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Direct Access to Acylated Azobenzenes and Amide Compounds by Reaction of Azoarenes with Benzylic Ethers as Acyl Equivalents

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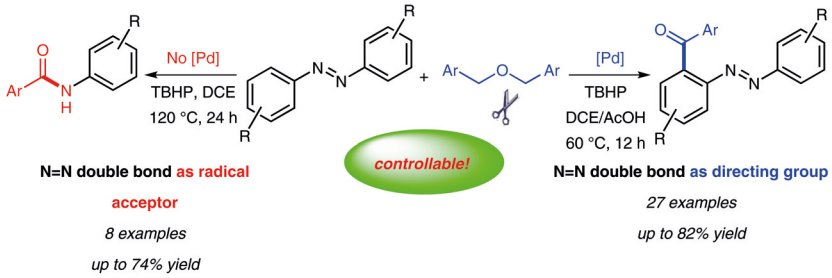

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Abstract Described herein is the use of N=N double bond of azobenzene as both directing group and radical acceptor in one-reaction protocol for the first time. An efficient pathway for the Pd-catalyzed regiospecific *ortho*-acylation of azoarenes using benzylic ethers as acyl equivalents has been achieved. In the absence of palladium catalyst, amide compounds were formed by the reaction of azoarenes with benzylic ethers under certain conditions. Various mono-acylazobenzene and amide compounds were obtained in good yields (35 examples). The mono-acylated products and amide products could be easily controlled by palladium catalyst.

Key words azobenzenes, synthetic methods, radical reaction, directing group, benzylic ether, amide compounds

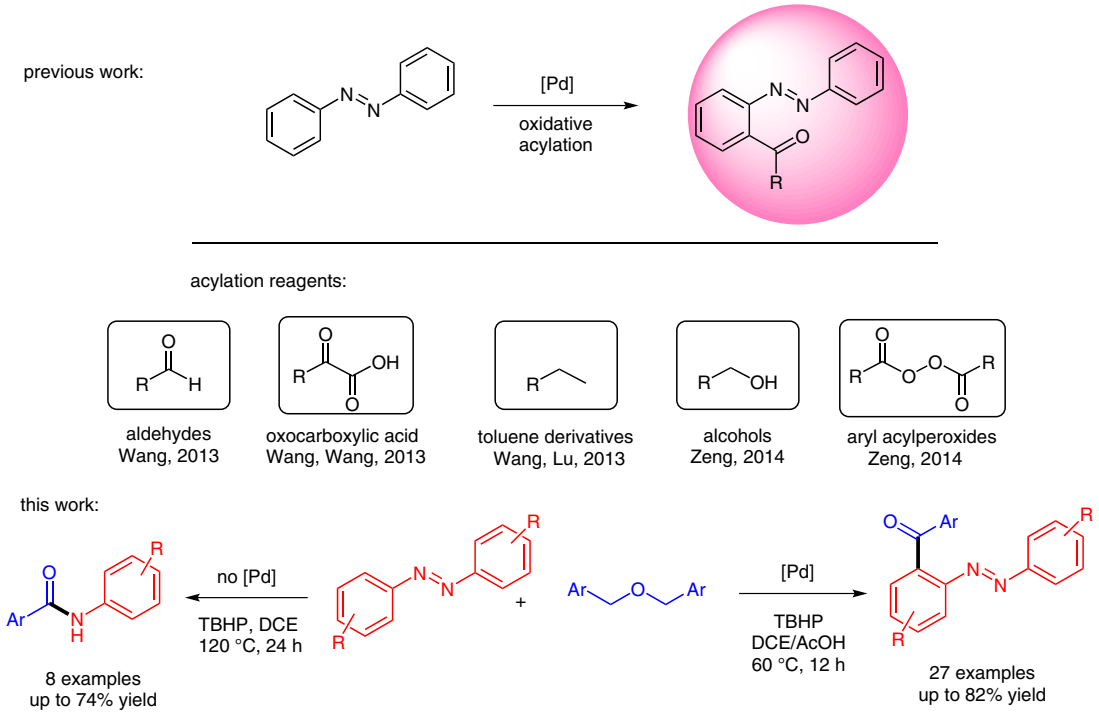
Aromatic azo compounds have received considerable attention for their applications as indicators, nonlinear optics, photochemical switches, and pharmaceuticals.[1] Recently, the functionalization of azoarenes has attracted significant attention for the synthesis of unsymmetrical azobenzenes using azo group as a directing group.[2] Among them, remarkable progress has been made by researchers on aldehydes,[3] α-oxocarboxylic acids,[4] toluene derivatives,[5] alcohols,[6] and aryl acylperoxides[7] as reactants for the acylation of azobenzenes based on transition-metal-catalyzed C–H activation (Scheme 1).

Benzylic ethers were widely used as the common protecting groups for alcohols. Its C–O bond can be easily cleaved under certain oxidizing or reducing conditions.[8] Since the first report on the formation of benzaldehydes from benzyl methyl ethers by Markees in 1958,[9] various methods have been developed to form benzaldehydes through oxidative cleavage of C–O bonds, such as TEMPO,[10] $Cu(NO_3)_2$,[11] NBS/H_2O,[12] DDQ,[13] etc. In addition, it can also serve as other widely-used synthetic equivalents such as carboxylic acids and esters under different conditions.[14] In 2014, Kim's group first reported benzyl ethers as aroyl surrogates using TBHP as oxidant.[15] With our continuing ef-

Table 1 Screening of the Reaction Conditions[a,b]

Entry	Catalyst (10 mol%)	Oxidant (equiv)	Solvent	Temp (°C)	Yield (%)
1	$Pd(OAc)_2$	TBHP (6)	DCE	60	66
2	$PdCl_2$	TBHP (6)	DCE	60	16
3	$Pd(PPh_3)_4$	TBHP (6)	DCE	60	28
4	$Pd(PPh_3)_2Cl_2$	TBHP (6)	DCE	60	24
5	$Pd(OAc)_2$	DTBP (6)	DCE	60	ND
6	$Pd(OAc)_2$	TBPB (6)	DCE	60	trace
7	$Pd(OAc)_2$	DDQ (6)	DCE	60	ND
8	$Pd(OAc)_2$	TBHP (6)	DCE	60	47[c]
9	$Pd(OAc)_2$	TBHP (4)	DCE	60	48
10	$Pd(OAc)_2$	TBHP (6)	MeCN	60	57
11	$Pd(OAc)_2$	TBHP (6)	DMSO	60	43
12	$Pd(OAc)_2$	TBHP (6)	1,4-dioxane	60	62
13	$Pd(OAc)_2$	TBHP (6)	DCE/AcOH[d]	60	82 (75)[e]
14	$Pd(OAc)_2$	TBHP (6)	DCE/AcOH[d]	60	67[f]
15	$Pd(OAc)_2$	TBHP (6)	DCE/AcOH[d]	100	73
16	$Pd(OAc)_2$	TBHP (6)	DCE/AcOH[d]	r.t.	60
17	$Cu(OAc)_2$	TBHP (6)	DCE/AcOH[d]	60	14
18	$Pd(OAc)_2$	TBHP (6)	DCE/AcOH[d]	60	22 (18, 32)[g]

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), catalyst (10 mol%), oxidant (4–6 equiv), and solvent (1 mL), r.t. → 100 °C, 12 h, air.
[b] Isolated yield. ND: Not detected.
[c] TBHP (70% solution in H_2O).
[d] DCE/AcOH (1:1, v/v).
[e] AcOH (3 equiv).
[f] Dibenzyl ether (2 equiv) was used.
[g] BnCl, styrene, and benzil were used as acylation reagents instead of **2a**, respectively.



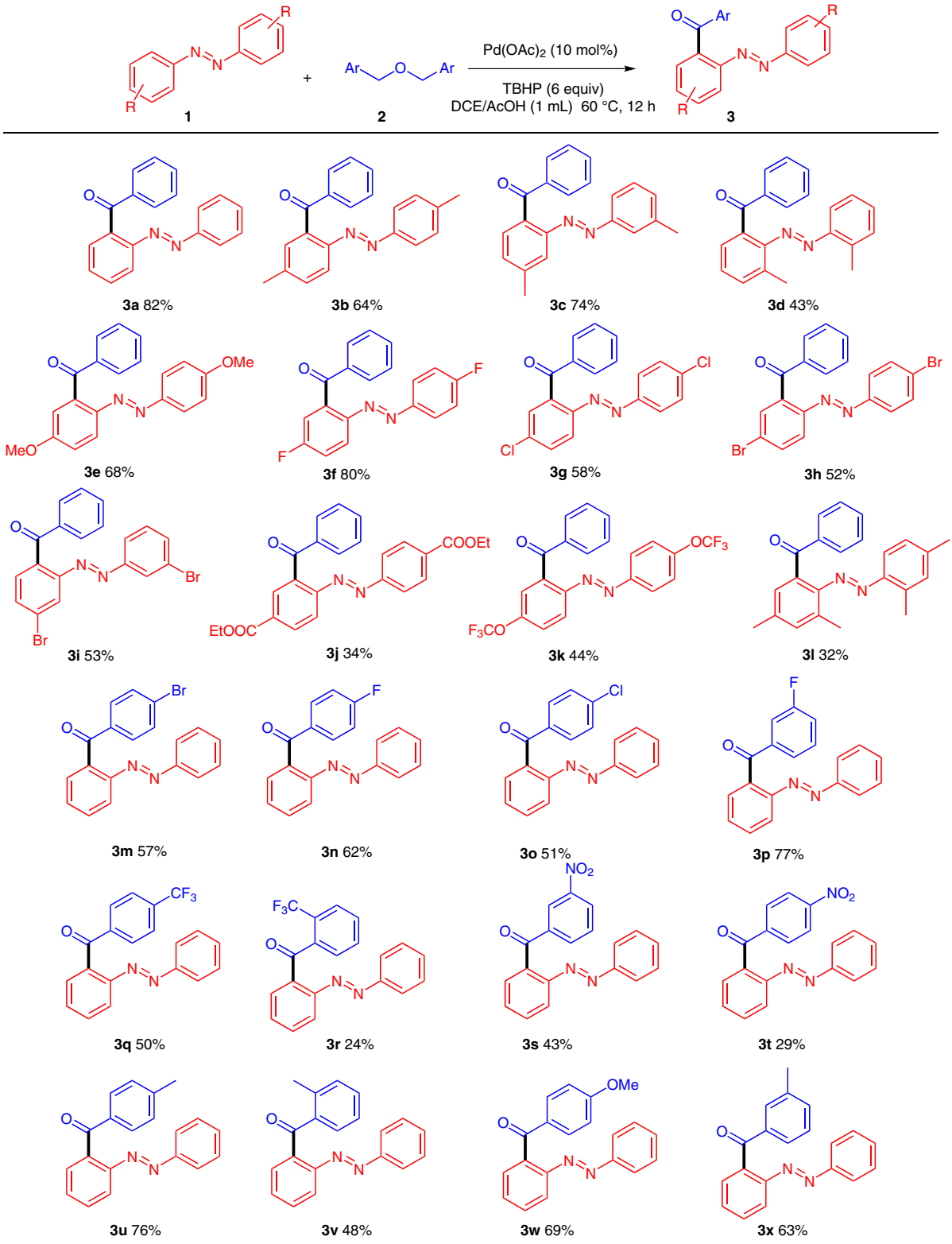
Scheme 1 Approaches for catalytic *ortho*-acylation of azobenzenes

forts towards the functionalization of azobenzenes,[2e] we reasoned that catalytic acylation reaction of azobenzenes with benzylic ethers using TBHP as oxidant is also feasible.

The amide functional group characterizes a vital class of organic compounds having a variety of biological activities and is prevalent in many natural products, pharmaceuticals, and polymers.[16] The synthesis of amides has therefore attracted considerable interest and a number of methods have been developed.[17] Very recently, the *ortho*-amidation of azobenzene under rhodium catalysis using N=N double bond as directing group was developed by Kim's group.[17c] Inspired by our recent work towards the synthesis of amide compounds by reacting azobenzenes with aldehydes and benzyl amines using N=N double bond as radical acceptor,[18] we envisioned that benzylic ethers as aroyl surrogates can also attack the N=N double bond of azobenzene affording the corresponding amide compounds under metal-free conditions (Scheme 1). We herein present the first example of N=N double bond of azobenzene used as both directing group and radical acceptor in one reaction protocol in a controllable fashion.

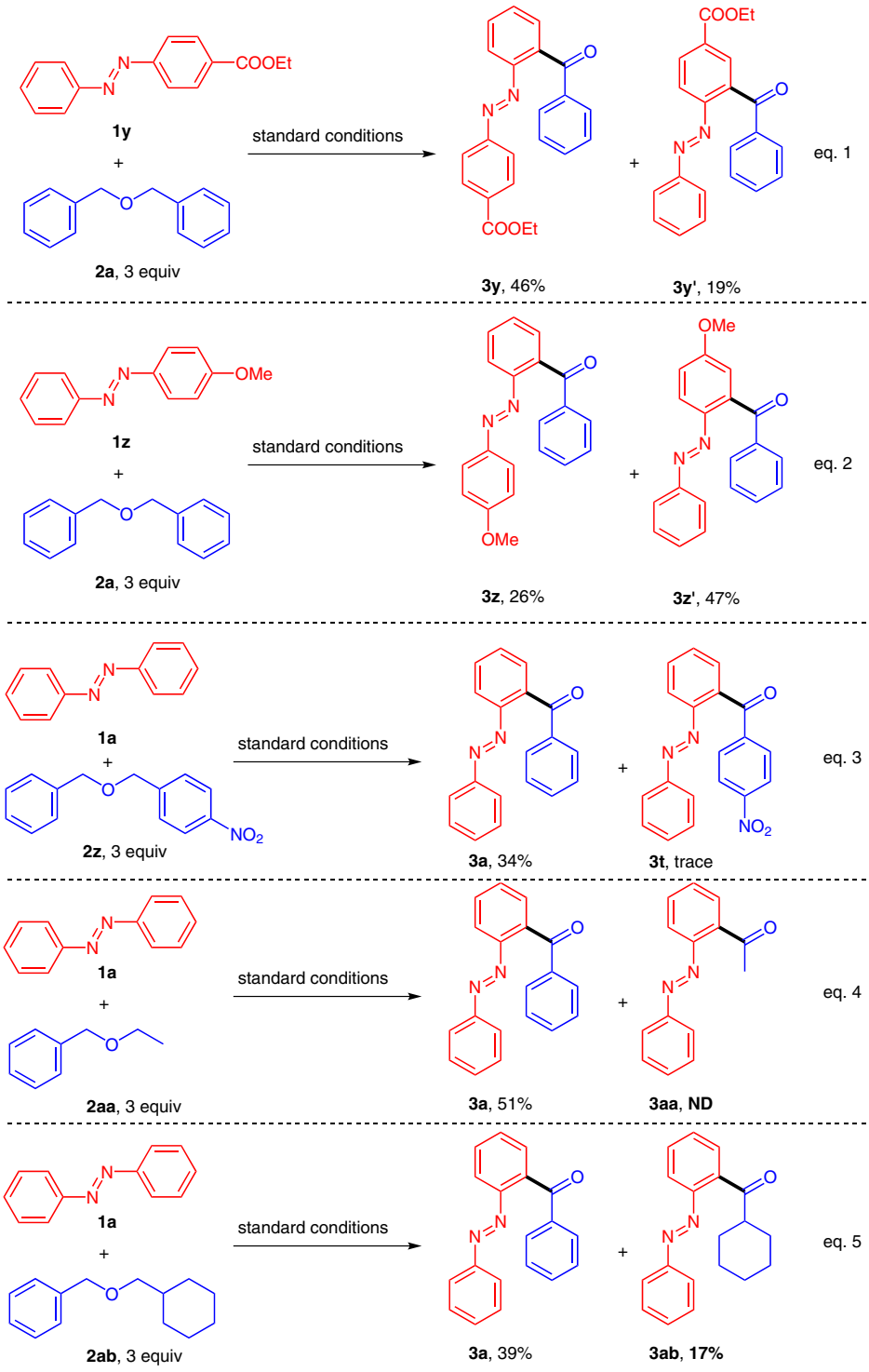
At the outset, the cross-coupling of azobenzene (**1a**) with dibenzyl ether (**2a**) was chosen as a model reaction for optimization of the reaction parameters. The optimization of Pd source and oxidant are summarized in Table 1. It was found that the combination of azobenzene (**1a**) with dibenzyl ether (**2a**, 3 equiv), *tert*-butyl hydroperoxide (TBHP, 6 equiv), and $Pd(OAc)_2$ (10 mol%) in DCE at 60 °C for 12 hours generated the acylated product **3a** in 66% yield (Table 1, entry 1). Then, various Pd catalysts, including $PdCl_2$, $Pd(PPh_3)_2Cl_2$, and $Pd(PPh_3)_4$ were employed with no improvement in yield (entries 2–4). Further exploration of some commercially available oxidants such as di-*tert*-butyl peroxide (DTBP), *tert*-butyl perbenzoate (TBPB), DDQ, and TBHP (70% in H_2O) in the model reaction indicated that TBHP was superior to the others (entries 5–8). Decreasing the amount of TBHP to 4 equivalents had a negative effect on the yield of the product (entry 9). Solvents such as MeCN, DMSO, and 1,4-dioxane were also screened. Fortunately, it was found that DCE/AcOH (1:1, v/v, 1 mL in all) was superior to the others affording the desired product in 82% yield (entries 10–13), which revealed that AcOH is unique in its ability to facilitate high levels of conversion. When 3 equivalents of AcOH were used, a slight decrease in the yield was observed (entry 13). Decreasing the amount of **2a** gave the product in 67% yield (entry 14). The yield was not improved when the temperature was either increased or decreased (entries 15, 16). When $Cu(OAc)_2$ was used instead of $Pd(OAc)_2$, only 14% of the product was obtained, and most of the azobenzene remained intact (entry 17). Subsequently, other acylation reagents such as benzyl chloride, styrene, and benzil were employed to compare the efficiency of this protocol with dibenzyl ether. Lower yields were obtained using these acylation reagents (entry 18).

Based on the optimized reaction conditions, the scope of the oxidative acylation of azobenzenes was examined (Scheme 2). The results demonstrated that the substitution on the benzene ring of azobenzenes showed significant



Scheme 2 Scope of the acylation of azobenzenes with dibenzyl ethers. *Reaction conditions*: azobenzene **1** (0.25 mmol) and dibenzyl ether **2** (0.75 mmol) with $Pd(OAc)_2$ (10 mol%) in the presence of TBHP (6 equiv) in DCE/AcOH (1:1, v/v, 1.0 mL) at 60 °C under air atmosphere for 12 h. Isolated yields.

electronic effects. Substrates with a *para* or *meta* electron-rich groups (such as 4-Me, 3-Me, 4-MeO) on the phenyl ring gave the corresponding products in better yields (**3b**, **3c**, **3e**), while *para* or *meta* electron-withdrawing-group-substituted azobenzenes (4-Cl, 4-Br, 3-Br, 4-CO_2Et, 4-CF_3O) afforded relatively lower yields of the desired acylated products (34–58%, **3g**–**k**). Notably, the azobenzene substituted with F at both the 4-positions afforded the desired product



Scheme 3 Competition experiments

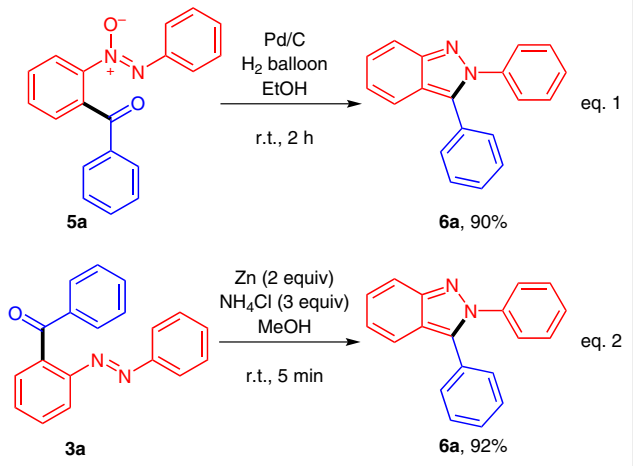
in 80% yield (**3f**). It should be noted that the *ortho*-substituted azobenzenes gave the products in relatively lower yields probably due to the steric hindrance (**3d**, **3l**).

To further explore the generality of this method, various dibenzyl ethers were employed under the optimized conditions (Scheme 2). The reactions of both electron-deficient (such as 4-F, 4-Cl, 4-Br; **3m**–**t**) and electron-rich (such as 4-Me, 2-Me; **3u**–**x**) dibenzyl ethers proceeded smoothly affording the corresponding acylated products in moderate to good yields. However, this transformation was slightly affected by the steric hindrance (**3r**, **3v**).

Next, acylation of unsymmetrically substituted azoarenes with dibenzyl ethers was investigated (Scheme 3, eq. 1 and 2). The reaction proceeded well in both the substrates (**1y** and **1z**), and two isomers of *ortho*-acylation products were obtained respectively. Overall, electron-rich aromatic ring of the azobenzene was more active than electron-poor aromatic ring. Subsequently, intramolecular competitive experiments employing unsymmetrical dibenzyl ethers (**2z**, **2aa** and **2ab**) were conducted (Scheme 3, eq. 3–5). Likewise, electron-rich aromatic ring of the dibenzyl ethers had a positive effect on this reaction. It should be noted that aliphatic part of dibenzyl ether could hardly transform into the corresponding product.

Azoxy compounds are important materials and useful intermediates in electronic devices and they have also been used as dyes, polymer inhibitors, and stabilizers.[19] In light of their importance, recently various methods for the synthesis of azoxybenzene derivatives have been developed through group-directed C–H activaiton.[20] To further explore this protocol, the reaction of azoxybenzene (**4a**) with dibenzyl ether (**2a**) was conducted under the same condition. Delightedly, the desired product **5a** was isolated in 62% yield as the sole isomer (Scheme 4).

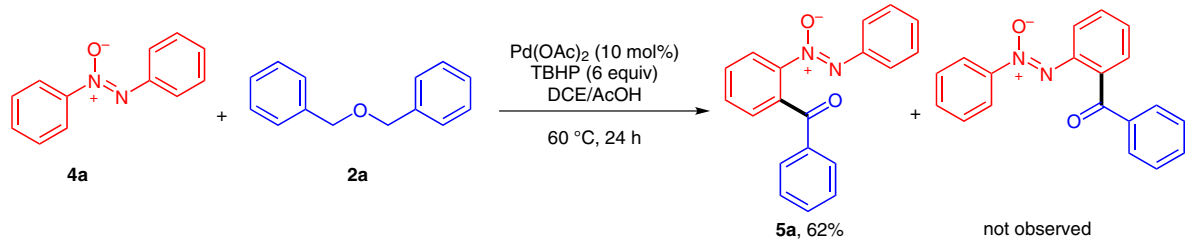
To showcase the applicability of the developed method, the further transformation of the acylated azoxybenzene and azobenzene into indazole under different catalytic systems was investigated (Scheme 5).[20c,21] The reduction of acylated azoxybenzene **5a** was promoted by Pd/C catalyst under H_2 atmosphere affording the desired indazole **6a** in 90% yield (Scheme 5, eq. 1), while the reduction of acylated azobenzene **3a** was based on Zn/NH_4Cl/MeOH system giving the indazole backbone **6a** in 92% yield (Scheme 5, eq. 2).



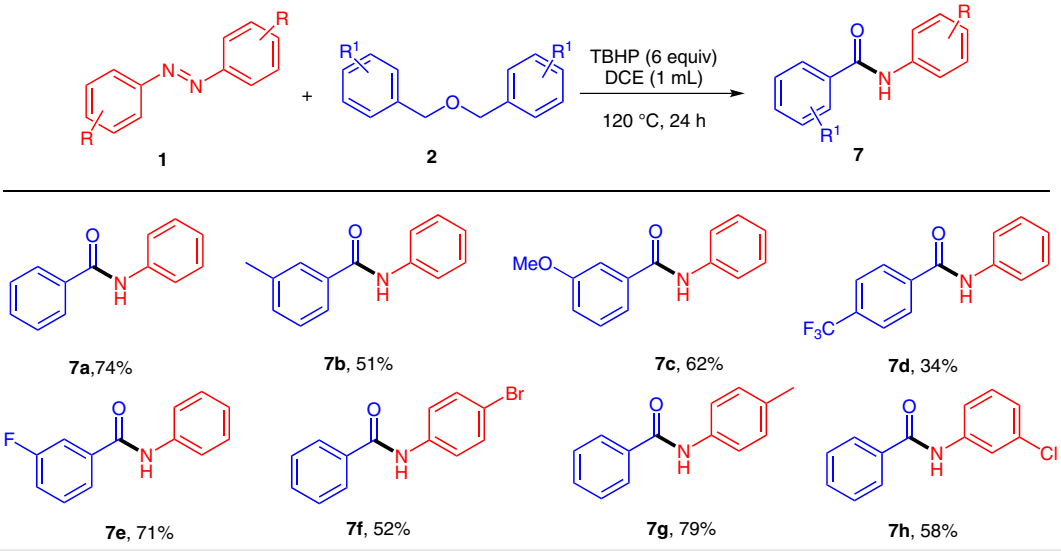
Scheme 5 Further reactions of acylated azoxybenzene and azobenzene

Based on our previous work on the formation of amides employing N=N double bond as radical acceptor attacked by acyl radical,[18] we reasoned that dibenzyl ether as aroyl surrogates could be also used to react with azobenzene generating the corresponding amide compounds. To test the feasibility of the aforementioned hypothesis, reaction conditions including oxidants, additives, temperature, and solvent were first screened for the synthesis of *N*-phenylbenzamide (**7a**) via the reaction of dibenzyl ether with azobenzene (Table 2,Scheme 6). It was found that the most effective reaction conditions were as follows: TBHP (6 equiv) as oxidant, DCE as solvent, at 120 °C, 24 hours. It should be noted that no acylated azobenzene was observed in the absence of palladium catalyst.

Next, the substrate scope of this reaction was investigated by testing various azobenzenes **1** and dibenzyl ether **2** (Scheme 6). We were pleased to find that various dibenzyl ethers could be transferred into the amide compounds in moderate to good yields. Electron-withdrawing groups (such as 4-CF_3, 3-F) and electron-donating groups (such as 3-Me, 3-MeO) substituted dibenzyl ethers were well tolerated under metal-free reaction conditions (**7b**–**e**). Gratifyingly, the presence of various groups (such as 4-Br, 4-Me, 3-Cl) on the azobenzenes allowed the formation of the corresponding desired products in 52–79% yields by reaction



Scheme 4 Pd-catalyzed *ortho*-acylation of azoxybenzene



Scheme 6 Direct amidation of dibenzyl ethers with azobenzenes. *Reaction conditions*: azobenzene **1** (0.25 mmol) and dibenzyl ether **2** (0.75 mmol) in the presence of TBHP (6 equiv) in DCE (1 mL) at 120 °C under air atmosphere for 24 h. Isolated yields.

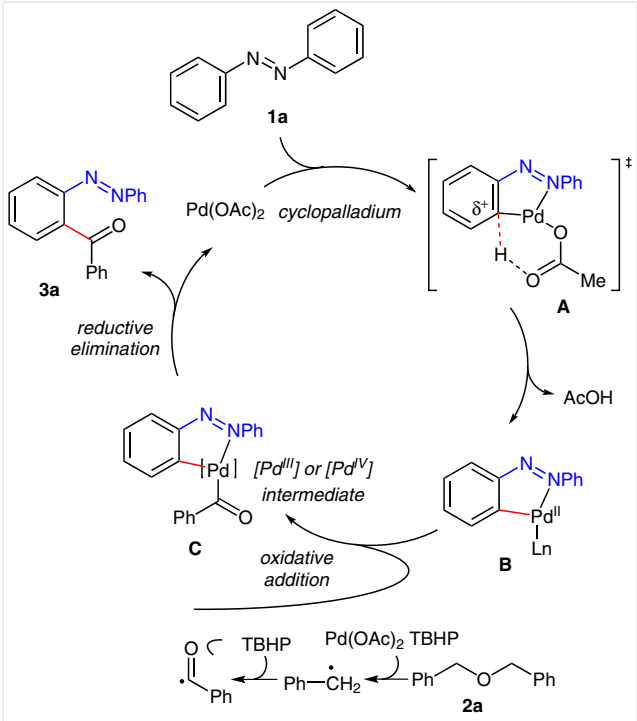
with dibenzyl ethers (**7f**–**h**). A notable feature of the developed method is the use of N=N double bond of the azobenzene as radical acceptor, which, to the best of our knowledge, is rarely reported by other research groups.

Table 2 Selected Results from Screening the Optimal Reaction Conditions[a]

Entry	Oxidant (equiv)	Additive (equiv)	Temp (°C)	Yield (%)[b]
1	TBHP (6)	–	60	ND
2	TBHP (6)	–	100	62
3	TBHP (6)	–	120	74
4	TBHP (6)	I_2 (0.2)	120	68
5	TBHP (6)	TBAI (0.2)	120	44
6	TBHP (6)	KI (1)	120	20
7	TBPB (6)	–	120	47
8	DTBP (6)	–	120	ND
9	DDQ (6)	–	120	ND

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), oxidant, additive, DCE (1 mL), 60–120 °C, 24 h.
[b] Isolated yield. ND: Not detected.

To verify the mechanism of the *ortho*-acylation of azobenzenes with dibenzyl ethers, a radical inhibitor, tetramethylpiperidin-1-oxyl (TEMPO), was introduced in the reaction: 2.5 equivalents of TEMPO could significantly suppress the formation of acylated azobenzene, which provided good evidence to support a radical pathway for the reaction. On the basis of the experimental results and previous reports, a tentative mechanism for Pd-catalyzed *ortho*-acylation of azobenzenes with dibenzyl ethers is outlined in Scheme 7. In the first step, azobenzene coordinating with Pd(II) catalyst by sp^2 C–H activation forms the palladacyclic intermediate **B**.[3] Dibenzyl ether **2a** can be oxidized to benzylic radicals via C–O cleavage by TBHP in the presence of $Pd(OAc)_2$, and these benzylic radicals can be further converted into benzoyl radicals.[15] Then, **B** reacting with benzoyl radicals affords either Pd(III)[22] or Pd(IV)[23] species **C**. Fi-



Scheme 7 Proposed mechanism

nally, product **3a** was formed by the reductive elimination of species **C** with the release of Pd(II) catalyst. As for the mechanism for the formation of amide compound, we reasoned that benzoyl radicals formed from dibenzyl ether attack the N=N double bond leading to the formation of amide product.[18]

In summary, the Pd(II)-catalyzed C–H *ortho*-acylation of azoarenes with dibenzyl ether using TBHP as oxidant has been developed, which provides an easy access to synthesize *ortho*-acylazoarenes in moderate to good yields under mild conditions. In the absence of palladium catalyst, amide compounds are obtained by the reaction of azoarenes with benzylic ethers. The N=N double bond of azobenzene is used for the first time as both directing group and radical acceptor in one-reaction protocol. Further investigations to extend the substrate scope and the applications of such chemistry in organic synthesis are underway.

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz, respectively, using TMS as an internal reference. Chemical shifts (δ) and coupling constants (*J*) are expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Solvents were purified before use. Aromatic azo compound substrates were prepared according to the literature procedure.[24] Dibenzyl ethers were synthesized according to the reported procedure.[25] The procedure for the synthesis of indazole is according to the reported procedure.[20c,21] Column chromatography was performed with silica gel (200–300 mesh ASTM).

ortho-Acylation of Azobenzenes 1 with Dibenzyl Ethers 2; General Procedure

To a sealed tube containing the respective azobenzene **1** (0.25 mmol), dibenzyl ether **2** (0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), and DCE/AcOH (1:1, v/v, 1 mL in all) was added TBHP (1.5 mmol). After stirring vigorously at 60 °C for 12 h, the mixture was evaporated under vacuum. The corresponding product **3** was isolated by silica gel column chromatography with a PE/EtOAc mixture as eluent.

(*E*)-Phenyl[2-(phenyldiazenyl)phenyl]methanone (3a)[6a]

Yield: 58 mg (82%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 6.8 Hz, 2 H), 7.67–7.62 (m, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.48–7.42 (m, 3 H), 7.39–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.2, 151.0, 149.4, 137.4, 135.9, 131.8, 130.4, 129.9, 129.8, 128.4, 127.9, 127.8, 127.3, 121.9, 119.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}N_2O$: 287.1184; found: 287.1181.

(*E*)-[5-Methyl-2-(*p*-tolyldiazenyl)phenyl](phenyl)methanone (3b)[6a]

Yield: 50 mg (64%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 1 H), 7.76 (d, *J* = 7.2 Hz, 2 H), 7.46–7.41 (m, 2 H), 7.36–7.29 (m, 5 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 2.47 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 150.2, 148.5, 141.7, 141.4, 138.6, 136.7, 132.6, 131.5, 129.5, 129.3, 129.2, 128.3, 122.7, 120.2, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O$: 315.1497; found: 315.1500.

(*E*)-[4-Methyl-2-(*m*-tolyldiazenyl)phenyl](phenyl)methanone (3c)[6a]

Yield: 58 mg (74%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.2 Hz, 2 H), 7.71 (s, 1 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.41–7.33 (m, 3 H), 7.25–7.16 (m, 3 H), 7.01 (s, 1 H), 2.51 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 152.2, 150.5, 141.5, 139.0, 138.7, 134.4, 132.5, 132.0, 131.5, 129.4, 129.1, 128.7, 128.2, 122.6, 120.9, 119.6, 21.5, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O$: 315.1497; found: 315.1501.

(*E*)-[3-Methyl-2-(*o*-tolyldiazenyl)phenyl](phenyl)methanone (3d)[6a]

Yield: 34 mg (43%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.6 Hz, 2 H), 7.50–7.41 (m, 2 H), 7.37 (t, *J* = 7.2 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.28–7.21 (m, 4 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.07 (t, *J* = 7.6 Hz, 1 H), 2.77 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 150.2, 150.1, 138.9, 138.1, 137.2, 132.5, 132.4, 131.3, 131.1, 130.0, 128.9, 128.2, 126.5, 126.0, 115.6, 18.4, 17.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{18}N_2ONa$: 337.1317; found: 337.1309.

(*E*)-{5-Methoxy-2-[(4-methoxyphenyl)diazenyl]phenyl}(phenyl)methanone (3e)[6a]

Yield: 59 mg (68%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 9.2 Hz, 1 H), 7.77 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.36 (t, *J* = 6.4 Hz, 4 H), 7.13 (dd, *J* = 8.8, 2.8 Hz, 1 H), 7.34 (d, *J* = 2.8 Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 3.91 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 161.8, 161.3, 146.4, 144.5, 138.4, 138.2, 132.7, 129.3, 128.6, 128.3, 127.0, 124.4, 121.9, 116.7, 113.9, 112.8, 55.8, 55.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O_3$: 347.1396; found: 347.1392.

(*E*)-{5-Fluoro-2-[(4-fluorophenyl)diazenyl]phenyl}(phenyl)methanone (3f)[6a]

Yield: 64 mg (80%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 9.2, 5.6 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 2 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.45–7.26 (m, 6 H), 7.00 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 165.5 (d, *J* = 65.1 Hz), 162.9 (d, *J* = 66.9 Hz), 148.5, 146.6, 139.2 (d, *J* = 7.0 Hz), 138.3, 133.1 (d, *J* = 10.3 Hz), 129.7, 128.6, 124.9 (d, *J* = 9.0 Hz), 122.1 (d, *J* = 8.8 Hz), 118.0, 117.8, 116.1, 115.7 (d, *J* = 20.9 Hz).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{13}F_2N_2O$: 323.0996; found: 323.0996.

(*E*)-{5-Chloro-2-[(4-chlorophenyl)diazenyl]phenyl}(phenyl)methanone (3g)[6a]

Yield: 51 mg (58%); orange solid; mp 120–122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.63–7.56 (m, 2 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.42–7.34 (m, 4 H), 7.29 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 150.2, 148.4, 138.5, 137.9, 137.7, 137.4, 133.2, 130.9, 129.4, 129.3, 128.8, 128.5, 124.2, 121.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{13}Cl_2N_2O$: 355.0405; found: 355.0400.

(*E*)-{5-Bromo-2-[(4-bromophenyl)diazenyl]phenyl}(phenyl)methanone (3h)[6a]

Yield: 58 mg (52%); orange solid; mp 159–161 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 1 H), 7.79–7.72 (m, 4 H), 7.51 (t, *J* = 7.2 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.39 (t, *J* = 7.2 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 150.6, 148.8, 138.7, 138.3, 137.9, 133.9, 133.2, 132.3, 131.7, 129.4, 128.5, 128.4, 126.3, 125.7, 124.4, 121.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{13}Br_2N_2O$: 442.9395; found: 442.9391.

(*E*)-{4-Bromo-2-[(3-bromophenyl)diazenyl]phenyl}(phenyl)methanone (3i)[5b]

Yield: 59 mg (53%); red solid; mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 1.6 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 3 H), 7.55–7.49 (m, 3 H), 7.47–7.39 (m, 3 H), 7.36–7.34 (m, 1 H), 7.26–7.21 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 152.7, 150.5, 138.4, 138.3, 136.7, 134.4, 134.1, 133.2, 130.5, 130.3, 129.4, 128.5, 125.4, 124.5, 123.5, 123.0, 121.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{13}Br_2N_2O$: 442.9395; found 442.9398.

Ethyl (*E*)-3-Benzoyl-4-{[4-(ethoxycarbonyl)phenyl]diazenyl}benzoate (3j)[6a]

Yield: 37 mg (34%); red solid; mp 122–124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34–8.29 (m, 2 H), 8.00 (dd, *J* = 12.0, 8.4 Hz, 3 H), 7.76 (d, *J* = 6.8 Hz, 2 H), 7.50 (dd, *J* = 16.4, 7.2 Hz, 3 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 4.41 (dq, *J* = 24.8, 7.2 Hz, 4 H), 1.41 (dt, *J* = 14.0, 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 165.8, 165.2, 154.3, 152.5, 137.9, 137.3, 133.2, 132.9, 132.8, 132.1, 130.4, 130.3, 129.5, 128.5, 122.9, 119.8, 61.7, 61.4, 14.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{23}N_2O_5$: 431.1607; found: 431.1610.

(*E*)-Phenyl(5-(trifluoromethoxy)-2-{[4-(trifluoromethoxy)phenyl]diazenyl}phenyl)methanone (3k)[5b]

Yield: 50 mg (44%); red solid; mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 2 H), 7.55–7.40 (m, 7 H), 7.16 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1, 151.4, 151.3, 150.9, 148.0, 139.0, 138.3, 133.4, 129.7, 129.4, 124.6, 122.8, 121.5, 121.1, 120.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{13}F_6N_2O_3$: 455.0830; found: 455.0825.

(*E*)-{2-[(2,4-Dimethylphenyl)diazenyl]-3,5-dimethylphenyl}(phenyl)methanone (3l)[26]

Yield: 27 mg (32%); red solid; mp 106–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.38–7.33 (m, 1 H), 7.28–7.23 (m, 4 H), 7.02 (s, 1 H), 6.95 (s, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 2.73 (s, 3 H), 2.40 (s, 3 H), 2.27 (s, 3 H), 2.23 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 148.4, 148.0, 141.5, 140.4, 138.8, 138.1, 137.2, 133.1, 132.3, 131.7, 131.2, 128.9, 128.1, 126.9, 126.8, 115.5, 21.3, 21.2, 18.4, 17.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}N_2O$: 343.1810; found: 343.1804.

(*E*)-(4-Bromophenyl)[2-(phenyldiazenyl)phenyl]methanone (3m)[6a]

Yield: 52 mg (57%); orange solid; mp 92–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.2 Hz, 1 H), 7.67–7.61 (m, 3 H), 7.60–7.54 (m, 2 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.47–7.44 (m, 2 H), 7.40–7.34 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 151.9, 150.3, 137.2, 136.1, 131.7, 131.6, 131.1, 130.9, 130.8, 129.0, 128.7, 127.9, 122.9, 120.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}BrN_2O$: 365.0290; found: 365.0286.

(*E*)-(4-Fluorophenyl)[2-(phenyldiazenyl)phenyl]methanone (3n)[6a]

Yield: 47 mg (62%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 1 H), 7.82–7.77 (m, 2 H), 7.66 (td, *J* = 6.8, 1.6 Hz, 1 H), 7.62–7.54 (m, 2 H), 7.49–7.45 (m, 2 H), 7.39–7.32 (m, 3 H), 7.04 (t, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 165.5 (d, *J* = 253.1 Hz), 151.9, 150.2, 136.5, 134.8, 134.7, 132.0, 131.9, 131.5, 131.0, 130.9, 129.0, 128.7, 122.8, 120.3, 115.6 (d, *J* = 21.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}FN_2O$: 305.1090; found: 305.1084.

(*E*)-(4-Chlorophenyl)[2-(phenyldiazenyl)phenyl]methanone (3o)[6a]

Yield: 41 mg (51%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 8.8 Hz, 2 H), 7.67 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.62–7.54 (m, 2 H), 7.46 (dd, *J* = 7.6, 2.0 Hz, 2 H), 7.40–7.32 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 151.9, 150.3, 139.1, 136.8, 136.1, 131.6, 131.0, 130.9, 130.7, 128.9, 128.7, 128.6, 122.9, 120.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}ClN_2O$: 321.0795; found: 321.0788.

(*E*)-(3-Fluorophenyl)[2-(phenyldiazenyl)phenyl]methanone (3p)

Yield: 58 mg (77%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.6 Hz, 1 H), 7.68 (td, *J* = 6.8, 1.6 Hz, 1 H), 7.63–7.55 (m, 2 H), 7.53–7.45 (m, 4 H), 7.39–7.29 (m, 4 H), 7.20–7.14 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 162.7 (d, *J* = 246.2 Hz), 151.8, 150.4, 140.5 (d, *J* = 6.4 Hz), 135.8, 131.6, 131.1 (d, *J* = 13.3 Hz), 130.0 (d, *J* = 7.6 Hz), 128.9 (d, *J* = 22.9 Hz), 125.2, 122.9, 121.0, 119.7 (d, *J* = 21.4 Hz), 115.6, 115.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}FN_2O$: 305.1090; found: 305.1073.

(*E*)-[2-(Phenyldiazenyl)phenyl][4-(trifluoromethyl)phenyl]methanone (3q)[6a]

Yield: 44 mg (50%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 2 H), 7.73–7.68 (m, 1 H), 7.65–7.61 (m, 4 H), 7.39–7.32 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 151.7, 150.4, 141.4, 135.5, 131.7, 131.5, 131.1, 129.4, 128.9 (q, *J* = 1.4 Hz), 125.4 (q, *J* = 3.7 Hz), 122.8, 122.2, 120.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{14}F_3N_2O$: 355.1058; found: 355.1053.

(*E*)-[2-(Phenyldiazenyl)phenyl][2-(trifluoromethyl)phenyl]methanone (3r)[4a]

Yield: 21 mg (24%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.6 Hz, 1 H), 7.75–7.58 (m, 4 H), 7.48–7.33 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 152.3, 151.3, 140.9, 136.0, 133.2, 132.1, 131.6, 131.3, 130.7, 130.5, 130.1, 129.3, 129,1, 128.8, 126.7 (q, *J* = 4.8 Hz), 123.2 (q, *J* = 20.7 Hz), 122.9, 116.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{13}F_3N_2ONa$: 377.0878; found: 377.0869.

(*E*)-(3-Nitrophenyl)[2-(phenyldiazenyl)phenyl]methanone (3s)[6a]

Yield: 36 mg (43%); orange solid; mp 125–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 8.04 (dd, *J* = 14.8, 8.0 Hz, 2 H), 7.74 (t, *J* = 7.6 Hz, 1 H), 7.68–7.59 (m, 2 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 2 H), 7.39–7.31 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7, 151.5, 150.5, 148.3, 139.9, 134.5, 134.4, 131.9, 131.7, 131.2, 129.6, 129.1, 128.9, 126.8, 123.7, 122.8, 121.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}N_3O_3$: 332.1035; found: 332.1031.

(*E*)-(4-Nitrophenyl)[2-(phenyldiazenyl)phenyl]methanone (3t)[6a]

Yield: 24 mg (29%); orange solid; mp 76–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.8 Hz, 2 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 2 H), 7.74–7.71 (m, 1 H), 7.65–7.61 (m, 2 H), 7.42–7.33 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 151.7, 150.7, 150.1, 143.5, 134.7, 132.2, 131.9, 131.5, 130.1, 129.3, 129.2, 123.9, 123.0, 122.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}N_3O_3$: 332.1035; found: 332.1037.

(*E*)-[2-(Phenyldiazenyl)phenyl](*p*-tolyl)methanone (3u)[6a]

Yield: 57 mg (76%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.6 Hz, 2 H), 7.64–7.55 (m, 3 H), 7.47 (d, *J* = 7.2 Hz, 2 H), 7.37–7.33 (m, 3 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 152.4, 150.5, 143.9, 137.7, 136.2, 131.6, 131.1, 130.9, 129.9, 129.3, 129.2, 128.9, 123.2, 119.9, 22.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2O$: 301.1341; found: 301.1344.

(*E*)-[2-(Phenyldiazenyl)phenyl](*o*-tolyl)methanone (3v)[5b]

Yield: 36 mg (48%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.2 Hz, 1 H), 7.66–7.57 (m, 2 H), 7.40–7.31 (m, 5 H), 7.27 (t, *J* = 7.2 Hz, 2 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.07 (t, *J* = 6.4 Hz, 1 H), 2.57 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 152.8, 151.3, 139.5, 138.9, 138.6, 131.9, 131.8, 131.7, 131.6, 131.2, 131.1, 129.9, 129.3, 125.9, 123.4, 119.3, 21.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2O$: 301.1341; found: 301.1348.

(*E*)-(4-Methoxyphenyl)[2-(phenyldiazenyl)phenyl]methanone (3w)[5b]

Yield: 54 mg (69%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.6 Hz, 1 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 7.64–7.50 (m, 5 H), 7.38–7.21 (m, 3 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 163.4, 152.1, 150.1, 137.8, 131.9, 131.4, 131.3, 130.8, 130.4, 128.9, 128.5, 122.9, 119.3, 113.6, 55.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{16}N_2O_2Na$: 339.1109; found: 339.1101.

(*E*)-[2-(Phenyldiazenyl)phenyl](*m*-tolyl)methanone (3x)[5b]

Yield: 47 mg (63%); red liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.6 Hz, 1 H), 7.67–7.60 (m, 2 H), 7.59–7.55 (m, 2 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 7.46 (dd, *J* = 6.4, 1.6 Hz, 2 H), 7.38–7.31 (m, 3 H), 7.29–7.22 (m, 2 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 152.5, 150.8, 138.9, 138.6, 137.6, 134.0, 131.8, 131.3, 131.2, 130.2, 129.4, 129.2, 128.7, 127.4, 123.4, 120.4, 21.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2O$: 301.1341; found: 301.1338.

Ethyl (*E*)-4-[(2-Benzoylphenyl)diazenyl]benzoate (3y)[6a]

Yield: 41 mg (46%); red solid; mp 114–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2 H), 7.96 (d, *J* = 7.6 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 2 H), 7.68–7.61 (m, 3 H), 7.50–7.43 (m, 3 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 4.37 (q, *J* = 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 165.9, 154.4, 150.2, 138.4, 137.3, 132.9, 132.4, 131.6, 130.9, 130.4, 129.4, 129.0, 128.8, 122.6, 119.9, 61.3, 14.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}N_2O_3$: 359.1396; found: 359.1384.

Ethyl (*E*)-3-Benzoyl-4-(phenyldiazenyl)benzoate (3y')[6a]

Yield: 17 mg (19%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 2 H), 7.55–7.50 (m, 3 H), 7.42–7.36 (m, 5 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 165.2, 152.2, 149.8, 138.4, 137.9, 133.2, 133.0, 132.4, 131.9, 130.9, 130.0, 129.7, 128.5, 123.2, 119.8, 61.6, 14.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}N_2O_3$: 359.1396; found: 359.1391.

(*E*)-{2-[(4-Methoxyphenyl)diazenyl]phenyl}(phenyl)methanone (3z)[5a]

Yield: 21 mg (26%); orange solid; mp 91–93 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 7.75 (s, 1 H), 7.63–7.60 (m, 1 H), 7.56–7.53 (m, 2 H), 7.50–7.42 (m, 3 H), 7.32–7.27 (m, 2 H), 6.80 (d, *J* = 9.2 Hz, 2 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 162.3, 150.6, 146.5, 138.6, 136.5, 132.6, 130.8, 130.4, 130.2, 128.4, 128.3, 124.9, 120.0, 114.0, 55.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2O_2$: 317.1290; found: 317.1291.

(*E*)-[5-Methoxy-2-(phenyldiazenyl)phenyl](phenyl)methanone (3z')[5a]

Yield: 37 mg (47%); orange solid; mp 119–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.8 Hz, 1 H), 7.79 (d, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.41–7.35 (m, 4 H), 7.32–7.28 (m, 3 H), 7.15 (dd, *J* = 8.8, 2.8 Hz, 1 H), 7.05 (d, *J* = 2.8 Hz, 1 H), 3.91 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9, 161.8, 152.0, 144.4, 138.9, 138.3, 132.8, 130.7, 129.3, 128.8, 128.3, 122.6, 122.2, 116.7, 112.9, 55.8.

HRMS (ESI-TOF): *m*/*z* = [M + H]$^+$ calcd for $C_{20}H_{17}N_2O_2$: 317.1290; found: 317.1295.

(*E*)-Cyclohexyl[2-(phenyldiazenyl)phenyl]methanone (3ab)[3]

Yield: 13 mg (17%); orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.57–7.46 (m, 6 H), 2.99–2.93 (m, 1 H), 1.93 (d, *J* = 11.2 Hz, 2 H), 1.79–1.72 (m, 2 H), 1.67–1.59 (m, 2 H), 1.48–1.43 (m, 2 H), 1.26–1.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 152.4, 149.8, 138.9, 131.6, 130.6, 129.2, 128.1, 123.2, 118.5, 51.8, 28.7, 25.8, 25.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{21}N_2O$: 293.1654; found: 293.1651.

(*E*)-1-(2-Benzoylphenyl)-2-phenyldiazene Oxide (5a)[20b]

Yield: 47 mg (62%); pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26–8.22 (m, 1 H), 7.77 (d, *J* = 7.2 Hz, 2 H), 7.72–7.65 (m, 4 H), 7.55–7.52 (m, 1 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.36 (t, *J* = 8.0 Hz, 2 H), 7.33–7.28 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 147.2, 143.1, 136.9, 134.7, 133.1, 131.4, 130.5, 129.9, 128.9, 128.8, 128.5, 128.4, 124.9, 123.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{14}N_2O_2Na$: 325.0953; found: 325.0958.

2,3-Diphenyl-2*H*-indazole (6a)[3]

Yield: 62 mg (92%); white solid; mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.45–7.34 (m, 11 H), 7.16–7.11 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 140.2, 135.4, 129.9, 129.7, 129.0, 128.8, 128.3, 128.2, 127.0, 126.0, 122.5, 121.8, 120.5, 117.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}N_2$: 271.1235; found: 271.1235.

Synthesis of Amide Compounds by Reacting Dibenzyl Ethers 2 with Azobenzenes 1; General Procedure

A mixture of azobenzene **1** (0.25 mmol), dibenzyl ether **2** (0.75 mmol), TBHP (1.5 mmol), and DCE (1 mL) was charged into a sealed tube. After stirring vigorously at 120 °C for 24 h, the mixture was evaporated under vacuum. The corresponding product **7** was isolated by silica gel column chromatography with a PE/EtOAc mixture as eluent.

***N*-Phenylbenzamide (7a)**[27]

Yield: 36 mg (74%); white solid; mp 162–164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.2 Hz, 2 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.16 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 137.9, 135.0, 131.9, 129.1, 128.8, 127.0, 124.5, 120.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{12}NO$: 198.0919; found: 198.0902.

3-Methyl-*N*-phenylbenzamide (7b)[27]

Yield: 27 mg (51%); pale yellow solid; mp 123–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (br s, 1 H), 7.68–7.63 (m, 4 H), 7.38–7.33 (m, 4 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 138.7, 138.0, 135.0, 132.6, 129.1, 128.6, 127.8, 124.5, 124.0, 120.3, 21.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1075; found: 212.1070.

3-Methoxy-*N*-phenylbenzamide (7c)[27]

Yield: 35 mg (62%); white solid; mp 114–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.46–7.44 (m, 1 H), 7.41–7.36 (m, 4 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.11–7.07 (m, 1 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 160.0, 137.9, 136.5, 129.8, 129.1, 124.6, 120.1, 118.6, 118.0, 112.5, 55.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{13}NO_2Na$: 250.0844; found: 250.0840.

***N*-Phenyl-4-(trifluoromethyl)benzamide (7d)**[28]

Yield: 23 mg (34%); white solid; mp 196–198 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.0 Hz, 2 H), 7.82 (s, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 7.6 Hz, 2 H), 7.20 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 138.8, 133.9, 131.0, 129.2, 127.5, 125.9, 125.1, 123.6, 120.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}F_3NO$: 266.0793; found: 266.0791.

3-Fluoro-*N*-phenylbenzamide (7e)[27]

Yield: 38 mg (71%); white solid; mp 174–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (br s, 1 H), 7.64–7.56 (m, 4 H), 7.46–7.41 (m, 1 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.25–7.23 (m, 1 H), 7.17 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 162.8 (d, *J* = 247.5 Hz), 137.6, 137.2 (d, *J* = 6.7 Hz), 130.5 (d, *J* = 7.9 Hz), 129.1, 124.9, 122.5, 120.3, 118.9 (d, *J* = 21.2 Hz), 114.5 (d, *J* = 22.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}FNO$: 216.0825; found: 216.0829.

***N*-(4-Bromophenyl)benzamide (7f)**[29]

Yield: 36 mg (52%); pale yellow solid; mp 201–203 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 6.8 Hz, 2 H), 7.81 (s, 1 H), 7.58–7.47 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 134.5, 133.6, 132.0, 131.9, 130.1, 128.8, 126.9, 121.6. 117.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}BrNO$: 276.0024; found: 276.0029.

***N*-(*p*-Tolyl)benzamide (7g)**[27]

Yield: 42 mg (79%); white solid; mp 158–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 3 H), 7.52 (d, *J* = 8.4 Hz, 3 H), 7.49–7.43 (m, 2 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 135.4, 135.1, 134.2, 131.7, 129.6, 128.7, 127.0, 120.3, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1075; found: 212.1078.

***N*-(3-Chlorophenyl)benzamide (7h)**[27]

Yield: 34 mg (58%); pale yellow solid; mp 118–120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (br s, 1 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.76 (s, 1 H), 7.54–7.42 (m, 4 H), 7.29–7.22 (m, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 139.0, 134.7, 134.5, 132.1, 130.0, 128.8, 127.1, 124.6, 120.4, 118.3.

HRMS (ESI-TOF): *m*/*z* [M – H]$^+$ calcd for $C_{13}H_9ClNO$: 230.0373; found: 230.0371.

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Supporting Information

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