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Hypervalent Iodine(III)-Promoted Phenyl Transfer Reaction from Phenyl Hydrazides to Nitriles

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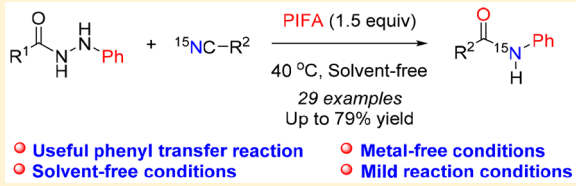
Supporting Information

ABSTRACT: A useful transformation of nitriles to *N*-phenyl amides has been achieved through a novel intermolecular phenyl transfer reaction from phenyl hydrazides and N-addition to nitriles in the presence of PIFA under mild and solvent-free conditions. This cross-coupling reaction includes the oxidative cleavage of sp^2 C−N bonds of phenyl hydrazides to form a phenyl radical and the subsequent N-addition to cyanos to form new sp^2 C−N bonds and provides efficient access to various *N*-phenyl amides in moderate to good yields under mild reaction conditions.

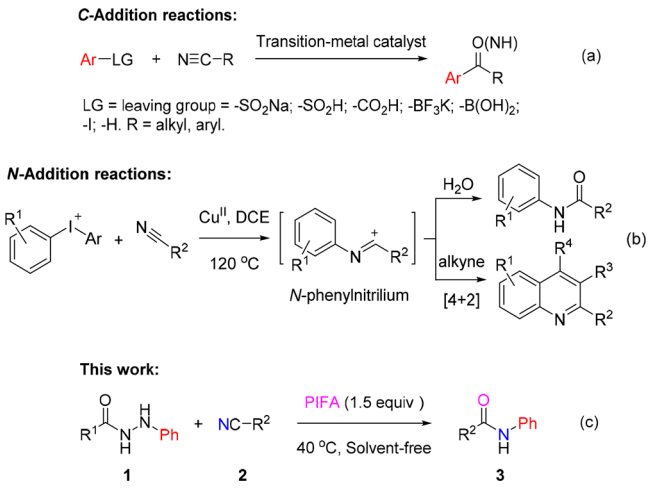


INTRODUCTION

Nitriles are commercially available and commonly used for functional group conversions in organic reactions, including the formation of amides, aldehydes, carboxyl derivatives, amines, and heterocycles.[1−7] When nitriles react with aryl donors, such as sodium arylsulfinates,[8] arylsulfinic acids,[9,10] potassium aryltrifluoroborates,[11] arylboronic acids,[12−16] aryl iodides,[17] and arenes,[18] the arylketone or ketimine products are afforded via an aryl transfer reaction, frequently in the presence of transition-metal catalysts (Scheme 1, a). These C-addition reactions directly add the aryl group to the carbon atom of the cyano group. However, a review of the literature showed that a direct N-addition reaction by tethering the aryl and nitrile portion to afford amides or their analogues is relatively rare. To the best of our knowledge, only two examples of this type reaction have been reported, and both involve copper catalysis. In 2013, Chen and co-workers[19] established a regioselective [2 + 2 + 2] cyclization for the synthesis of substituted quinolines, involving a diaryliodonium salt, a nitrile, and an alkyne. The aryl group of the diaryliodoniums served as the aryl source in this three-component reaction. The reaction proceeded through a key *N*-phenylnitrilium intermediate, which upon hydrolysis gave the anilides (only one case was listed in their work) or formal [4 + 2] annulation to the quinolines via direct N-addition assisted by $Cu(OTf)_2$ (Scheme 1b). Soon after, they found that this aryl transfer reaction could be extended to the preparation of tricyclic quinolines starting from an alkyne and nitriles.[20] In light of the above results, we were interested in developing a new route using both the aryl and nitrile portions as the reaction partners to construct a new carbon−nitrogen bond in the presence of nonmetallic reagents under mild and green conditions. We now present the first example of furnishing *N*-phenyl amides via [bis(trifluoroacetoxy)iodo]-benzene (PIFA)-promoted intermolecular direct N-addition of a phenyl radical (generated in situ from phenyl hydrazides) to nitriles under solvent-free conditions at 40 °C (Scheme 1, c).

Hydrazines and their analogues are versatile synthetic building blocks in the construction of various nitrogen-containing compounds in organic chemistry.[21−28] It is well-known that dehydrogenation of aryl hydrazines by a variety of oxidants will produce arenes and nitrogen via a transient aryl diazene (Scheme 2).[29−31] Hydrazine derivatives can serve as an

Scheme 1. C/N-Addition Reaction of Aryl and Nitrile Portion



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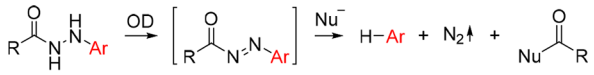
Scheme 2. Oxidative Cleavage of an Aryl Hydrazide



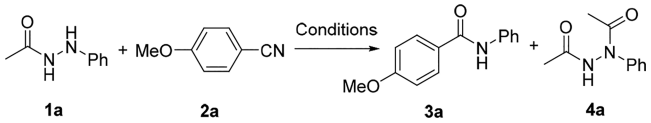
aryl donor in the presence of a palladium catalyst,[32−35] as well as a donor of sulfonyl,[36−38] amino,[39] and other groups[40,41] in transfer reactions to construct new C−C, C−P, C−S, and C−N bonds by cleavage of the hydrazide linker. However, new methods which proceed efficiently under relatively mild and catalytic reaction conditions are in high demand.

RESULTS AND DISCUSSION

Very recently, we developed[42] a PIFA-promoted ring-closing reaction for the synthesis of spirocyclopropane quinolinediones in good to excellent yields from readily available 2,2-disubstituted-2-benzoylacetamides under mild conditions. The spirocyclopropane quinolinedione products can readily convert to pyrrolo[3,2-*c*]quinolinones via an intermolecular amine ring-opening cyclization reaction. On the basis of our recent research[42−46] and that of others[19,20] related to the synthesis of nitrogen-containing functional small molecules, it was envisioned that *N*′-phenylacetohydrazide (**1**) would react with nitriles (**2**) leading to *N*-phenylamides (**3**) via intermolecular direct N-addition (Scheme 1c).

Initially, several solvents were screened for the reaction, including CH_2Cl_2, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol (CH_3OH), 2,2,2-trifluoroethanol (TFE), hexafluoroisopropanol (HFIP), and ethyl acetate (EtOAc). It was found that the rate of the reaction gradually accelerated as the CH_2Cl_2 (1 mL) evaporated. The desired product **3a** was isolated in 69% yield as a white solid when we treated the mixture of **1a** (0.3 mmol) and **2a** (0.6 mmol) with 1.5 equiv of PIFA at 40 °C (Table 1, entry 1). However, none of compound **3a** was obtained in other higher boiling-point solvents under the same conditions, and mostly starting material **1a** was recovered. These observations indicate that increasing the concentration of the reactants is favorable for this phenyl transfer reaction. Therefore, we decided to carry out the reaction in the absence of solvent. To our delight, the desired product **3a** was isolated in 76% yield, along with 16% of *N*′-acetyl-*N*′-phenylacetohydrazide (**4a**) generated from **1a** (Table 1, entry 3).[47] Further investigation revealed that increasing the amount of PIFA had almost no effect on the yield of **3a** (Table 1, entry 4), but a significantly lower yield of **3a** was obtained if we decreased the amount of PIFA to 1.0 equiv (Table 1, entry 2). In addition, we found that it was detrimental to the transformation if the amount of **2a** was reduced (Table 1, entries 5 and 6). Similar results were observed during temperature optimization experiments (Table 1, entries 7 and 8). Further investigation was carried out into other oxidants including PIDA, PhIO, and IBX. All of these showed a lower oxidative activity than PIFA, and mostly starting material **2a** was recovered (Table 1, entries 9−11).

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a** **4a**

entry	2a (equiv)	hypervalent iodine reagent (equiv)	*T* (°C)	yield of 3a (%)	yield of 4a (%)
1[b]	2.0	PIFA (1.5)	40	69	19
2	2.0	PIFA (1.0)	40	55	26
3	2.0	PIFA (1.5)	40	76	16
4	2.0	PIFA (2.0)	40	78	13
5	1.0	PIFA (1.5)	40	23	35
6	1.5	PIFA (1.5)	40	39	32
7	2.0	PIFA (1.5)	25	39	34
8	2.0	PIFA (1.5)	55	62	15
9[c]	2.0	PIDA (1.5)	40	trace	53
10[d]	2.0	PhIO (1.5)	40	trace	59
11[e]	2.0	IBX (1.5)	40	0	56

[a]Unless otherwise indicated, all reactions were carried out with **1a** (0.3 mmol) for 3 h under solvent-free conditions. [b]Reaction was performed in CH_2Cl_2 (1 mL). [c]88% of **2a** was recovered. [d]90% of **2a** was recovered. [e]87% of **2a** was recovered.

The optimal conditions were established as a ratio of **1**, **2**, and PIFA of 1:2:1.5 at 40 °C for this phenyl transfer process (Table 1, entry 3). The scope of the reaction was then investigated, and the results are summarized in Table 2. The scope of nitriles **2** was investigated first (entries 1−21 in Table 2). A phenyl group (**2e**) and a variety of phenyl groups substituted with electron-donating groups (EDGs, e.g., Me and OMe) (**2a−d**) and electron-withdrawing groups (EWGs, e.g., Cl and CO_2Et) (**2f−j**) at the ortho-, meta-, or para-positions were well tolerated and afforded the corresponding primary amides **3a−j** in 36−76% yields. The reaction also proceeded well with furan-2-carbonitrile (**2k**), thiophene-2-carbonitrile (**2l**), and 1-methyl-1*H*-pyrrole-2-carbonitrile (**2m**) and afforded the desired products (**3k−m**) in 36−71% yield. Aliphatic-substituted nitriles were more active, and a range of amides **3n−p** were isolated in 68−79% yields. It is noteworthy that this method has been proven to be efficient for the synthesis of some useful α-substituted primary amides, including 2-cyano-*N*-phenylacetamide (**3q**), *N*-2-diphenylacetamide (**3r**), and methyl 3-oxo-3-(phenylamino)propanoate (**3s**), with a lower loading of **2** (1.5 equiv). The case of **3q** is expecially interesting, as this application demonstrated high chemoselectivity, and no double N-addition product was detected by LCMS. Moreover, the reaction also proceeded smoothly to afford the desired products **3t** and **3u** in moderate yields without affecting the alkenyl and carbonyl functional groups at the α-position.

Encouraged by the above-mentioned results (entries 1 and 22), the scope of the direct N-addition protocol was further expanded using various hydrazides **1** (entries 22−29, Table 2). We observed that phenylhydrazine **1b** only gave the desired **3a** in 49% yield (entry 22). Starting materials **1c** and **1d** converted to the oxidative dehydrogenation products **4c** and **4d** in the yields of 0% and 59%, respectively, instead of compounds **3a** and **3ad** (entries 23 and 24). The substrate with a CF_3 group on the benzene was transformed to the corresponding cross-coupled amide **3ae** in 54% yield (entry 25). To our delight, the *tert*-butyl group on **1f** was also easily transferred to the nitrile and gave **3af** in 69% yield (entry 26). Several other sulfamides **1g−i** were also successfully reacted, and product **3a** was obtained in 59−72% (entries 27−29). It should be noted that the relatively low yields of products **3** were due to the formation of the diacetylhydrazine **4**, which was generated from starting material **1**. Several control experiments were performed to clarify the mechanism for this byproduct formation. It was found that an oxidative dehydrogenation intermediate **5a** was afforded in 63% yield when we treated compound **1a** (1.0

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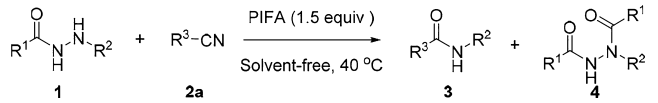
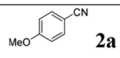
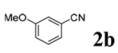
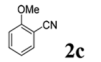
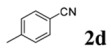
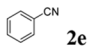
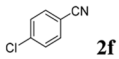
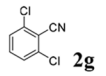
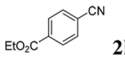
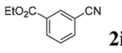
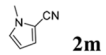
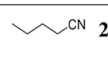
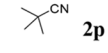
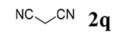
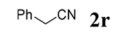
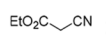
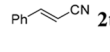
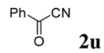
Table 2. Extension of the Substrate Scope[a]



Entry	Substrates 1	Substrates 2	Time(h)	3: Yield (%)	4: Yield (%)
1	1a	 2a	3	3a: 76	4a: 16
2	1a	 2b	3	3b: 63	4a: 25
3	1a	 2c	2	3c: 39	4a: 42
4	1a	 2d	2	3d: 55	4a: 25
5	1a	 2e	2	3e: 53	4a: 29
6	1a	 2f	2	3f: 41	4a: 35
7	1a	 2g	2	3g: 36	4a: 38
8	1a	 2h	2	3h: 36	4a: 43
9	1a	 2i	2	3i: 45	4a: 30
10	1a	 2j	2	3j: 41	4a: 33
11	1a	 2k	2	3k: 71[b]	4a: 19
12	1a	 2l	2	3l: 62[b]	4a: 24
13	1a	 2m	2	3m: 36	4a: 45
14	1a	 2n	2	3n: 79[b]	4a: 12
15	1a	 2o	2	3o: 68[b]	4a: 24
16	1a	 2p	2	3p: 69[b]	4a: 22
17	1a	 2q	2	3q: 74[b]	4a: 16
18	1a	 2r	2	3r: 72[b]	4a: 19
19	1a	 2s	2	3s: 59[b]	4a: 29
20	1a	 2t	2	3t: 57[b]	4a: 27
21	1a	 2u	2	3u: 54[b]	4a: 31
22	 1b	2a	3	3a: 49	--
23	 1c	2a	3	3a: trace[c]	4c: 0
24	 1d	2a	3	3ad: 0[d]	4d: 59[e]
25	 1e	2a	2	3ae: 54[d]	4e: 23
26	 1f	2a	2	3af: 69	4f: 11
27	 1g	2a	3	3a: 67	4g: 0
28	 1h	2a	3	3a: 72	4h: 0
29	 1i	2a	3	3a: 59	4i: 0

[a]Unless otherwise indicated, all reactions were carried out with **1** (0.3 mmol), **2a** (0.6 mmol) and PIFA (0.45 mmol) under solvent-free conditions at 40 °C. [b]1.5 mmol of **2** was used. [c]Complex mixture was observed. [d]The reaction was performed at 80 °C. [e]Mixture of *N*-acetyl-*N*′-(4-methoxyphenyl)acetohydrazide and *N*′-acetyl-*N*′-(4-methoxyphenyl)acetohydrazide in a ratio of 2:1.

equiv) in MeCN (5.0 equiv) at 0 °C for 5 min in the presence of 1.5 equiv of PIFA (eq 1).[48] The isolated intermediate **5a** was then smoothly transformed to the desired compound **3n** in 85% yield under the optimized conditions, without the formation of byproduct **4a** (eq 2). A blank experiment performed with **1a** in the absence of carbonitriles **2** under the optimized conditions afforded byproduct **4a** in 82% yield (eq 3). These observation indicated that **4a** was being formed directly form **1a**, not from **5a**. Furthermore, a separate experiment performed under an atmosphere of N_2 still proceeded smoothly to give the target compound **3a** in 71% yield (eq 4). This observation indicates that the oxygen atom of **2** may come from the PIFA.[29−31,49] To further clarify the source of the nitrogen atom in the product **3**, an experiment was conducted using **1a** (1.0 equiv) and ^{15}N-labeled Me$C^{15}N$ (5.0 equiv) under the optimized conditions (eq 5). Mass spectrometry (MS) analysis suggested that ^{15}N was incorporated in product **3**, which indicated that the CN group served as the nitrogen donor and attacked the phenyl group of the phenyl hydrazides. Radical trapping experiments were also conducted to determine whether a radical process was involved in this reaction (Table 3). It was found that compound **3a** could be isolated in 19% and 22% yield in the presence of 1 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 1,1-diphenylethylene, respectively, under the optimized conditions. However, none of **3a** was generated with *N*-*tert*-butyl-α-phenylnitrone (PBN) and galvinoxyl. These results indicate that radicals might be involved in the transformation.[50−53]

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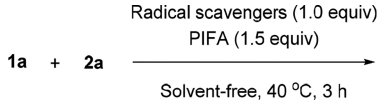
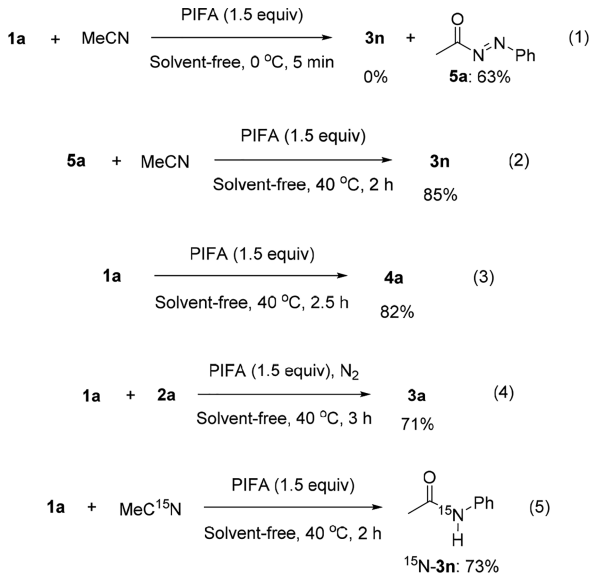
Table 3. Radical Trapping Experiments

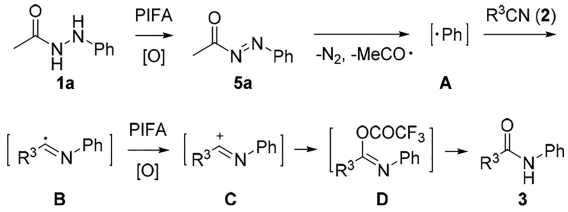


	radical scavengers				
	none	TEMPO	1,1-diphenylethylene	PBN	galvinoxyl
yield of **3a** (%)	76	19	22	0	0



Based on the results of these control experiments and information from previous work, a plausible mechanism is proposed in Scheme 3. Initially, phenyl hydrazide **1a** is oxidized

Scheme 3. Proposed Mechanism



by the oxidant PIFA to form dehydrogenation intermediate **5**, which is subsequently decomposed into phenyl radical **A**.[29−31,49] The radical **A** reacts intermolecularly with **2a** to form a new radical intermediate **B**.[19] This intermediate is then oxidized to give the nonisolable positively charged imine ion **C**,[54,55] which is trapped by a free ligand delivered by PIFA. This results in the formation of the nonisolable carbocation **D**[54] and subsequently leads to the amide **3a** after workup. It should be noted that byproduct **4a** might be formed from the acetyl radical (MeCO) and **1** via a radical coupling reaction.

CONCLUSION

A PIFA-promoted intermolecular tandem amidation and successive oxidation reaction of phenyl hydrazides and nitriles was developed for the synthesis of various secondary amide derivatives. Advantages of this aryl transfer reaction over existing methods include the use of metal-free reagents, readily available starting materials, good yields, and the drug-like nature of the products.

EXPERIMENTAL SECTION

General Remarks. All reactions were carried out under air atmosphere, unless otherwise indicated. Other all reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Petroleum ether (PE) used refers to the 60−90 °C boiling point fraction of petroleum. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance/600 (^{1}H: 600 MHz, ^{13}C: 150 MHz at 25 °C) or Bruker Avance/400 (^{1}H: 400 MHz, ^{13}C: 100 MHz at 25 °C) and TMS as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz). All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization (ESI-oa-TOF), and the purity of all samples used for HRMS (>95%) were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopic analysis. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All reactions were monitored by TLC with GF254 silica gel-coated plates. Flash chromatography was carried out on SiO_2 (silica gel 200−300 mesh).

Typical experimental procedure for **3** (**3a** as an example): To a tube were added *N*′-phenylacetohydrazide **1a** (45 mg, 0.3 mmol), 4-methoxybenzonitrile **2a** (80 mg, 0.6 mmol), and PIFA (194 mg, 0.45 mmol). The mixture was well stirred for 3 h at 40 °C (the whole process was closely monitored by TLC). After cooling, the reaction mixture was purified by a flash silica gel column chromatography with ethyl acetate and PE as eluent to give *N*-(4-methoxyphenyl)benzamide **3a** as a white solid (52 mg, 76%).

*4-Methoxy-N-phenylbenzamide (**3a**).*[56] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (52 mg, 76%). mp 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.8 Hz, 2H), 7.71 (s, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.6, 138.3, 129.2, 129.0, 127.3, 124.5, 120.6, 114.1, 55.6. HRMS (ESI), m/z calcd for $C_{14}H_{13}NO_2Na$ ([M + Na]$^+$) 250.0838, found: 250.0838.

*3-Methoxy-N-phenylbenzamide (**3b**).*[57] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (43 mg, 63%). mp 111−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.41−7.34 (m, 4H), 7.16 (t, J = 7.6 Hz, 1H), 7.11−7.08 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 138.0, 136.7, 130.0, 129.3, 124.8, 120.3, 118.8, 118.2, 112.7, 55.7. (One carbon is not observed). HRMS (ESI), m/z calcd for $C_{14}H_{13}NO_2Na$ ([M + Na]$^+$) 250.0838, found: 250.0843.

*2-Methoxy-N-phenylbenzamide (**3c**).*[57] The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a white solid (26 mg, 39%). mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.30 (dd, J = 7.6, 2.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.51−7.48 (m, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.16−7.11 (m, 2H), 7.04 (d, J = 8.0 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 157.4, 138.6, 133.4, 132.7, 129.1, 124.3, 121.9, 120.6, 111.7, 56.4. HRMS (ESI), m/z calcd for $C_{14}H_{13}NO_2Na$ ([M + Na]$^+$) 250.0838, found: 250.0842.

*4-Methyl-N-phenylbenzamide (**3d**).*[56] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (35 mg, 55%). mp 140−143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 3H), 7.64 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 138.1, 132.3, 129.6, 129.2, 127.2, 124.6, 120.2, 21.6. (One carbon is not observed). HRMS (ESI), m/z calcd for $C_{14}H_{13}NONa$ ([M + Na]$^+$) 234.0889, found: 234.0883.

*N-Phenylbenzamide (**3e**).*[56] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (31 mg, 53%). mp 164−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.8 Hz, 2H), 7.83 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 138.1, 135.2, 132.0, 129.3, 129.0, 127.2, 124.7, 120.3. HRMS (ESI), m/z calcd for $C_{13}H_{11}NONa$ ([M + Na]$^+$) 220.0733, found: 220.0741.

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J. Org. Chem. 2017, 82, 7957−7963

*4-Chloro-N-phenylbenzamide (**3f**)*.[56] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (28 mg, 41%). mp 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.74 (s, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 137.8, 133.5, 129.3, 129.2, 128.6, 125.0, 120.4. (One carbon is not observed). HRMS (ESI), m/z calcd for $C_{13}H_{10}ClNONa$ ([M + Na]$^+$) 254.0343, found: 254.0337.

*2,6-Dichloro-N-phenylbenzamide (**3g**)*.[58] The product was isolated by flash chromatography (eluent: PE/EA = 30/1) as a white solid (29 mg, 36%). mp 140−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 2H), 7.45−7.34 (m, 5H), 7.33−7.29 (m, 1H), 7.20 (t, J = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 137.3, 136.1, 132.6, 131.1, 129.4, 128.4, 125.4, 120.5. HRMS (ESI), m/z calcd for $C_{13}H_9Cl_2NONa$ ([M + Na]$^+$) 287.9953, found: 287.9953.

*Methyl 4-(Phenylcarbamoyl)benzoate (**3h**)*.[59] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (24 mg, 32%). mp 184−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 7.81 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 139.0, 137.7, 133.2, 130.2, 129.3, 127.2, 125.1, 120.4, 52.6. HRMS (ESI), m/z calcd for $C_{15}H_{13}NO_3Na$ ([M + Na]$^+$) 278.0788, found: 278.0793.

*Methyl 3-(Phenylcarbamoyl)benzoate (**3i**)*.[60] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (34 mg, 45%). mp 131−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.88 (s, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 137.8, 135.5, 132.9, 132.2, 130.8, 129.4, 127.6, 125.0, 120.5, 52.6. HRMS (ESI), m/z calcd for $C_{15}H_{13}NO_3Na$ ([M + Na]$^+$) 278.0788, found: 278.0792.

*Methyl 2-(Phenylcarbamoyl)benzoate (**3j**)*.[61] The product was isolated by flash chromatography (eluent: PE/EA = 10/1) as a white solid (31 mg, 41%). mp 110−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 1H), 7.70−7.56 (m, 5H), 7.53 (s, 1H), 7.37 (t, J = 6.2 Hz, 2H), 7.16 (t, J = 6.3 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 167.3, 138.4, 138.1, 132.4, 130.5, 130.1, 129.3, 129.1, 127.9, 124.8, 120.2, 52.9. HRMS (ESI), m/z calcd for $C_{15}H_{13}NO_3Na$ ([M + Na]$^+$) 278.0788, found: 278.0789.

*N-Phenylfuran-2-carboxamide (**3k**)*..[56,62] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (40 mg, 71%). mp 123−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.52 (m, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.24 (m, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 147.9, 144.3, 137.5, 129.3, 124.7, 120.0, 115.4, 112.8. HRMS (ESI), m/z calcd for $C_{11}H_9NO_2Na$ ([M + Na]$^+$) 210.0525, found: 210.0547.

*N-Phenylthiophene-2-carboxamide (**3l**)*..[56,62] The product was isolated by flash chromatography (eluent: PE/EA = 30/1) as a white solid (38 mg, 62%). mp 140−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.62 (m, 3H), 7.60 (s, 1H), 7.56−7.54 (m, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.17−7.13 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 137.7, 130.9, 129.3, 128.6, 128.0, 124.8, 120.3. HRMS (ESI), m/z calcd for $C_{11}H_9NONaS$ ([M + Na]$^+$) 226.0297, found: 226.0298.

*1-Methyl-N-phenyl-1H-pyrrole-2-carboxamide (**3m**)*.[62] The product was isolated by flash chromatography (eluent: PE/EA = 10/1) as a white solid (22 mg, 36%). mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 3H), 7.35 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.81−6.77 (m, 1H), 6.70−6.69 (m, 1H), 6.16−6.14 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 129.2, 129.0, 124.2, 120.8, 120.1, 112.2, 107.6. HRMS (ESI), m/z calcd for $C_{12}H_{12}N_2ONa$ ([M + Na]$^+$) 223.0842, found: 223.0844.

*N-Phenylacetamide (**3n**)*.[56] The product was isolated by flash chromatography (eluent: PE/EA = 5/1) as a white solid (32 mg, 79%). mp 113−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 139.3, 128.6, 122.9, 119.0, 24.0. HRMS (ESI), m/z calcd for C_8H_9NONa ([M + Na]$^+$) 158.0576, found: 158.0574.

*N-Phenylpentanamide (**3o**)*.[56] The product was isolated by flash chromatography (eluent: PE/EA = 10/1) as a white solid (36 mg, 68%). mp 60−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.20 (s, 1H), 7.10 (t, J = 7.6 Hz, 1H), 2.36 (t, J = 7.2 Hz, 2H), 1.77−1.67 (m, 2H), 1.46−1.35 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 138.1, 129.1, 124.3, 119.9, 37.7, 27.8, 22.5, 14.0. HRMS (ESI), m/z calcd for $C_{11}H_{16}NO$ ([M + H]$^+$) 178.1226, found: 178.1232.

*N-Phenylpivalamide (**3p**)*.[63] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (37 mg, 69%). mp 129−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 3H), 7.10 (t, J = 7.6 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 138.2, 129.1, 124.3, 120.1, 39.8, 27.8. HRMS (ESI), m/z calcd for $C_{11}H_{15}NONa$ ([M + Na]$^+$) 200.1046, found: 200.1047.

*2-Cyano-N-phenylacetamide (**3q**)*.[64] The product was isolated by flash chromatography (eluent: PE/EA = 5/1) as a white solid (36 mg, 74%). mp 197−199 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 3.90 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.0, 138.4, 128.9, 123.9, 119.2, 115.9, 26.7. HRMS (ESI), m/z calcd for $C_9H_8N_2ONa$ ([M + Na]$^+$) 183.0529, found: 183.0534.

*N,2-Diphenylacetamide (**3r**)*.[56] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (46 mg, 72%). mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.38 (m, 4H), 7.36−7.33 (m, 3H), 7.29 (d, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 3.74 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 137.6, 134.5, 129.7, 129.4, 129.1, 127.9, 124.6, 119.8, 45.0. HRMS (ESI), m/z calcd for $C_{14}H_{13}NONa$ ([M + Na]$^+$) 234.0889, found: 234.0888.

*Methyl 3-Oxo-3-(phenylamino)propanoate (**3s**)*.[65] The product was isolated by flash chromatography (eluent: PE/EA = 10/1) as a white solid (34 mg, 59%). mp 43−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 3.49 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 162.8, 137.6, 129.2, 124.8, 120.3, 52.8, 41.4. HRMS (ESI), m/z calcd for $C_{10}H_{11}NO_3Na$ ([M + Na]$^+$) 216.0631, found: 216.0631.

*N-Phenylcinnamamide (**3t**)*.[62] The product was isolated by flash chromatography (eluent: PE/EA = 10/1) as a white solid (38 mg, 57%). mp 151−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 15.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.55−7.52 (m, 2H), 7.42 (s, 1H), 7.40−7.34 (m, 5H), 7.14 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 142.6, 138.1, 134.8, 130.2, 129.3, 129.0, 128.1, 124.6, 120.9, 120.0. HRMS (ESI), m/z calcd for $C_{15}H_{13}NONa$ ([M + Na]$^+$) 246.0889, found: 246.0889.

*2-Oxo-N,2-diphenylacetamide (**3u**)*.[66] The product was isolated by flash chromatography (eluent: PE/EA = 40/1) as a white solid (36 mg, 54%). mp 62−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.43 (d, J = 7.2 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.5, 159.0, 136.8, 134.8, 133.2, 131.7, 129.4, 128.7, 125.5, 120.1. HRMS (ESI), m/z calcd for $C_{14}H_{11}NO_2Na$ ([M + Na]$^+$) 248.0682, found: 248.0682.

*4-Methoxy-N-(4-(trifluoromethyl)phenyl)benzamide (**3ae**)*.[67] The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a white solid (48 mg, 54%). mp 212−214 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.01−7.97 (m, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 162.2, 143.0, 129.8, 126.4, 125.88, 125.85, 120.0, 113.7, 55.5. HRMS (ESI), m/z calcd for $C_{15}H_{12}F_3NO_2Na$ ([M + Na]$^+$) 318.0712, found: 318.0718.

*N-(tert-Butyl)-4-methoxybenzamide (**3af**)*.[68] The product was isolated by flash chromatography (eluent: PE/EA = 40/1) as a white solid (48 mg, 54%). mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.85 (s, 1H), 3.84 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 162.0, 128.6, 128.4, 113.8, 55.5, 51.6, 29.1. HRMS (ESI), m/z calcd for $C_{12}H_{17}NO_2Na$ ([M + Na]$^+$) 230.1151, found: 230.1150.

*Acetic Acid, 2-Acetyl-2-phenyl Hydrazide (**4a**) and N-Acetyl-N′-phenylacetohydrazide*.[69] The product was isolated by flash

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chromatography (eluent: PE/EA = 1/2) as a colorless oil (9 mg, 16%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.88 (s, 1H), 10.38 (s, 1H), 7.36 (s, 5H), 7.19 (s, 1H), 2.07 (s, 3H), 1.96 (s, 3H), 1.87 (d, J = 27.6 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.2, 168.8, 141.5, 128.5, 125.7, 123.4, 21.7, 20.5. HRMS (ESI), m/z calcd for $C_{10}H_{12}N_2O_2Na$ ([M + Na]$^+$) 215.0791, found: 215.0800.

*Acetic Acid, 2-Acetyl-2-(4-methoxyphenyl) Hydrazide (**4d**) and N-Acetyl-N′-(4-methoxyphenyl)acetohydrazide.* The product was isolated by flash chromatography (eluent: PE/EA = 1/3) as a yellow oil (39 mg, 59%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.81 (s, 1H), 10.29 (s, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 7.8 Hz, 2H), 3.77 (s, 1H), 3.74 (s, 3H), 2.03 (s, 3H), 1.92 (s, 3H), 1.83 (d, J = 7.9 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.1, 168.6, 157.3, 134.6, 128.6, 125.8, 114.4, 113.6, 55.3, 21.3, 20.5. HRMS (ESI), m/z calcd for $C_{11}H_{14}N_2O_3Na$ ([M + Na]$^+$) 245.0897, found: 245.0907.

*Acetic Acid, 2-Acetyl-2-(4-(trifluoromethyl)phenyl) Hydrazide (**4e**).* The product was isolated by flash chromatography (eluent: PE/EA = 1/2) as a white solid (18 mg, 23%). mp 106−108 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.99 (s, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 2.11 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.6, 168.9, 144.7, 126.8, 125.7, 125.0, 123.2, 122.6, 121.4, 22.0, 20.4. HRMS (ESI), m/z calcd for $C_{11}H_{12}F_3N_2O_2$ ([M + H]$^+$) 261.0845, found: 261.0854.

*Acetic Acid, 2-Acetyl-2-(tert-butyl) Hydrazide (**4f**).* The product was isolated by flash chromatography (eluent: PE/EA = 1/2) as a colorless oil (6 mg, 11%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.15 (s, 1H), 1.87 (s, 3H), 1.81 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.6, 169.0, 59.2, 27.5, 23.0, 20.2. HRMS (ESI), m/z calcd for $C_8H_{16}N_2O_2Na$ ([M + Na]$^+$) 195.1104, found: 195.1114.

*(E)-1-(Phenyldiazenyl)ethan-1-one (**5a**).*[70] The product was isolated by flash chromatography (eluent: PE/EA = 2/1) as a red oil (28 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.7, 151.6, 133.7, 129.5, 123.8, 21.4. HRMS (ESI), m/z calcd for $C_8H_8N_2ONa$ ([M + Na]$^+$) 171.0529, found: 171.0529.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01215.

^{1}H and ^{13}C NMR spectra for all compounds and radical trapping and labeling experiments (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Rach, S. F.; Kühn, F. E. *Chem. Rev.* **2009**, *109*, 2061.
(2) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.
(3) Fleming, F. F.; Wang, Q. *Chem. Rev.* **2003**, *103*, 2035.
(4) Zhang, Y.; Pan, L.; Zou, Y.; Xu, X.; Liu, Q. *Chem. Commun.* **2014**, *50*, 14334.
(5) Xu, X.; Zhang, L.; Liu, X.; Pan, L.; Liu, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 9271.
(6) Hu, Z.; Dong, J.; Men, Y.; Lin, Z.; Cai, J.; Xu, X. *Angew. Chem., Int. Ed.* **2017**, *56*, 1805.
(7) Liu, X.; Zhang, L.; Xu, X.; Wang, S.; Pan, L.; Zhang, Q.; Liu, Q. *Chem. Commun.* **2014**, *50*, 8764.
(8) Chen, J.; Li, J.; Su, W. *Molecules* **2014**, *19*, 6439.
(9) Miao, T.; Wang, G.-W. *Chem. Commun.* **2011**, *47*, 9501.
(10) Behrends, M.; Sävmarker, J.; Sjöberg, P. J. R.; Larhed, M. *ACS Catal.* **2011**, *1*, 1455.
(11) Wang, X.; Liu, M.; Xu, L.; Wang, Q.; Chen, J.; Ding, J.; Wu, H. *J. Org. Chem.* **2013**, *78*, 5273.
(12) Tsui, G. C.; Glenadel, Q.; Lau, C.; Lautens, M. *Org. Lett.* **2011**, *13*, 208.
(13) Wong, Y.-C.; Parthasarathy, K.; Cheng, C.-H. *Org. Lett.* **2010**, *12*, 1736.
(14) Zhou, C.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3551.
(15) Zhao, B.; Lu, X. *Org. Lett.* **2006**, *8*, 5987.
(16) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.
(17) Hsieh, J.-C.; Chen, Y.-C.; Cheng, A.-Y.; Tseng, H.-C. *Org. Lett.* **2012**, *14*, 1282.
(18) Zhou, C.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 2302.
(19) Wang, Y.; Chen, C.; Peng, J.; Li, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5323.
(20) Wang, Y.; Chen, C.; Zhang, S.; Lou, Z.; Su, X.; Wen, L.; Li, M. *Org. Lett.* **2013**, *15*, 4794.
(21) Léavai, A. *J. Heterocycl. Chem.* **2002**, *39*, 1.
(22) Ferwanah, A.-R.; Awadallah, A. *Molecules* **2005**, *10*, 492.
(23) Sun, J.; Qiu, J.-K.; Zhu, Y.-L.; Guo, C.; Hao, W.-J.; Jiang, B.; Tu, S.-J. *J. Org. Chem.* **2015**, *80*, 8217.
(24) Sun, J.; Qiu, J.-K.; Jiang, B.; Hao, W.-J.; Guo, C.; Tu, S.-J. *J. Org. Chem.* **2016**, *81*, 3321.
(25) Sun, K.; Wang, X.; Fu, F.; Zhang, C.; Chen, Y.; Liu, L. *Green Chem.* **2017**, *19*, 1490.
(26) Wan, X.; Sun, K.; Zhang, G. *Sci. China: Chem.* **2017**, *60*, 353.
(27) Sun, K.; Lv, Y.; Shi, Z.; Fu, F.; Zhang, C.; Zhang, Z. *Sci. China: Chem.* **2017**, *60*, 730.
(28) Yang, Y.; Bao, Y. J.; Guan, Q. Q.; Sun, Q.; Zha, Z. G.; Wang, Z. Y. *Green Chem.* **2017**, *19*, 112.
(29) Rosenbaum, C.; Waldmann, H. *Tetrahedron Lett.* **2001**, *42*, 5677.
(30) White, E. H.; Field, K. W.; Hendrickson, W. H.; Dzadzic, P.; Roswell, D. F.; Paik, S.; Mullen, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 8023.
(31) Millington, C. R.; Quarrell, R.; Lowe, G. *Tetrahedron Lett.* **1998**, *39*, 7201.
(32) Zhao, Y. W.; Song, Q. L. *Chem. Commun.* **2015**, *51*, 13272.
(33) Xu, W.; Hu, G.; Xu, P.; Gao, Y.; Yin, Y.; Zhao, Y. *Adv. Synth. Catal.* **2014**, *356*, 2948.
(34) Zhou, H.-P.; Liu, J.-B.; Yuan, J.-J.; Peng, Y.-Y. *RSC Adv.* **2014**, *4*, 25576.
(35) Peng, Z.; Hu, G.; Qiao, H.; Xu, P.; Gao, Y.; Zhao, Y. *J. Org. Chem.* **2014**, *79*, 2733.
(36) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. *J. Org. Chem.* **2015**, *80*, 4697.
(37) Wu, X.-m.; Wang, Y. *Synlett* **2014**, *25*, 1163.
(38) Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 4202.
(39) Taylor, J. E.; Daniels, D. S. B.; Smith, A. D. *Org. Lett.* **2013**, *15*, 6058.
(40) Okimoto, M.; Chiba, T. *J. Org. Chem.* **1990**, *55*, 1070.
(41) Lerchen, A.; Vásquez-Céspedes, S.; Glorius, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 3208.

DOI: 10.1021/acs.joc.7b01215
J. Org. Chem. 2017, 82, 7957−7963

(42) Zhang, Z.; Gao, X.; Li, Z.; Zhang, G.; Ma, N.; Liu, Q.; Liu, T. *Org. Chem. Front.* **2017**, *4*, 404.
(43) Liu, Y.; Zhang, Z.; Wan, Y.; Zhang, G.; Li, Z.; Bi, J.; Ma, N.; Liu, T.; Liu, Q. *J. Org. Chem.* **2017**, *82*, 3901.
(44) Sun, K.; Wang, X.; Liu, L.; Sun, J.; Liu, X.; Li, Z.; Zhang, Z.; Zhang, G. *ACS Catal.* **2015**, *5*, 7194.
(45) Zhang, Z.; Zheng, D.; Ma, N.; Bi, J. *Chin. J. Org. Chem.* **2017**, *37*, DOI: 10.6023/cjoc201612032.
(46) Zhang, Z.; Huang, Y.; Huang, G.; Zhang, G.; Liu, Q. *J. Heterocycl. Chem.* **2017**, DOI: 10.1002/jhet.2839.
(47) Behrend, R.; Reinsberg, W. *Liebigs Ann. Chem.* **1910**, *377*, 189.
(48) Because the benzonitrile **2a** and **4a** are of the same polarity, the control experiment was carried out with MeCN.
(49) Guo, J.-Y.; Wu, R.-X.; Jin, J.-K.; Tian, S.-K. *Org. Lett.* **2016**, *18*, 3850.
(50) Liu, X.; Cong, T.; Liu, P.; Sun, P. *Org. Biomol. Chem.* **2016**, *14*, 9416.
(51) Xia, C.; Wang, K.; Xu, J.; Wei, Z.; Shen, C.; Duan, G.; Zhu, Q.; Zhang, P. *RSC Adv.* **2016**, *6*, 37173.
(52) Li, W.; Yin, G.; Huang, L.; Xiao, Y.; Fu, Z.; Xin, X.; Liu, F.; Li, Z.; He, W. *Green Chem.* **2016**, *18*, 4879.
(53) Aruri, H.; Singh, U.; Kumar, S.; Kushwaha, M.; Gupta, A. P.; Vishwakarma, R. A.; Singh, P. P. *Org. Lett.* **2016**, *18*, 3638.
(54) Serna, S.; Tellitu, I.; Domínguez, E.; Moreno, I.; SanMartín, R. *Org. Lett.* **2005**, *7*, 3073.
(55) Tellitu, I.; Serna, S.; Herrero, M. T.; Moreno, I.; Domínguez, E.; SanMartin, R. *J. Org. Chem.* **2007**, *72*, 1526.
(56) Huang, H.; Jiang, Z.; Wu, Y.; Gan, C.; Li, J.; Xiang, S.; Feng, C.; Wang, B.; Yang, W. *Synlett* **2016**, *27*, 951.
(57) Hong, G.; Mao, D.; Zhu, X.; Wu, S.; Wang, L. *Org. Chem. Front.* **2015**, *2*, 985.
(58) Jain, S. K.; Aravinda Kumar, K. A.; Bharate, S. B.; Vishwakarma, R. A. *Org. Biomol. Chem.* **2014**, *12*, 6465.
(59) Seo, H.-A.; Cho, Y.-H.; Lee, Y.-S.; Cheon, C.-H. *J. Org. Chem.* **2015**, *80*, 11993.
(60) Katritzky, A. R.; Oniciu, D. C.; Mancheño, B.; Barcock, R. A. *J. Chem. Soc., Perkin Trans. 1* **1994**, 113.
(61) Stoermer, R.; Steinbeck, H. J. *Ber. Dtsch. Chem. Ges. B* **1932**, *65*, 413.
(62) Kobs, U.; Neumann, W. P. *Chem. Ber.* **1990**, *123*, 2191.
(63) Rasheed, S.; Rao, D. N.; Reddy, A. S.; Shankar, R.; Das, P. *RSC Adv.* **2015**, *5*, 10567.
(64) Hu, H.; Jiang, M.; Xie, L.; Hu, G.; Zhang, C.; Zhang, L.; Zhou, S.; Zhang, M.; Gong, P. *Chem. Res. Chin. Univ.* **2015**, *31*, 746.
(65) Graziano, M. L.; Cimminiello, G. *Synthesis* **1989**, 54.
(66) Deshidi, R.; Kumar, M.; Devari, S.; Shah, B. A. *Chem. Commun.* **2014**, *50*, 9533.
(67) Lavoie, C. M.; MacQueen, P. M.; Stradiotto, M. *Chem. - Eur. J.* **2016**, *22*, 18752.
(68) Kotha, S. S.; Badigenchala, S.; Sekar, G. *Adv. Synth. Catal.* **2015**, *357*, 1437.
(69) Valyashko, N. A. *Zh. Obshch. Khim.* **1950**, *20*, 1667.
(70) Jürmanna, G.; Tšubrika, O.; Tammeveskib, K.; Mäeorg, U. *J. Chem. Res.* **2015**, *10*, 661.

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J. Org. Chem. 2017, 82, 7957−7963