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Peroxide-mediated direct synthesis of amides from aroyl surrogates

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ABSTRACT

An efficient and metal-free method has been developed for the direct synthesis of amides from readily available azobenzenes reacting with aroyl surrogates such as alcohols, methylarenes. A variety of amides were afforded in moderate to good yields through this reaction. It is another example reported by our group for the use of azobenzene as the new radical acceptor.

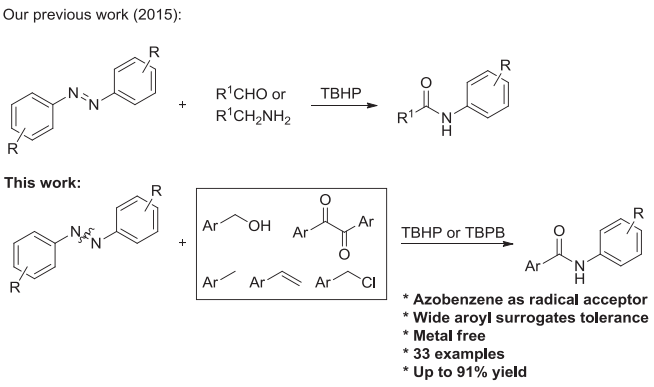
1. Introduction

The amide functional group is ubiquitous in numerous significant valuable compounds.[1] Traditionally, the synthesis of amides involves the coupling of carboxylic acid derivatives with amines.[2] Later on, considerable alternative methods such as Staudinger reaction,[3] Beckmann rearrangement,[4] Ugi reaction,[5] iodonium-promoted coupling of amine with α-halonitroalkane,[6] transamidation of amines[7] were developed to create amide compounds. Recently, alcohols[8] and methylarenes[9] were also successfully adopted to synthesize amides.

Nevertheless, the above mentioned methodologies often suffer from drawbacks such as the use of expensive transition metal catalysts, the limited substrate scope and the utilization of co-reagents. Hence, a new method for the synthesis of amides is still highly desirable.

Lately, aromatic azo compounds have attracted much attention for their unique properties[10] and extensive applications.[11] Our group also utilized azobenzene as a new directing group to realize *ortho*-C–H phosphonation,[12] which further expanded the synthesis of steric azo compounds. On the other hand, the reduction of azo compounds to the corresponding amines is a useful transformation both in the laboratory and in industry. Thus, various methods were developed to transform these azo compounds.[13] Our recent studies have been focusing on the development of new synthetic pathways for the synthesis of amides through the cleavage of N=N double bond of azobenzenes,[14] where aldehydes and benzyl amines as aroyl surrogates generated acyl radical to attack the N=N double bond. Since primary alcohols, especially benzyl alcohols,[15] and toluene derivatives can be easily oxidized into the corresponding aldehydes,[16] it can be reasoned that azobenzenes as new radical acceptors can also be attacked by other aroyl surrogates such as alcohols and toluene derivatives in similar pattern affording the corresponding amide compounds.

Herein we describe the direct synthesis of amide compounds from readily accessible azobenzenes and aroyl surrogates (Scheme 1). The present method features a much broad scope on amide synthesis, and eliminates the requirement of metal catalyst.



Scheme 1. Different methods for the formation of amides.

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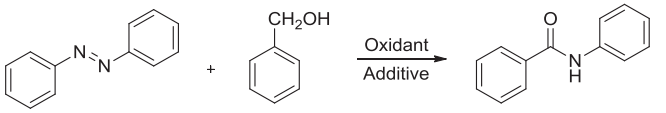
2. Results and discussion

Initially, azobenzene (**1a**) and benzyl alcohol (**2a**) were used as the model substrates to screen the reaction conditions (Table 1). We were pleased to find that when the mixture of azobenzene (0.25 mmol) and benzyl alcohol (0.5 mmol) was treated with various oxidants including *tert*-butyl hydroperoxide (TBHP, 70% solution in water), di-*tert*-butyl peroxide (DTBP), DDQ, MnO_2, and *tert*-butyl peroxybenzoate (TBPB) in DCE (1 mL) at 120 °C for 24 h, TBHP provided a 68% yield of the desired product **4a** (Table 1, entries 1–5). Some additives such as KOH, $Fe(acac)_2$, $Cu(OAc)_2$, I_2, TBAI, etc. were also tested, but no improvement in yield was observed (Table 1, entries 6–14). Increasing the amount of TBHP to 5 equiv led to a lower yield (Table 1, entry 15). Then several solvents (dioxane, CH_3CN, PhCl, and DMF) were evaluated and it was found that CH_3CN turned out to be the best solvent affording the desired product **4a** in 83% yield (Table 1, entries 16–19). Decreasing the temperature to 100 °C or 80 °C brought a reduction in the yield (Table 1, entry 20).

Table 1
Optimization of the reaction conditions[a]



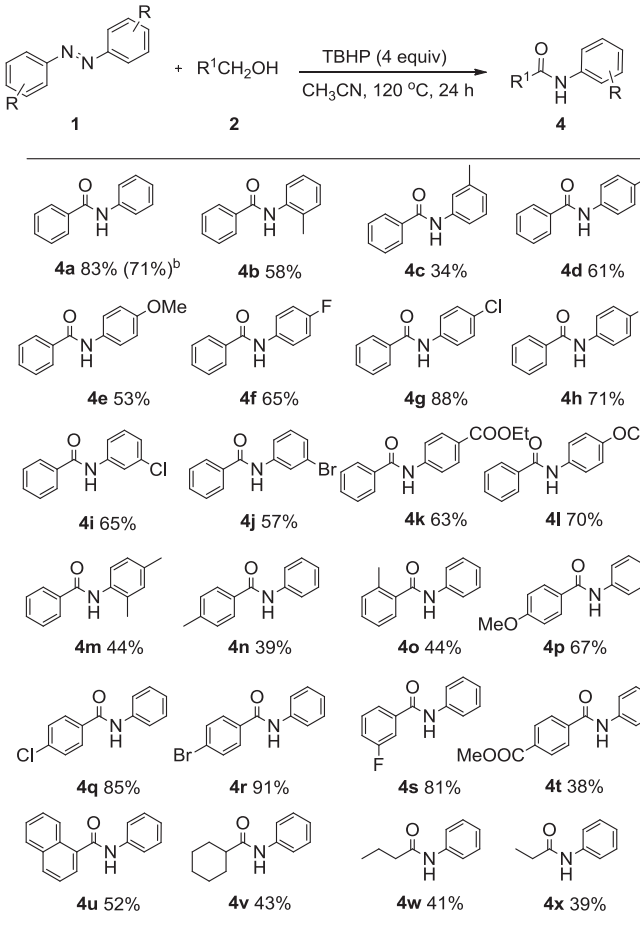
1a 2a 4a

Entry	Oxidant	Additive (equiv)	Solvent	*T* [°C]	Yield [%][b]
1	TBHP	/	DCE	120	68
2	DTBP	/	DCE	120	Trace
3	DDQ	/	DCE	120	0
4	MnO_2	/	DCE	120	0
5	TBPB	/	DCE	120	32
6	TBHP	KOH (1)	DCE	120	36
7	TBHP	$Fe(acac)_2$ (0.1)	DCE	120	26
8	TBHP	$Cu(OAc)_2$ (0.2)	DCE	120	0
9	TBHP	I_2 (0.2)	DCE	120	0
10	TBHP	TBAI (0.2)	DCE	120	Trace
11	TBHP	^{t}BuOK (1)	DCE	120	35
12	TBHP	NBS (0.2)	DCE	120	0
13	TBHP	PivOH (2)	DCE	120	16
14	TBHP	TBAB (1)	DCE	120	40
15	TBHP	/	DCE	120	45[c]
16	TBHP	/	dioxane	120	12
17	TBHP	/	CH_3CN	120	83
18	TBHP	/	PhCl	120	40
19	TBHP	/	DMF	120	0
20	TBHP	/	CH_3CN	100	47 (29)[d]

[a] Unless otherwise noted, general reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), oxidant (4 equiv), additive and solvent (1 mL), 24 h, air.
[b] Isolated yield.
[c] TBHP (5 equiv) was used.
[d] 80 °C.

Using our optimized conditions, we proceeded to investigate the substrate scope of this reaction, and the results are revealed in Table 2. It was found that the moderate to excellent yields were obtained for most cases. Azobenzenes bearing electron-donating such as methyl, methoxy groups at various position of the phenyl ring reacted smoothly to give the corresponding products **4b**–**e** in 34–61% yields. It should be noted that substrates with *para* or *meta* electron-withdrawing group (such as 4-F, 4-Cl, 4-Br, 3-Cl, 3-Br, 4-COOEt, 4-OCF_3) could give the desired products in moderate to excellent yields (57–88%, Table 2, **4f**–**l**). Overall, electron-poor azobenzenes were relatively more reactive than electron-rich azobenzenes. The steric effects of substituents of the azobenzene were well tolerated. 2,4-Dimethylazobenzene delivered the desired product **4m** in 44% yield.

Table 2
Direct amidation of alcohols with azobenzenes[a]



[a]General reaction conditions: azobenzenes **1** (0.25 mmol), alcohols **2** (0.5 mmol), TBHP (4 equiv) and CH_3CN (1 mL) at 120 °C for 24 h; Isolated yield.

[b]Reaction performed on a 5 mmol scale.

Next, the scope and generality of alcohols were explored under the standard reaction conditions (Table 2, **4n**–**x**). The reaction did not show an obvious electronic effect. As for the substitution pattern, higher yields were obtained with *para*-substituted benzyl alcohols containing halo groups in comparison with those bearing methyl, methoxy and ester groups (Table 2, **4n**–**t**). To our delight, the reaction could also be applied to naphthalene-1-methanol to give **4u** in 52% yield. Furthermore, aliphatic alcohols such as cyclohexylmethanol, *n*-butanol, and 1-propanol could also be transformed into corresponding products in 39–43% yields (Table 2, **4v**–**x**).

Since toluene derivatives can also work as aroyl surrogate under certain conditions,[16] we investigated the amidation reaction of azobenzenes with toluene derivatives. Reaction conditions including oxidants, additives, temperature were first investigated for the synthesis of *N*-phenylbenzamide (**4a**) via reaction of toluene with azobenzene, and the results showed that the optimal conditions were as follows: using 4 equiv TBPB as the oxidant, toluene derivatives as the solvent at 120 °C for 24 h (Table S1, see Supplementary data). After getting the optimum reaction conditions, we investigated the scope for TBPB-mediated amidation of azobenzene (**1a**) with toluene derivatives (**3**). As shown in Table 3, the tested substrates provided good to excellent yields. Substituents present in the phenyl ring of alkylbenzenes played a role in controlling the product yields as evident from their yields (Table 3). It should be noted that methylbenzenes bearing additional methyl groups in various position provided good

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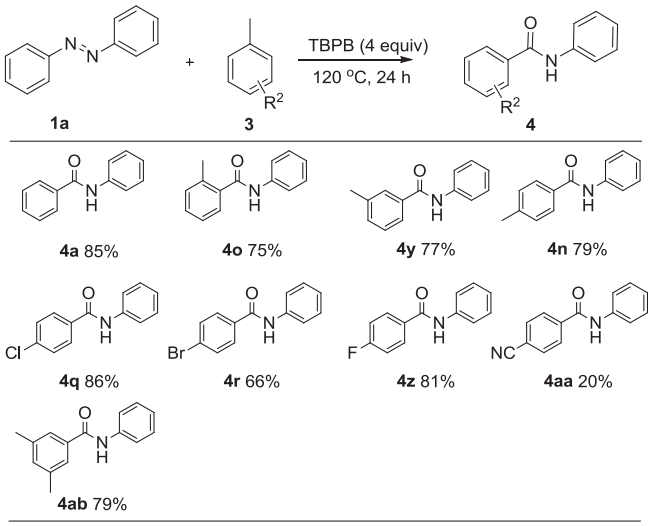
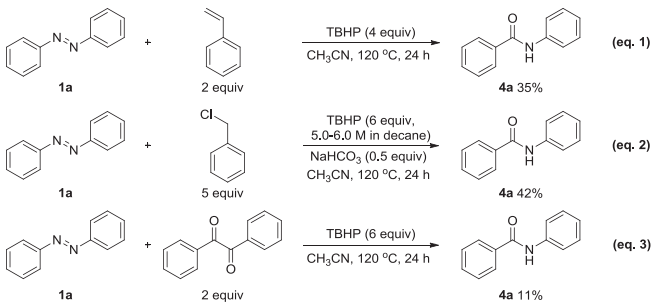
Table 3
Direct amidation of toluene derivatives with azobenzene[a]



[a]General reaction conditions: azobenzene **1a** (0.25 mmol), toluene derivatives **3** (1 mL), TBPB (4 equiv) at 120 °C for 24 h; Isolated yield.

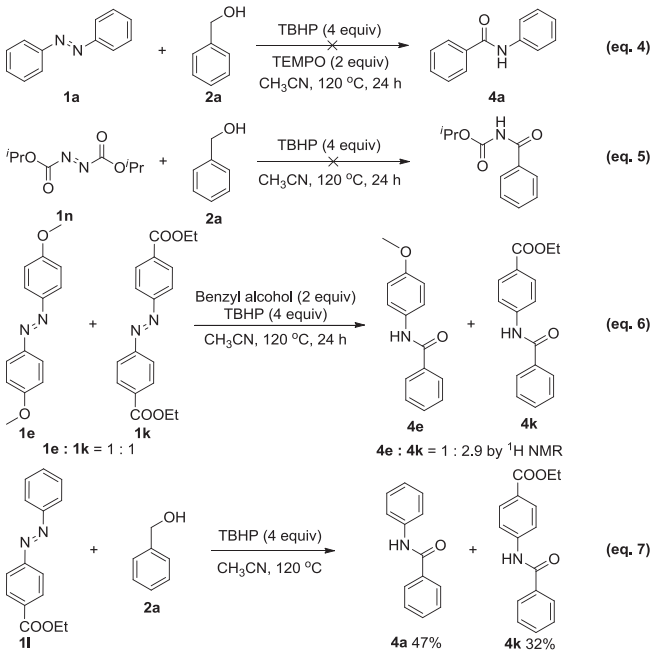
yields of corresponding products with the retention of other methyl groups (Table 3, **4o**, **4y**, **4n** and **4ab**). Additionally, the reaction conditions were also compatible with halo-substituted toluenes, such as F, Cl, Br groups providing the desired products in 66–86% yields (Table 3, **4q**, **4r** and **4z**). Unfortunately, electron withdrawing group (4-CN) on the phenyl ring afforded the desired products only in 20% yield (Table 3, **4aa**).

Proceeding further toward the substrate exploration of this protocol, other acylation reagents such as benzil,[17] styrene,[18] and benzyl chloride[19] were investigated according to related literature. Styrene reacted with **1a** providing product **4a** in 35% yield (Scheme 2, Eq. 1), while the reaction of benzyl chloride with **1a** delivered the desired product **4a** in 42% yield (Scheme 2, Eq. 2). However, most starting materials remained when benzil was used as acylation reagents (Scheme 2, Eq. 3). Overall, the initially systematic research concerning this interesting reaction has been conducted by our group.



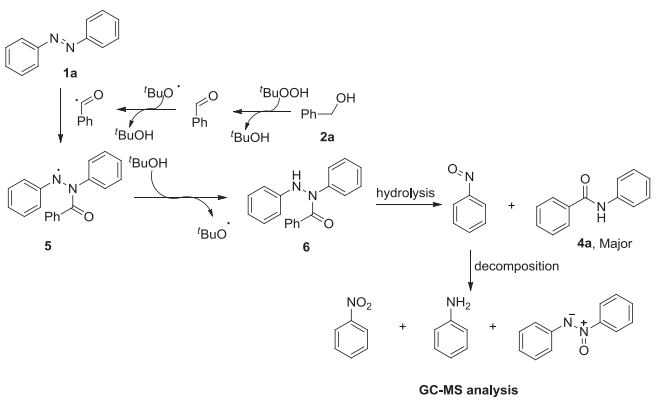
Scheme 2. Direct amidation of different acylation reagents with azobenzene.

To gain insight into the reaction mechanism, several control reactions were carried out, as shown in Scheme 3. First, addition of the radical-trapping reagents TEMPO can completely inhibit the reaction and no desired product was observed, which suggests the transformation may proceed via a radical course (Scheme 3, Eq. 4). When nonaromatic azo compound (diisopropyl diazene-1,2-dicarboxylate) reacted with benzyl alcohol, no desired product was formed, which indicates azo aromatic compounds as substrates are essential for this reaction (Scheme 3, Eq. 5). To further investigate the electronic effect of the substrate on the reaction, a scrambling test of **1e** and **1k** with benzyl alcohol under the optimized conditions was conducted. Product **4k** was slightly favored over **4e** indicating the electron-poor azobenzene shows relatively higher reactivity (Scheme 3, Eq. 6). Unsymmetrically substituted azobenzene proceeded successfully in this reaction affording **4a** and **4k** in 47% and 32% yields, respectively (Scheme 3, Eq. 7), which suggests different position of the N=N double bond can be attacked by acyl radical when unsymmetrically substituted azobenzene is used.



Scheme 3. Preliminary mechanistic studies.

Based on these experimental results and previous reports including our previous work,[14] the proposed mechanism is outlined in Scheme 4. In step one, benzylic alcohol (**2a**) could be converted to benzaldehyde readily by TBHP, and transferred to acyl radical.[20] Then azobenzene (**1a**) would react with the acyl radicals to afford intermediate **5**,[21] which could abstract a H atom from the ^{t}BuOH to give intermediate **6**.[22] Finally, the major product **4a** and nitrosobenzene could be obtained by the hydrolysis of intermediate **6**.[23] At the same time, trace of aniline, azoxybenzene and nitrobenzene could be observed due to the decomposition of the unstable nitrosobenzene (see ESI for GC–MS analysis of the reaction mixtures). It can be reasoned that similar process is involved in the reaction of other acylation reagents with azobenzenes.



Scheme 4. Proposed mechanism.

3. Conclusion

In conclusion, we have successfully developed an efficient and metal-free synthesis of amide compounds, starting from aroyl surrogates and azobenzenes. The reaction condition is mild and it has broad substrate scope. This method further extends the application of azobenzenes as synthon in organic synthesis. It is another example for the application of azobenzenes as new radical acceptors. Further investigations to extend the substrate scope and the applications of such chemistry in organic synthesis are underway.

4. Experimental section

4.1. General information

^{1}H NMR, ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz, respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Aromatic azo compound substrates were prepared according to the literature procedure.[24] Chromatography: Column chromatography was performed with silica gel (200–300 mesh ASTM).

4.2. Typical procedure for TBHP-mediated reaction of alcohols with azobenzenes

The mixture of azobenzenes **1** (0.25 mmol), alcohols **2** (0.5 mmol), TBHP (1 mmol) and CH_3CN (1 mL) were added into a sealed tube under air. After being stirred vigorously at 120 °C for 24 h, the mixture was evaporated under vacuum. The corresponding product was isolated by silica gel column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

*4.2.1. N-Phenylbenzamide (**4a**).*[25] White solid (41 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (br s, 1H), 7.85 (d, J=7.2 Hz, 2H), 7.64 (d, J=7.6 Hz, 2H), 7.54–7.51 (m, 1H), 7.46 (t, J=7.6 Hz, 2H), 7.35 (t, J=7.6 Hz, 2H), 7.14 (t, J=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 137.9, 135.0, 131.9, 129.1, 128.8, 127.1, 124.6, 120.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}NO$ 198.0919; found 198.0928.

*4.2.2. N-(o-Tolyl)benzamide (**4b**).*[25] White solid (31 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J=8.0 Hz, 1H), 7.88 (d, J=7.2 Hz, 2H), 7.72 (br s, 1H), 7.56 (t, J=7.2 Hz, 1H), 7.51–7.47 (m, 2H), 7.28–7.22 (t, J=7.6 Hz, 2H), 7.14–7.10 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 135.8, 135.0, 131.9, 130.6, 129.4, 128.9, 127.1, 126.9, 125.4, 123.2, 17.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075; found 212.1066.

*4.2.3. N-(m-Tolyl)benzamide (**4c**).*[25] White solid (18 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (br s, 1H), 7.85 (d, J=7.2 Hz, 2H), 7.54–7.40 (m, 5H), 7.23 (t, J=8.0 Hz, 1H), 6.96 (d, J=7.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 139.0, 137.9, 135.1, 131.8, 128.9, 128.8, 127.0, 125.4, 120.9, 117.3, 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075; found 212.1071.

*4.2.4. N-(p-Tolyl)benzamide (**4d**).*[25] White solid (32 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (br s, 1H), 7.84 (d, J=7.2 Hz, 2H), 7.54–7.49 (m, 3H), 7.46–7.41 (m, 2H), 7.14 (d, J=8.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 135.4, 135.1, 134.2, 131.7, 129.6, 128.7, 127.1, 120.4, 20.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075; found 212.1078.

*4.2.5. N-(4-Methoxyphenyl)benzamide (**4e**).*[25] Pale yellow solid (30 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J=7.2 Hz, 3H), 7.55–7.51 (m, 3H), 7.46 (t, J=7.6 Hz, 2H), 6.90 (d, J=8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 156.6, 135.0, 131.7, 131.0, 128.8, 127.0, 122.2, 114.2, 55.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1025; found 228.1027.

*4.2.6. N-(4-Fluorophenyl)benzamide (**4f**).*[25] Pale yellow solid (35 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J=7.2 Hz, 2H), 7.84 (br s, 1H), 7.62–7.58 (m, 2H), 7.55 (d, J=7.2 Hz, 1H), 7.49 (t, J=7.2 Hz, 2H), 7.07 (t, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 160.8, 158.3, 134.7, 133.9, 132.0, 128.8, 127.0, 122.1 (J=7.8 Hz), 115.9, 115.7. HRMS (ESI-TOF) m/z: $[M-H]^-$ calcd for $C_{13}H_9FNO$ 214.0668; found 214.0647.

*4.2.7. N-(4-Chlorophenyl)benzamide (**4g**).*[25] Pale yellow solid (51 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J=7.2 Hz, 2H), 7.85 (br s, 1H), 7.62–7.55 (m, 3H), 7.50 (t, J=7.6 Hz, 2H), 7.34 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 136.5, 134.6, 132.1, 129.6, 129.1, 128.9, 127.0, 121.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529; found 232.0522.

*4.2.8. N-(4-Bromophenyl)benzamide (**4h**).*[26] Pale yellow solid (48 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J=7.2 Hz, 2H), 7.83 (br s, 1H), 7.59–7.54 (m, 3H), 7.52–7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 137.0, 134.6, 132.1, 128.9, 127.0, 121.7, 117.2. HRMS (ESI-TOF) m/z: $[M-H]^-$ calcd for $C_{13}H_9BrNO$ 273.9868; found 273.9861.

*4.2.9. N-(3-Chlorophenyl)benzamide (**4i**).*[25] Pale yellow solid (38 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (br s, 1H), 7.81 (d, J=7.2 Hz, 2H), 7.76–7.74 (m, 1H), 7.52–7.40 (m, 4H), 7.23 (t, J=8.0 Hz, 1H), 7.11–7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 139.1, 134.7, 134.5, 132.1, 130.0, 128.8, 127.1, 124.6, 120.5, 118.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529; found 232.0523.

*4.2.10. N-(3-Bromophenyl)benzamide (**4j**).*[25] White solid (39 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (br s, 1H), 7.91–7.89 (m, 1H), 7.84–7.82 (m, 2H), 7.54 (t, J=7.2 Hz, 2H), 7.45 (t, J=7.6 Hz, 2H), 7.27–7.25 (m, 1H), 7.20 (t, J=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 139.2, 134.5, 132.1, 130.3, 128.8, 127.6, 127.1, 123.2, 122.7, 118.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}BrNO$ 276.0024; found 276.0022.

*4.2.11. Ethyl 4-benzamidobenzoate (**4k**).*[27] White solid (42 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br s, 1H), 8.03 (d, J=8.8 Hz, 2H), 7.87 (d, J=7.2 Hz, 2H), 7.75 (d, J=8.8 Hz, 2H), 7.57–7.53 (m, 1H), 7.47 (t, J=7.2 Hz, 2H), 4.36 (q, J=7.2 Hz, 2H), 1.39 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 166.0, 142.2, 134.5, 132.2, 130.8, 128.9, 127.1, 126.1, 119.3, 60.9, 14.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_3$ 270.1130; found 270.1134.

*4.2.12. N-(4-(Trifluoromethoxy)phenyl)benzamide (**4l**).* White solid (49 mg, 70%). Mp: 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J=7.6 Hz, 3H), 7.68 (d, J=8.8 Hz, 2H), 7.59–7.48 (m, 3H), 7.23 (d, J=8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 136.5, 134.6, 133.7, 132.1, 130.2, 128.9, 128.5, 127.0, 121.9, 121.4. HRMS (ESI-TOF) m/z: $[M-H]^-$ calcd for $C_{14}H_9F_3NO_2$ 280.0585; found 280.0579.

*4.2.13. N-(2,4-Dimethylphenyl)benzamide (**4m**).*[26] Pale yellow solid (25 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J=7.2 Hz, 2H), 7.73 (d, J=8.0 Hz, 1H), 7.64 (br s, 1H), 7.57–7.53 (m, 1H), 7.50–7.46

(m, 2H), 7.05 (d, *J*=7.6 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 135.2, 135.1, 133.1, 131.8, 131.3, 129.7, 128.8, 127.4, 127.1, 123.5, 20.9, 17.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232; found 226.1229.

*4.2.14. 4-Methyl-N-phenylbenzamide (**4n**).*[25] White solid (21 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (br s, 1H), 7.76 (d, *J*=8.0 Hz, 2H), 7.63 (d, *J*=7.6 Hz, 2H), 7.35 (t, *J*=7.6 Hz, 2H), 7.26 (d, *J*=8.0 Hz, 2H), 7.14 (t, *J*=7.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 142.4, 138.1, 132.1, 129.4, 129.1, 127.1, 124.5, 120.2, 21.5. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $C_{14}H_{13}NNaO$ 234.0895; found 234.0891.

*4.2.15. 2-Methyl-N-phenylbenzamide (**4o**).*[25] White solid (23 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J*=7.6 Hz, 2H), 7.55 (br s, 1H), 7.46 (d, *J*=7.6 Hz, 1H), 7.38–7.34 (m, 3H), 7.27–7.22 (m, 2H), 7.15 (t, *J*=7.2 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 138.0, 136.4, 131.3, 130.3, 129.1, 126.6, 125.9, 124.6, 119.9, 19.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075; found 212.1073.

*4.2.16. 4-Methoxy-N-phenylbenzamide (**4p**).*[25] White solid (38 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (br s, 1H), 7.81 (d, *J*=8.8 Hz, 2H), 7.61 (d, *J*=7.6 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 2H), 7.13 (t, *J*=7.6 Hz, 1H), 6.93 (d, *J*=9.2 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 162.4, 138.1, 129.0, 129.0, 127.1, 124.4, 120.3, 113.9, 55.3. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1025; found 228.1028.

*4.2.17. 4-Chloro-N-phenylbenzamide (**4q**).*[25] White solid (49 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J*=8.4 Hz, 2H), 7.62 (d, *J*=7.6 Hz, 2H), 7.47 (d, *J*=8.8 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.17 (t, *J*=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 138.2, 137.6, 133.3, 129.2, 129.1, 128.7, 124.8, 120.3. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529; found 232.0534.

*4.2.18. 4-Bromo-N-phenylbenzamide (**4r**).*[25] White solid (62 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.75–7.61 (m, 3H), 7.49–7.35 (m, 3H), 7.26–7.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 137.6, 132.0, 131.6, 129.2, 128.7, 128.6, 124.8, 120.3. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $C_{13}H_{10}BrNNaO$ 297.9843; found 297.9837.

*4.2.19. 3-Fluoro-N-phenylbenzamide (**4s**).*[25] White solid (43 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (br s, 1H),7.62 (d, *J*=8.0 Hz, 3H), 7.59–7.55 (m, 1H), 7.47–7.41 (m, 1H), 7.37 (t, *J*=7.6 Hz, 2H), 7.26–7.23 (m, 1H), 7.19–7.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.1, 161.6, 137.6, 137.2, 130.5, 129.2, 124.9, 122.5, 120.4, 119.0 (*J*=21.1 Hz), 114.6 (*J*=22.8 Hz). HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $C_{13}H_{10}FNNaO$ 238.0644; found 238.0642.

*4.2.20. Methyl 4-(phenylcarbamoyl)benzoate (**4t**).*[28] White solid (24 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J*=8.4 Hz, 2H), 7.94 (d, *J*=8.4 Hz, 2H), 7.85 (s, 1H), 7.65 (d, *J*=7.6 Hz, 2H), 7.39 (t, *J*=8.0 Hz, 2H), 7.19 (t, *J*=7.6 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 166.5, 137.6, 130.1, 129.2, 127.1, 124.9, 120.3, 52.5. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{15}H_{14}NO_3$ 256.0974; found 256.0982.

*4.2.21. N-Phenyl-1-naphthamide (**4u**).*[29] White solid (32 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40–8.37 (m, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 7.93–7.91 (m, 1H), 7.77–7.69 (m, 4H), 7.62–7.51 (m, 3H), 7.42 (t, *J*=8.0 Hz, 2H), 7.19 (t, *J*=7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 138.0, 133.8, 131.1, 130.9, 129.2, 128.5, 127.4, 126.6, 125.3, 125.1, 124.8, 124.7, 120.0. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{14}NO$ 248.1075; found 248.1068.

*4.2.22. N-Phenylcyclohexanecarboxamide (**4v**).*[30] White solid (22 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=7.6 Hz, 2H), 7.31 (t, *J*=7.6 Hz, 2H), 7.09 (t, *J*=7.6 Hz, 1H), 2.27–2.19 (m, 1H), 1.97–1.81 (m, 4H), 1.73–1.52 (m, 4H), 1.32–1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 138.1, 128.9, 124.1, 119.8, 46.6, 29.7, 25.7. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{13}H_{18}NO$ 204.1388; found 204.1371.

*4.2.23. N-Phenylbutyramide (**4w**).*[31] White solid (17 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=7.6 Hz, 2H), 7.42 (br s, 1H), 7.31 (t, *J*=7.6 Hz, 2H), 7.09 (t, *J*=7.2 Hz, 1H), 2.33 (t, *J*=7.6 Hz, 2H), 1.80–1.72 (m, 2H), 0.99 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 138.0, 129.0, 124.2, 119.9, 39.7, 19.1, 13.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{10}H_{14}NO$ 164.1075; found 164.1063.

*4.2.24. N-Phenylpropionamide (**4x**).*[31] White solid (15 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=7.6 Hz, 2H), 7.31 (t, *J*=7.6 Hz, 2H), 7.09 (t, *J*=7.2 Hz, 1H), 2.39 (q, *J*=7.6 Hz, 2H), 1.25 (t, *J*=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 137.9, 128.9, 124.2, 119.8, 30.8, 9.7. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_9H_{12}NO$ 150.0919; found 150.0917.

4.3. Typical procedure for TBPB-mediated reaction of toluene derivatives with azobenzene

The mixture of azobenzene **1a** (0.25 mmol), TBPB (1 mmol) and toluene derivatives (1 mL) were added into a sealed tube under air. After being stirred vigorously at 120 °C for 24 h, the mixture was evaporated under vacuum. The corresponding product was isolated by silica gel column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

*4.3.1. 3-Methyl-N-phenylbenzamide (**4y**).*[25] Pale yellow solid (41 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.67–7.61 (m, 4H), 7.37–7.32 (m, 4H), 7.13 (t, *J*=7.6 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 138.7, 138.0, 135.0, 132.6, 129.1, 128.7, 127.8, 124.5, 123.9, 120.3, 21.4. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075; found 212.1068.

*4.3.2. 4-Fluoro-N-phenylbenzamide (**4z**).*[26] Pale yellow solid (44 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.85 (m, 2H), 7.82 (br s, 1H), 7.62 (d, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.19–7.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 164.7, 163.7, 137.8, 131.2, 129.5, 129.1, 124.7, 120.3, 115.9 (*J*=21.9 Hz). HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{13}H_{11}FNO$ 216.0825; found 216.0821.

*4.3.3. 4-Cyano-N-phenylbenzamide (**4aa**).*[32] White solid (12 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J*=8.4 Hz, 2H), 7.94 (br s, 1H), 7.77 (d, *J*=8.4 Hz, 2H), 7.63 (d, *J*=8.0 Hz, 2H), 7.39 (t, *J*=7.6 Hz, 2H), 7.20 (t, *J*=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 138.9, 137.3, 132.6, 129.2, 127.8, 125.3, 120.4, 117.9, 115.4. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O$ 223.0871; found 223.0878.

*4.3.4. 3,5-Dimethyl-N-phenylbenzamide (**4ab**).*[33] White solid (45 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.64 (d, *J*=7.6 Hz, 2H), 7.46 (s, 2H), 7.34 (t, *J*=7.6 Hz, 2H), 7.17–7.13 (m, 2H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 138.5, 138.1, 135.0, 133.4, 129.1, 124.8, 124.4, 120.2, 21.3. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232; found 226.1225.

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Supplementary data

Supplementary data (Copies of the ^{1}H and ^{13}C NMR spectra of all products, optimization of reaction conditions, GC–MS spectra) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.11.063.

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