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Palladium-Catalyzed Decarboxylative Ortho Acylation of Azobenzenes with α-Oxocarboxylic Acids

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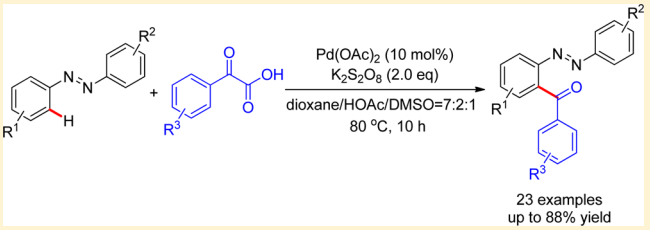
Supporting Information

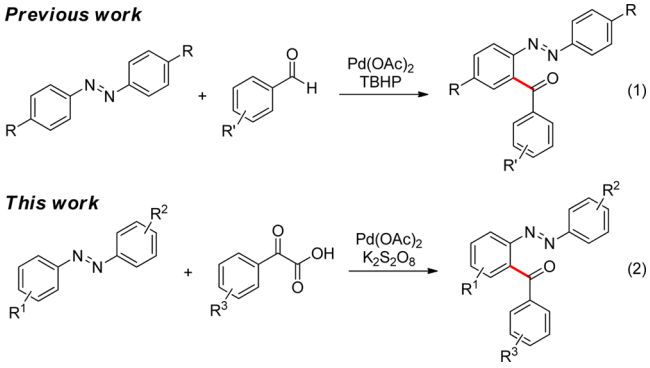
ABSTRACT: A palladium-catalyzed decarboxylative ortho acylation of azobenzenes with α-oxocarboxylic acids via ligand-directed C−H activation has been explored. The reaction proceeded smoothly with potassium persulfate as the oxidant to afford acylated unsymmetrical azobenzenes in moderate to good yields and tolerated chloro, bromo, iodo, and methoxy groups. Para, ortho, and disubstituted as well as unsymmetrical azobenzenes could be used.



INTRODUCTION

Aromatic azo compounds are very important in many fields such as nonlinear optics,[1] dyes,[2] indicators,[3] photochemical switches,[4] and therapeutic agents[5] due to their unique structures. Over the past few years, the synthesis of azobenzene derivatives has attracted a great deal of attention.[6] However, palladium-catalyzed C−H activation directed by the azo group has rarely been reported. Recently, Sanford[7] reported the acetoxylation of (*E*)-1,2-diphenyldiazene via C−H bond activation; other reactions such as acylation and halogenation of azobenzenes were disclosed by the Wang[8] and Tian[9] groups, respectively.

Ortho-acylated aromatic compounds are important structural motifs for preparing natural products, dyes, and drug intermediates.[10] Many methods had been known to realize this type of product. Traditional methods such as Friedel−Crafts acylation and oxidation of secondary alcohols by various oxidants[11] have been limited to specific structures. Recently, Ge[12] and others[13] reported palladium-catalyzed ortho acylation with α-oxocarboxylic acids. Additionally, many other compounds such as aldehydes,[8,14] benzyl alcohols,[15] toluene derivatives,[16] aminotoluenes,[17] carboxylic acids and anhydrides,[18] and α-diketones[19] could be applied to the synthesis of aryl ketones. Although the ortho acylation of aromatic azo compounds with aldehydes was demonstrated, it was limited to the symmetrical para-substituted azobenzenes (eq 1).[8] Furthermore, the palladium-catalyzed decarboxylative acylation of sp^2 C−H bonds with azo as the directing group has never been reported. With our continuing interest in developing more convenient sp^2 C−H bond cross-coupling-reactions,[20] herein we have devised an alternative protocol to achieve the ortho acylation of azobenzenes with α-oxocarboxylic acids via palladium-catalyzed sp^2 C−H activation with wider substrate scope (eq 2).[21]



RESULTS AND DISCUSSION

In our initial investigation, the reaction of azobenzene **1a** and α-oxocarboxylic acid **2a** was chosen as the model reaction. First, we chose dioxane as the solvent. To our delight, product **3a** was isolated in 12% yield in the presence of $K_2S_2O_8$ and $Pd(OAc)_2$ (Table 1, entry 1). Addition of AcOH and DMSO moderately improved the yield of **3a** (Table 1, entries 2 and 3), indicating that AcOH and DMSO were beneficial to this transformation. After further solvent screening, the yield was increased to 78% with a dioxane/AcOH/DMSO mixture (7/2/1, v/v/v) (Table 1, entries 4−8). Other oxidants such as $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, oxone, $Cu(OAc)_2$, 1,4-benzoquinone (BQ), *tert*-butyl hydroperoxide (TBHP), and $PhI(OAc)_2$ were less effective and afforded **3a** in low yields (Table 1, entries 9−15). Among all of the examined oxidants, $K_2S_2O_8$ was the best for this catalytic reaction. When the oxidant loading was decreased to 1.0 equiv, the desired product was obtained in a lower yield of 69% (Table 1, entry 16). Changing the **1a**/**2a** ratio from 1/1.1 to 1/1.2 and 1/1 reduced the yield of **3a** from 78% to 74% and 70%,

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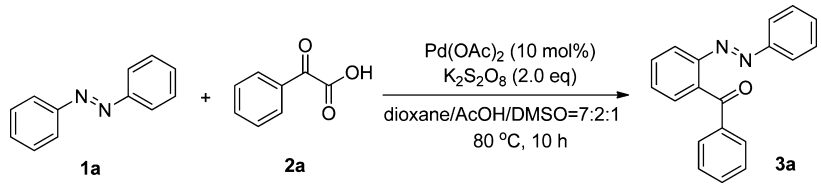
Table 1. Optimization of the Reaction Conditions[a]



entry	oxidant (equiv)	T (°C)	solvent (v/v/v)	t (h)	yield (%)[b]
1	$K_2S_2O_8$ (2.0)	80	10/0/0	10	12
2	$K_2S_2O_8$ (2.0)	80	8/2/0	10	20
3	$K_2S_2O_8$ (2.0)	80	9/0/1	10	49
4	$K_2S_2O_8$ (2.0)	80	6/2/2	10	76
5	$K_2S_2O_8$ (2.0)	80	5/2/3	10	75
6	$K_2S_2O_8$ (2.0)	80	7.5/1.5/1	10	72
7	$K_2S_2O_8$ (2.0)	80	7.5/2/0.5	10	70
8	**$K_2S_2O_8$ (2.0)**	**80**	**7/2/1**	**10**	**78**
9	$Na_2S_2O_8$ (2.0)	80	7/2/1	10	75
10	$(NH_4)_2S_2O_8$ (2.0)	80	7/2/1	10	63
11	oxone (2.0)	80	7/2/1	10	24
12	$Cu(OAc)_2$ (2.0)	80	7/2/1	10	trace
13	BQ (2.0)	80	7/2/1	10	trace
14	TBHP (5.0)	80	7/2/1	10	trace
15	$PhI(OAc)_2$ (2.0)	80	7/2/1	10	33
16	$K_2S_2O_8$ (1.0)	80	7/2/1	10	69
17[c]	$K_2S_2O_8$ (2.0)	80	7/2/1	10	74
18[d]	$K_2S_2O_8$ (2.0)	80	7/2/1	10	70
19[e]	$K_2S_2O_8$ (2.0)	80	7/2/1	10	68
20	$K_2S_2O_8$ (2.0)	70	7/2/1	12	71
21	$K_2S_2O_8$ (2.0)	90	7/2/1	10	73
22	$K_2S_2O_8$ (2.0)	80	7/2/1	12	78
23	$K_2S_2O_8$ (2.0)	80	7/2/1	8	66
24[f]	$K_2S_2O_8$ (2.0)	80	7/2/1	10	72

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.33 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (2 equiv), dioxane/AcOH/DMSO (7/2/1, 2 mL), 80 °C, 10 h. [b]Isolated yields based on **1a**. [c]0.36 mmol of **2a** was used. [d]0.30 mmol of **2a** was used. [e]5 mol % of $Pd(OAc)_2$ was used. [f]0.6 mmol of Ag_2O was added.

respectively (Table 1, entries 8, 17, and 18). From the obtained results, it could be found that the ratio 1/1.1 was the best choice. Reducing the amount of $Pd(OAc)_2$ from 10 to 5 mol % resulted in a worse result (Table 1, entry 19). Lower temperature suppressed the efficiency, whereas higher temperature did not lead to a better result (Table 1, entries 20 and 21). The effect of reaction time was also studied, and 10 h was a better choice (Table 1, entry 8 vs entries 22 and 23). Interestingly, the addition of 2 equiv of Ag_2O, which was essential in similar protocols, led to a lower yield (Table 1, entry 24). Therefore, the standard conditions for the palladium-catalyzed ortho acylation of **1a** with **2a** were as follows: 10 mol % of $Pd(OAc)_2$ as the catalyst, 2.0 equiv of $K_2S_2O_8$ as the oxidant, and 1.1 equiv of α-oxocarboxylic acid as the partner of azobenzene. The reaction was performed best at 80 °C for 10 h in a dioxane/AcOH/DMSO mixture (7/2/1, v/v/v).

To explore the applicability of this protocol, the substrate scope of α-oxocarboxylic acids was examined (Table 2). The reaction of azobenzene with phenylglyoxylic acids provided products **3a**−**p** in 50−88% yields and tolerated a variety of functional groups including chloro, bromo, iodo, and methoxy groups (Table 2, entries 1−16). The reaction did not show an obvious electronic effect. As for the substitution pattern, higher yields were obtained with para-substituted phenylglyoxylic acids containing methyl, halo, and aryl groups in comparison with those bearing trifluoromethyl and methoxy groups (Table 2, entries 2−7). Meta-substituted phenylglyoxylic acids worked well in the reaction to give the desired products **3h**−**k** in good to excellent yields (71−88%) (Table 2, entries 8−11). The reaction could also be applied to ortho-substituted phenylglyoxylic acids to give **3l**−**n** in moderate to good yields (Table 2, entries 12−14). Furthermore, disubstituted phenylglyoxylic acids showed good reactivity and provided products **3o**,**p** in good yields (Table 2, entries 15 and 16).

Next, we investigated the scope of azobenzenes, and the results are shown in Table 3. Good yields (68−87%) were obtained for the examined aromatic azo compounds. Para-substituted azobenzenes proved to be good substrates for this reaction (Table 3, entries 1−3). To our surprise, ortho-substituted azobenzenes **1e**,**f** provided products **3t**,**u** in higher yields (Table 3, entries 4 and 5 vs entries 1−3). 3,5-Disubstituted azobenzene **1g** furnished **3v** in a relatively lower yield (68%), probably due to the steric effect of the methyl group. When unsymmetrical azobenzene **1h** was employed, a good yield (83%) was obtained, yet the reaction was nonselective for the two phenyl rings (Table 3, entry 7).

It is of interest to note that the halo group in products **3d**,**e**,**i**−**k**,**n**,**p**,**r** may be utilized as the handle for further functionalization. The present protocol using α-oxocarboxylic acids as the acylation reagents provides an alternative approach to the acylated azobenzenes and generally affords product yields comparable to those for Wang's methodology using

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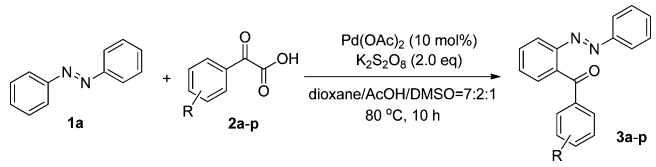
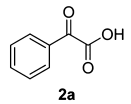
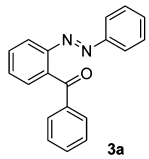
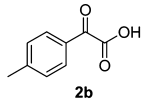
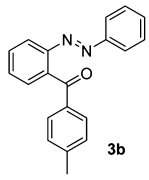
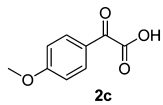
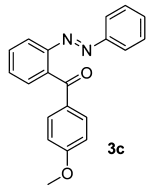
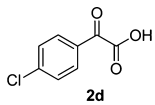
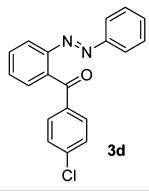
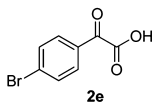
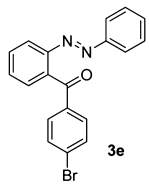
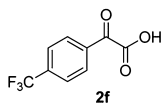
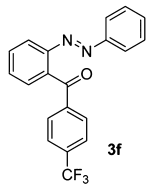
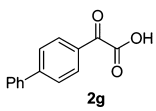
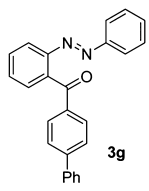
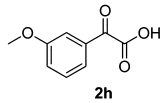
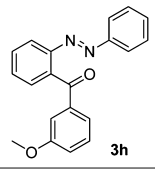
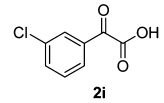
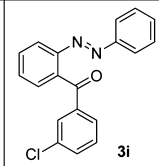
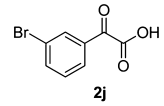
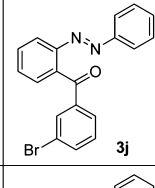
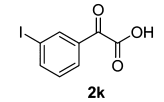
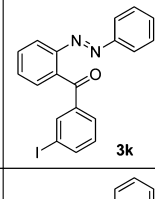
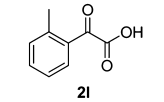
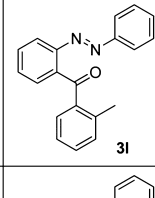
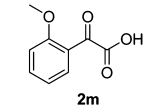
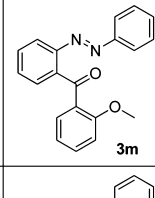
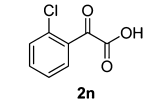
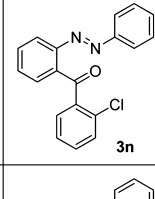
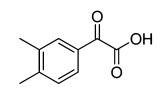
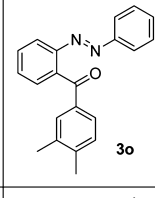
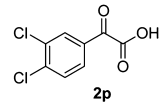
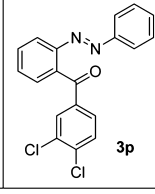
Table 2. Reaction of Azobenzene with α-Oxocarboxylic Acids[a]



entry	substrate **2**	product **3**	yield (%)[b]
1	 **2a**	 **3a**	78
2	 **2b**	 **3b**	77
3	 **2c**	 **3c**	65
4	 **2d**	 **3d**	71
5	 **2e**	 **3e**	72
6	 **2f**	 **3f**	61
7	 **2g**	 **3g**	75
8	 **2h**	 **3h**	71

entry	substrate **2**	product **3**	yield (%)[b]
9	 **2i**	 **3i**	88
10	 **2j**	 **3j**	72
11	 **2k**	 **3k**	73
12	 **2l**	 **3l**	60
13	 **2m**	 **3m**	50
14	 **2n**	 **3n**	77
15	 **2o**	 **3o**	77
16	 **2p**	 **3p**	65

[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.33 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (2 equiv), dioxane/AcOH/DMSO (7/2/1, 2 mL), 80 °C, 10 h. [b]Isolated yields based on **1a**.

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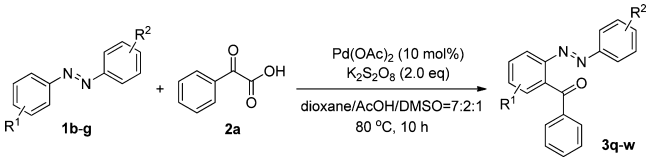
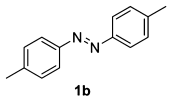
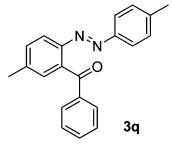
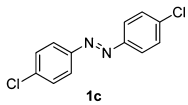
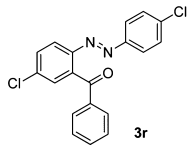
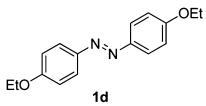
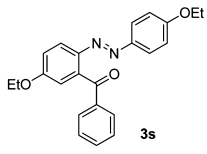
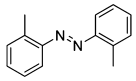
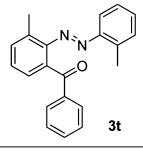
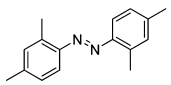
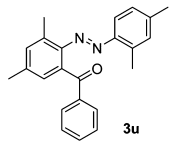
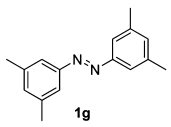
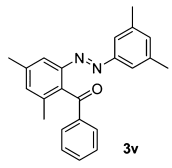
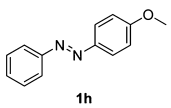
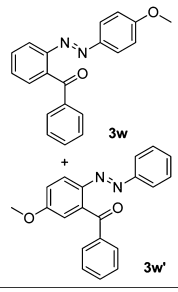
Table 3. Reaction of Azobenzenes with Phenylglyoxylic Acid[a]



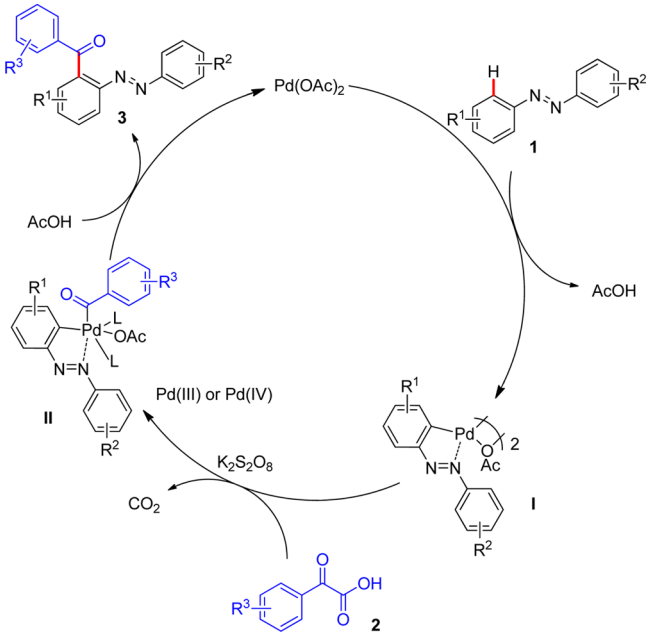
entry	substrate **1**	product **3**	yield (%)[b]
1	 **1b**	 **3q**	71
2	 **1c**	 **3r**	68
3	 **1d**	 **3s**	75
4	 **1e**	 **3t**	81
5	 **1f**	 **3u**	87
6	 **1g**	 **3v**	68
7	 **1h**	 **3w** + **3w'**	83[c]

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.33 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (2 equiv), dioxane/AcOH/DMSO (7/2/1, 2 mL), 80 °C, 10 h. [b]Isolated yields based on **1**. [c]The ratio of **3w to 3w'** was 1.1/1.

aldehydes as the partners.[8] It should be emphasized that the present reaction has very good selectivity, affording mono-acylated unsymmetrical azobenzenes exclusively. With the reaction of **1a** with **2a** as an example, increasing the amount of **2a** from 1.1 equiv to 2.3 equiv and prolonging the reaction time from 10 to 24 h still provided **3a** in 72% yield, along with a very small amount of byproducts.

On the basis of our experimental results and previous literature, a plausible mechanism is shown in Scheme 1. First,

Scheme 1. Plausible Reaction Mechanism



this transformation may begin with the ortho palladation of **1** with $Pd(OAc)_2$ to provide the five-membered palladacycle **I**, which reacts with **2** to provide intermediate **II** along with decarboxylation.[12a,13e−g,21] Finally, product **3** is generated by reductive elimination, and meanwhile a Pd(II) species is released to complete the catalytic cycle. Alternatively, the reaction mechanism involving a Pd(0/II) catalytic cycle cannot be excluded.[13a,g,i]

CONCLUSION

In summary, we have described an efficient approach to the Pd-catalyzed ortho acylation of aromatic azo compounds with *α*-oxocarboxylic acids via C−H bond activation using potassium persulfate as a convenient oxidant without any silver salt. This new protocol provides a series of ortho-acylated unsymmetrical azobenzenes, tolerating a wide range of functional groups such as chloro, bromo, iodo, and methoxy groups. In addition to para-substituted azobenzenes, ortho and disubstituted as well as unsymmetrical azobenzenes can be employed.

EXPERIMENTAL SECTION

General Procedure for the Palladium-Catalyzed Decarboxylative Ortho Acylation of Azobenzenes with *α*-Oxocarboxylic Acids. A mixture of azobenzene **1** (0.3 mmol), *α*-oxocarboxylic acid **2** (0.33 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), $K_2S_2O_8$ (162.3 mg, 0.6 mmol) in 1,4-dioxane/AcOH/DMSO (7/2/1, v/v/v, 2 mL) was stirred at 80 °C for 10 h. The mixture was filtered by a silica gel plug with ethyl acetate as the eluent and evaporated in vacuum. Product **3** was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (20:1) as the eluent.

*(E)-Phenyl(2-(phenyldiazenyl)phenyl)methanone (**3a**).*[8] By following the general procedure, the reaction of **1a** (54.7 mg, 0.3 mmol) with **2a** (49.5 mg, 0.33 mmol) gave **3a** (66.7 mg, 78% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.9 Hz, 1H), 7.78 (d, J =

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7.8 Hz, 2H), 7.68–7.63 (m, 1H), 7.60–7.58 (m, 2H), 7.50–7.42 (m, 3H), 7.40–7.32 (m, 5H).

*(E)-(2-(Phenyldiazenyl)phenyl)(p-tolyl)methanone (**3b**).*[8] By following the general procedure, the reaction of **1a** (54.8 mg, 0.3 mmol) with **2b** (54.8 mg, 0.33 mmol) gave **3b** (69.3 mg, 77% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.66–7.61 (m, 1H), 7.60–7.55 (m, 2H), 7.49–7.46 (m, 2H), 7.38–7.31 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H).

*(E)-(4-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)methanone (**3c**).*[8] By following the general procedure, the reaction of **1a** (54.6 mg, 0.3 mmol) with **2c** (59.9 mg, 0.33 mmol) gave **3c** (61.3 mg, 65% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.9 Hz, 2H), 7.65–7.60 (m, 1H), 7.59–7.50 (m, 4H), 7.38–7.34 (m, 3H), 6.86 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H).

*(E)-(4-Chlorophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3d**).*[8] By following the general procedure, the reaction of **1a** (54.5 mg, 0.3 mmol) with **2d** (60.9 mg, 0.33 mmol) gave **3d** (67.8 mg, 71% yield): red solid, mp 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.0, 0.7 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.69–7.64 (m, 1H), 7.62–7.57 (m, 1H), 7.56 (dd, J = 7.5, 1.6 Hz, 1H), 7.48–7.45 (m, 2H), 7.40–7.33 (m, 5H).

*(E)-(4-Bromophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3e**).*[8] By following the general procedure, the reaction of **1a** (54.7 mg, 0.3 mmol) with **2e** (76.0 mg, 0.33 mmol) gave **3e** (79.1 mg, 72% yield): red solid, mp 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.0, 0.7 Hz, 1H), 7.69–7.65 (m, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.61–7.57 (m, 1H), 7.56 (dd, J = 7.5, 1.6 Hz, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.47–7.44 (m, 2H), 7.40–7.33 (m, 3H).

*(E)-(2-(Phenyldiazenyl)phenyl)(4-(trifluoromethyl)phenyl)-methanone (**3f**).* By following the general procedure, the reaction of **1a** (54.6 mg, 0.3 mmol) with **2f** (72.0 mg, 0.33 mmol) gave **3f** (64.9 mg, 61% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.73–7.68 (m, 1H), 7.65–7.61 (m, 4H), 7.39–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 151.9, 150.6, 141.6 (q, J_{C-F} = 1.5 Hz), 135.7, 134.0 (q, J_{C-F} = 32.3 Hz), 131.8, 131.6, 131.2, 129.6 (2C), 129.13, 129.12 (2C), 125.5 (q, J_{C-F} = 3.7 Hz, 2C), 123.7 (q, J_{C-F} = 272.8 Hz), 122.9 (2C), 121.0; FT-IR ν/cm^{-1} (neat) 2924, 1675, 1587, 1412, 1324, 1284, 1168, 1132, 1065, 1017, 929, 774, 682; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{20}H_{13}N_2OF_3$ 354.0980, found 354.1003.

*(E)-Biphenyl-4-yl(2-(phenyldiazenyl)phenyl)methanone (**3g**).*[8] By following the general procedure, the reaction of **1a** (54.9 mg, 0.3 mmol) with **2g** (74.8 mg, 0.33 mmol) gave **3g** (81.8 mg, 75% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.69–7.65 (m, 1H), 7.64–7.55 (m, 6H), 7.50–7.42 (m, 4H), 7.40–7.29 (m, 4H).

*(E)-(3-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)methanone (**3h**).*[8] By following the general procedure, the reaction of **1a** (54.9 mg, 0.3 mmol) with **2h** (60.0 mg, 0.33 mmol) gave **3h** (67.6 mg, 71% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 1H), 7.67–7.62 (m, 1H), 7.59–7.55 (m, 2H), 7.50–7.47 (m, 2H), 7.43–7.41 (m, 1H), 7.38–7.32 (m, 3H), 7.25–7.22 (m, 2H), 7.05–7.01 (m, 1H), 3.81 (s, 3H).

*(E)-(3-Chlorophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3i**).* By following the general procedure, the reaction of **1a** (54.9 mg, 0.3 mmol) with **2i** (61.4 mg, 0.33 mmol) gave **3i** (80.6 mg, 88% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.0, 0.7 Hz, 1H), 7.78 (t, J = 1.8 Hz, 1H), 7.71–7.66 (m, 1H), 7.63–7.55 (m, 3H), 7.49–7.42 (m, 3H), 7.40–7.33 (m, 3H), 7.29 (t, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 152.0, 150.5, 140.3, 135.9, 134.8, 132.7, 131.7, 131.3, 131.1, 129.8, 129.1 (3C), 128.9, 127.7, 123.0 (2C), 121.1; FT-IR ν/cm^{-1} (neat) 2924, 2856, 1664, 1599, 1452, 1304, 1273, 1192, 774, 690; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{19}H_{13}N_2O^{35}Cl$ 320.0716, found 320.0717.

*(E)-(3-Bromophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3j**).* By following the general procedure, the reaction of **1a** (55.1 mg, 0.3 mmol) with **2j** (75.6 mg, 0.33 mmol) gave **3j** (79.4 mg, 72% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.0, 0.7 Hz, 1H), 7.95 (t, J = 1.8 Hz, 1H), 7.68 (ddd, J = 8.0, 6.7, 1.8 Hz, 1H), 7.64–7.55 (m, 4H), 7.49–7.45 (m, 2H), 7.40–7.34 (m, 3H), 7.22 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 152.0, 150.5, 140.5, 135.8, 135.6, 132.0, 131.7, 131.3, 131.1, 130.1, 129.1 (2C), 128.9, 128.1, 123.0 (2C), 122.8, 121.0; FT-IR ν/cm^{-1} (neat) 2924, 1668, 1564, 1452, 1292, 1244, 1148, 941, 769, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{19}H_{13}N_2O^{79}Br$ 364.0211, found 364.0202.

*(E)-(3-Iodophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3k**).* By following the general procedure, the reaction of **1a** (55.1 mg, 0.3 mmol) with **2k** (91.2 mg, 0.33 mmol) gave **3k** (90.3 mg, 73% yield): red solid, mp 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, J = 1.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.78 (ddd, J = 7.8, 1.6, 1.0 Hz, 1H), 7.68 (ddd, J = 8.0, 7.0, 2.0 Hz, 1H), 7.64–7.55 (m, 3H), 7.48–7.45 (m, 2H), 7.40–7.34 (m, 3H), 7.08 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 152.0, 150.6, 141.5, 140.5, 137.9, 135.8, 131.7, 131.4, 131.1, 130.2, 129.1 (2C), 129.0, 128.7, 123.0 (2C), 120.9, 94.2; FT-IR ν/cm^{-1} (neat) 2924, 1668, 1592, 1560, 1416, 1292, 1240, 1149, 949, 774, 718, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{19}H_{13}N_2OI$ 412.0073, found 412.0098.

*(E)-(2-(Phenyldiazenyl)phenyl)(o-tolyl)methanone (**3l**).*[8] By following the general procedure, the reaction of **1a** (54.7 mg, 0.3 mmol) with **2l** (54.8 mg, 0.33 mmol) gave **3l** (54.1 mg, 60% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.9, 1.0 Hz, 1 H), 7.70 (dd, J = 7.4, 1.5 Hz, 1H), 7.64 (td, J = 7.6, 1.6 Hz, 1H), 7.58 (td, J = 7.4, 1.3 Hz, 1H), 7.41–7.25 (m, 7H), 7.21 (d, J = 7.4 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 2.57 (s, 3H).

*(E)-(2-Methoxyphenyl)(2-(phenyldiazenyl)phenyl)methanone (**3m**).* By following the general procedure, the reaction of **1a** (55.0 mg, 0.3 mmol) with **2m** (59.8 mg, 0.33 mmol) gave **3m** (47.5 mg, 50% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 3H), 7.61–7.53 (m, 2H), 7.39–7.31 (m, 6H), 7.00 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 158.5, 152.4, 150.6, 139.6, 133.5, 131.3, 131.1, 130.8, 130.7, 130.2, 129.1, 128.9 (2C), 123.1 (2C), 120.6, 117.6, 111.9, 55.7; FT-IR ν/cm^{-1} (neat) 2928, 1644, 1596, 1484, 1464, 1436, 1308, 1252, 1148, 1025, 937, 769, 682; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{20}H_{16}N_2O_2$ 316.1212, found 316.1213.

*(E)-(2-Chlorophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3n**).* By following the general procedure, the reaction of **1a** (54.7 mg, 0.3 mmol) with **2n** (60.5 mg, 0.33 mmol) gave **3n** (73.9 mg, 77% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.5, 1.6 Hz, 1H), 7.74 (dd, J = 7.9, 1.1 Hz, 1H), 7.66 (td, J = 7.6, 1.6 Hz, 1H), 7.59 (td, J = 7.4, 1.4 Hz, 1H), 7.55–7.52 (m, 1H), 7.42–7.23 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 152.4, 151.1, 140.0, 137.1, 132.5, 132.3, 131.9, 131.6, 131.0, 130.8, 130.7, 130.1, 128.9 (2C), 126.7, 123.3 (2C), 117.8; FT-IR ν/cm^{-1} (neat) 2932, 2856, 1675, 1592, 1468, 1436, 1300, 1240, 1121, 1057, 934, 774, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{19}H_{13}N_2O^{35}Cl$ 320.0716, found 320.0709.

*(E)-(3,4-Dimethylphenyl)(2-(phenyldiazenyl)phenyl)methanone (**3o**).* By following the general procedure, the reaction of **1a** (54.8 mg, 0.3 mmol) with **2o** (59.3 mg, 0.33 mmol) gave **3o** (72.3 mg, 77% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.65–7.60 (m, 1H), 7.60–7.45 (m, 6H), 7.38–7.31 (m, 3H), 7.12 (d, J = 7.8 Hz, 1H), 2.26 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 152.3, 150.5, 142.6, 137.8, 136.9, 136.4, 131.4, 130.9, 130.63, 130.61, 129.7, 129.0 (2C), 128.7, 127.7, 123.1 (2C), 119.6, 20.2, 19.8; FT-IR ν/cm^{-1} (neat) 2924, 2852, 1663, 1607, 1452, 1304, 1276, 1252, 1117, 773, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{21}H_{18}N_2O$ 314.1419, found 314.1438.

*(E)-(3,4-Dichlorophenyl)(2-(phenyldiazenyl)phenyl)methanone (**3p**).* By following the general procedure, the reaction of **1a** (54.9 mg, 0.3 mmol) with **2l** (72.6 mg, 0.33 mmol) gave **3l** (69.3 mg, 65% yield): red solid, mp 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.0, 0.8 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 7.71–7.67 (m, 1H), 7.61 (td, J = 7.4, 1.2 Hz, 1H), 7.56–7.53 (m, 2H), 7.51–7.47 (m, 2H), 7.45–7.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 151.9, 150.5, 138.3, 137.3, 135.3, 133.2, 131.9, 131.5, 131.2, 131.0, 130.6, 129.2 (2C), 128.8, 128.5, 123.0 (2C), 121.4; FT-IR ν/cm^{-1} (neat) 2924, 2848, 1668, 1584, 1460, 1384, 1289, 1237, 1157, 1029, 949, 774, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{19}H_{12}N_2O^{35}Cl_2$ 354.0327, found 354.0320.

*(E)-(5-Methyl-2-(p-tolyldiazenyl)phenyl)(phenyl)methanone (**3q**).*[8] By following the general procedure, the reaction of **1b** (63.1 mg, 0.3 mmol) with **2a** (49.7 mg, 0.33 mmol) gave **3q** (67.2 mg, 71% yield): red solid, mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1H), 7.78−7.75 (m, 2H), 7.48−7.42 (m, 2H), 7.38−7.29 (m, 5H), 7.10 (d, J = 8.1 Hz, 2H), 2.48 (s, 3H), 2.33 (s, 3H).

*(E)-(5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)(phenyl)-methanone (**3r**).*[8] By following the general procedure, the reaction of **1c** (75.6 mg, 0.3 mmol) with **2a** (50.1 mg, 0.33 mmol) gave **3r** (72.7 mg, 68% yield): red solid, mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.6 Hz, 1H), 7.77−7.74 (m, 2H), 7.61 (dd, J = 8.6, 2.3 Hz, 1H), 7.57 (d, J = 2.2 Hz, 1H), 7.54−7.49 (m, 1H), 7.42−7.34 (m, 4H), 7.29 (d, J = 8.9 Hz, 2H).

*(E)-(5-Ethoxy-2-((4-ethoxyphenyl)diazenyl)phenyl)(phenyl)-methanone (**3s**).* By following the general procedure, the reaction of **1d** (81.1 mg, 0.3 mmol) with **2a** (49.8 mg, 0.33 mmol) gave **3s** (84.1 mg, 75% yield): orange solid, mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 1H), 7.79−7.76 (m, 2H), 7.49−7.44 (m, 1H), 7.38−7.33 (m, 4H), 7.12 (dd, J = 8.9, 2.8 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 6.78 (d, J = 8.9 Hz, 2H), 4.14 (q, J = 7.0 Hz, 2H), 4.02 (q, J = 7.0 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 161.3, 160.8, 146.5, 144.6, 138.6, 138.4, 132.8, 129.4 (2C), 128.4 (2C), 124.6 (2C), 122.1, 117.3, 114.6 (2C), 113.5, 64.3, 63.9, 14.87, 14.86; FT-IR ν/cm^{-1} (neat) 2932, 1660, 1600, 1580, 1500, 1472, 1392, 1293, 1245, 1141, 1041, 913, 838, 710; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{23}H_{22}N_2O_3$ 374.1630, found 374.1632.

*(E)-(3-Methyl-2-(o-tolyldiazenyl)phenyl)(phenyl)methanone (**3t**).* By following the general procedure, the reaction of **1e** (63.7 mg, 0.3 mmol) with **2a** (49.8 mg, 0.33 mmol) gave **3t** (75.9 mg, 81% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.63 (m, 2H), 7.48 (d, J = 6.8 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.39−7.35 (m, 1H), 7.32−7.21 (m, 5H), 7.16 (d, J = 7.5 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 2.77 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 150.4, 150.3, 139.1, 138.2, 137.3, 132.7, 132.6, 131.4 (2C), 131.3, 130.1, 129.1 (2C), 128.3 (2C), 126.6, 126.1, 115.8, 18.6, 17.4; FT-IR ν/cm^{-1} (neat) 3060, 2924, 1668, 1600, 1580, 1452, 1316, 1277, 1157, 969, 774, 710, 694; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{21}H_{18}N_2O$ 314.1419, found 314.1410.

*(E)-(2-((2,4-Dimethylphenyl)diazenyl)-3,5-dimethylphenyl)-(phenyl)methanone (**3u**).* By following the general procedure, the reaction of **1f** (71.4 mg, 0.3 mmol) with **2a** (49.9 mg, 0.33 mmol) gave **3u** (90.6 mg, 87% yield): red solid, mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.63 (m, 2H), 7.38−7.33 (m, 1H), 7.28−7.22 (m, 4H), 7.02 (s, 1H), 6.95 (s, 1H), 6.86 (d, J = 8.2 Hz, 1H), 2.73 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 148.6, 148.2, 141.6, 140.5, 138.9, 138.3, 137.4, 133.2, 132.5, 131.8, 131.3, 129.1 (2C), 128.3 (2C), 127.1, 126.9, 115.7, 21.5, 21.4, 18.6, 17.4; FT-IR ν/cm^{-1} (neat) 2924, 2856, 1668, 1596, 1448, 1320, 1217, 822, 698; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{23}H_{22}N_2O$ 342.1732, found 342.1740.

*(E)-(2-((3,5-Dimethylphenyl)diazenyl)-4,6-dimethylphenyl)-(phenyl)methanone (**3v**).* By following the general procedure, the reaction of **1g** (71.9 mg, 0.3 mmol) with **2a** (50.0 mg, 0.33 mmol) gave **3v** (70.1 mg, 68% yield): red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.78 (m, 2H), 7.56 (s, 1H), 7.49 (tt, J = 7.4, 1.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.22 (s, 1H), 7.01 (s, 1H), 6.98 (s, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 152.5, 150.4, 139.8, 139.0, 138.6 (2C), 136.5, 135.3, 133.9, 132.93, 132.86, 129.2 (2C), 128.6 (2C), 120.8 (2C), 116.6, 21.5, 21.2 (2C), 19.1; FT-IR ν/cm^{-1} (neat) 2920, 1668, 1604, 1580, 1448, 1312, 1269, 1185, 918, 862, 710, 686; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{23}H_{22}N_2O$ 342.1732, found 342.1739.

*(E)-(2-((4-Methoxyphenyl)diazenyl)phenyl)(phenyl)methanone (**3w**) and (E)-(5-Methoxy-2-(phenyldiazenyl)phenyl)(phenyl)-methanone (**3w′**).* By following the general procedure, the reaction of **1h** (63.9 mg, 0.3 mmol) with **2a** (50.2 mg, 0.33 mmol) gave **3w** and **3w′** (78.5 mg, 83% yield) in a ratio of 1.1/1. The isomeric mixture was separated repeatedly by column chromatography over silica gel to obtain pure **3w** and **3w′**: red oil. **3w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.78−7.74 (m, 2H), 7.66−7.61 (m, 1H), 7.58−7.52 (m, 2H), 7.49−7.41 (m, 3H), 7.39−7.33 (m, 2H), 6.82 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 162.5, 150.7, 146.6, 138.7, 136.6, 132.8, 130.9, 130.4, 129.5 (2C), 128.9, 128.4 (2C), 125.0 (2C), 120.2, 114.2 (2C), 55.7; FT-IR ν/cm^{-1} (neat) 2924, 1668, 1596, 1450, 1286, 1236, 1071, 1031, 691; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{20}H_{16}N_2O_2$ 316.1212, found 316.1205. **3w′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.40−7.28 (m, 7H), 7.15 (dd, J = 8.9, 2.7 Hz, 1H), 7.05 (d, J = 2.7 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 162.0, 152.2, 144.6, 139.1, 138.5, 132.9, 130.8, 129.5 (2C), 129.0 (2C), 128.5 (2C), 122.7 (2C), 122.3, 116.9, 113.1, 56.0; FT-IR ν/cm^{-1} (neat) 2925, 1666, 1598, 1500, 1448, 1254, 1143, 1028, 840, 701; HRMS (EI-TOF) m/z [M$^+$] calcd for $C_{20}H_{16}N_2O_2$ 316.1212, found 316.1206.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of products **3a−w**. 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.

■ REFERENCES

(1) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (c) Ishow, E.; Bellaïche, C.; Bouteiller, L.; Nakatani, K.; Delaire, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 15744. (d) Papagiannouli, I.; Iliopoulos, K.; Gindre, D.; Sahraoui, B.; Krupka, O.; Smokal, V.; Kolendo, A.; Couris, S. *Chem. Phys. Lett.* **2012**, *554*, 107.

(2) (a) Hunger, K. *Industrial Dyes: Chemistry, Properties, Applications*; Wiley-VCH: Weinheim, Germany, 2003. (b) Bafana, A.; Devi, S. S.; Chakrabarti, T. *Environ. Rev.* **2011**, *19*, 350.

(3) Anderson, R. G.; Nickless, G. *Analyst* **1967**, *92*, 207.

(4) (a) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915. (b) Harvey, A. J.; Abell, A. D. *Tetrahedron* **2000**, *56*, 9763.

(5) (a) Hoult, J. R. S. *Drugs* **1986**, *32*, 18. (b) Sandborn, W. J. *Am. J. Gastroenterol.* **2002**, *97*, 2939.

(6) (a) Miyamura, S.; Tsurugi, H.; Satoh, T.; Miura, M. *J. Organomet. Chem.* **2008**, *693*, 2438. (b) Drug, E.; Gozin, M. *J. Am. Chem. Soc.* **2007**, *129*, 13784. (c) Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 6174. (d) Takeda, Y.; Okumura, S.; Minakata, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 7804. (e) Cai, S.; Rong, H.; Yu, X.; Liu, X.; Wang, D.; He, W.; Li, Y. *ACS Catal.* **2013**, *3*, 478. (f) Zhu, Y.; Shi, Y. *Org. Lett.* **2013**, *15*, 1942.

(7) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300.

(8) Li, H.; Li, P.; Wang, L. *Org. Lett.* **2013**, *15*, 620.

(9) Ma, X.-T.; Tian, S.-K. *Adv. Synth. Catal.* **2013**, *355*, 337.

(10) (a) Hirai, K.; Ishiba, T.; Sugimoto, H.; Sasakura, K.; Fujishita, T.; Toyoda, T.; Tsukinoki, Y.; Joyama, H.; Hatakeyama, H.; Hirose, K. *J. Med. Chem.* **1980**, *23*, 764. (b) Hirai, K.; Fujishita, T.; Ishiba, T.; Sugimoto, H.; Matsutani, S.; Tsukinoki, Y.; Hirose, K. *J. Med. Chem.* **1982**, *25*, 1466. (c) Ogita, H.; Isobe, Y.; Takaku, H.; Sekine, R.; Goto, Y.; Misawa, S.; Hayashi, H. *Bioorg. Med. Chem.* **2002**, *10*, 3473. (d) Mitsch, A.; Wißner, P.; Böhm, M.; Silber, K.; Klebe, G.; Sattler, I.; Schlitzer, M. *Arch. Pharm. Pharm. Med. Chem.* **2004**, *337*, 493.

(11) (a) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley: New York, 1973. (b) Sartori, G.; Maggi, R. *Chem. Rev.* **2006**, *106*, 1077. (c) Fernandez, M.; Tojo, G. In *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice*; Tojo, E., Ed.; Springer: New York, 2006.

(12) (a) Li, M.; Ge, H. *Org. Lett.* **2010**, *12*, 3464. (b) Fang, P.; Li, M.; Ge, H. *J. Am. Chem. Soc.* **2010**, *132*, 11898. (c) Li, M.; Wang, C.; Ge,

H. *Org. Lett.* **2011**, *13*, 2062. (d) Li, M.; Wang, C.; Fang, P.; Ge, H. *Chem. Commun.* **2011**, *47*, 6587. (e) Miao, J.; Ge, H. *Org. Lett.* **2013**, *15*, 2930.

(13) (a) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Lett.* **2012**, *14*, 4358. (b) Kim, M.; Park, J.; Sharma, S.; Kim, A.; Park, E.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2013**, *49*, 925. (c) Sharma, S.; Kim, A.; Park, E.; Park, J.; Kim, M.; Kwak, J. H.; Lee, S. H.; Jung, Y. H.; Kim, I. S. *Adv. Synth. Catal.* **2013**, *355*, 667. (d) Sharma, S.; Khan, I. A.; Saxena, A. K. *Adv. Synth. Catal.* **2013**, *355*, 673. (e) Yao, J.; Feng, R.; Wu, Z.; Liu, Z.; Zhang, Y. *Adv. Synth. Catal.* **2013**, *355*, 1517. (f) Yang, Z.; Chen, X.; Liu, J.; Gui, Q.; Xie, K.; Li, M.; Tan, Z. *Chem. Commun.* **2013**, *49*, 1560. (g) Park, J.; Kim, M.; Sharma, S.; Park, E.; Kim, A.; Lee, S. H.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2013**, *49*, 1654. (h) Yu, L.; Li, P.; Wang, L. *Chem. Commun.* **2013**, *49*, 2368. (i) Pan, C.; Jin, H.; Liu, X.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 2933. (j) Li, D.; Wang, M.; Liu, J.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 3640. (k) Cai, H.-T.; Li, D.-D.; Liu, Z.; Wang, G.-W. *Acta Chim. Sinica* **2013**, *71*, 717. (l) Zhang, S.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Org. Biomol. Chem.* **2013**, *11*, 4308.

(14) (a) Jia, X.; Zhang, S.; Wang, W.; Luo, F.; Cheng, J. *Org. Lett.* **2009**, *11*, 3120. (b) Baslé, O.; Bidange, J.; Shuai, Q.; Li, C.-J. *Adv. Synth. Catal.* **2010**, *352*, 1145. (c) Chan, C.-W.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 3926. (d) Wu, Y.; Li, B.; Mao, F.; Li, X.; Kwong, F. Y. *Org. Lett.* **2011**, *13*, 3258. (e) Park, J.; Park, E.; Kim, A.; Lee, Y.; Chi, K. W.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2011**, *11*, 4390. (f) Li, C.; Wang, L.; Li, P.; Zhou, W. *Chem. Eur. J.* **2011**, *17*, 10208. (g) Yang, Y.; Zhou, B.; Li, Y. *Adv. Synth. Catal.* **2012**, *354*, 2916. (h) Banerjee, A.; Santra, S. K.; Guin, S.; Rout, S. K.; Patel, B. K. *Eur. J. Org. Chem.* **2013**, *7*, 1367. (i) Szabó, F.; Daru, J.; Simkó, D.; Nagy, T. Z.; Stirling, A.; Novák, Z. *Adv. Synth. Catal.* **2013**, *355*, 685.

(15) (a) Xiao, F.; Shuai, Q.; Zhao, F.; Baslé, O.; Deng, G.; Li, C.-J. *Org. Lett.* **2011**, *13*, 1614. (b) Yuan, Y.; Chen, D.; Wang, X. *Adv. Synth. Catal.* **2011**, *353*, 3373. (c) Park, J.; Kim, A.; Sharma, S.; Kim, M.; Park, E.; Jeon, Y.; Lee, Y.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Biomol. Chem.* **2013**, *11*, 2766. (d) Kim, M.; Sharma, S.; Park, J.; Kim, M.; Choi, Y.; Jeon, Y.; Kwak, J. H.; Kim, I. S. *Tetrahedron* **2013**, *69*, 6552.

(16) (a) Guin, S.; Rout, S. K.; Banerjee, A.; Nandi, S.; Patel, B. K. *Org. Lett.* **2012**, *14*, 5294. (b) Yin, Z.; Sun, P. *J. Org. Chem.* **2012**, *77*, 11339. (c) Weng, J.; Yu, Z.; Liu, X.; Zhang, G. *Tetrahedron Lett.* **2013**, *54*, 1205. (d) Wu, Y.; Choy, P. Y.; Mao, F.; Kwong, F. Y. *Chem. Commun.* **2013**, *49*, 689.

(17) Zhang, Q.; Yang, F.; Wu, Y. *Chem. Commun.* **2013**, *49*, 6837.

(18) (a) Lu, J.; Zhang, H.; Chen, X.; Liu, H.; Jiang, Y.; Fu, H. *Adv. Synth. Catal.* **2013**, *355*, 529. (b) Mamone, P.; Danoun, G.; Gooßen, L. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6704.

(19) Zhou, W.; Li, H.; Wang, L. *Org. Lett.* **2012**, *14*, 4594.

(20) (a) Wang, G.-W.; Yuan, T.-T.; Wu, X.-L. *J. Org. Chem.* **2008**, *73*, 4717. (b) Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334. (c) Wang, G.-W.; Yuan, T.-T. *J. Org. Chem.* **2010**, *75*, 476. (d) Wang, G.-W.; Yuan, T.-T.; Li, D.-D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1380. (e) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *Chem. Commun.* **2011**, *47*, 12789. (f) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *J. Org. Chem.* **2012**, *77*, 3341. (g) Li, F.; Liu, T.-X.; Wang, G.-W. *Org. Lett.* **2012**, *14*, 2176. (h) Su, Y.-T.; Wang, Y.-L.; Wang, G.-W. *Chem. Commun.* **2012**, *48*, 8132. (i) Jiang, T.-S.; Wang, G.-W. *J. Org. Chem.* **2012**, *77*, 9504.

(21) After our work had been completed, a report on the palladium-catalyzed ortho-acylation reaction of azoxybenzenes with α-oxocarboxylic acids appeared: Li, H.; Li, P.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 9170.