Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2018, **16**, 7737

Synthesis of 2-aminobenzophenones through acylation of anilines with α-oxocarboxylic acids assisted by *tert*-butyl nitrite†

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Received 30th July 2018,
Accepted 2nd October 2018

DOI: 10.1039/c8ob01846d

rsc.li/obc

In this paper, a regioselective, efficient and convenient synthesis of 2-aminobenzophenones through acylation of anilines with α-oxocarboxylic acids assisted by *tert*-butyl nitrite is presented. Interestingly, *tert*-butyl nitrite acts as not only an efficient and mild nitrosation reagent, but also a sustainable oxidant required in the Pd(II)-catalyzed decarboxylative acylation. Meanwhile, the NO unit turned out to be an easily introduced and readily removable directing group for the regioselective acylation.

Introduction

The development of efficient and practical methods for the synthesis of 2-aminobenzophenone derivatives has remained a hot topic in organic and medicinal chemistry for a long time. This is mainly due to the fact that the 2-aminobenzophenone scaffold is present ubiquitously in natural products, drugs and functional materials.[1] Moreover, 2-aminobenzophenones also serve as versatile building blocks in the synthesis of a plethora of fine chemicals.[1] Due to their importance, a number of elegant methods for the preparation of 2-aminobenzophenones have been developed so far, which mainly include: (i) Friedel–Crafts acylation of arenes with 2-nitrobenzoyl chloride generated *in situ* from the reaction of 2-nitrobenzoic acid with oxalyl chloride followed by a separate reduction of the nitro unit;[2] (ii) reaction of 2-aminoaryl aldehydes with arylmagnesium bromide followed by oxidation with $CuCl_2$;[2] (iii) Friedel–Crafts acylation of arenes with 2-nitrobenzoic acid in the presence of Tf_2O and $BF_3{\cdot}Et_2O$ followed by a separate reduction of the nitro group;[2] (iv) Pd-catalyzed addition of arylboronic acids on 2-aminobenzonitriles;[3] (v) insertion of benzyne into an amide bond;[4] (vi) acylation of anilines with benzonitriles promoted by a stoichiometric amount of $BCl_3/AlCl_3$;[5] (vii) addition of 2-aminobenzonitriles with Grignard reagents;[2] *etc*. While these literature methods are generally reliable, some of them still suffer from limitations such as difficult-to-obtain substrates, expensive catalysts, perishable intermediates, harsh reaction conditions, and uncontrollable regioselectivity. Therefore, the search for new synthetic methods for the preparation of 2-aminobenzophenones starting from easily obtainable substrates and employing nontoxic, stable and easy-to-handle acylating reagents is still of urgent demand.

In recent years, direct functionalizations of the inert aromatic C(sp^2)–H bonds under the catalysis of transition-metal (TM) catalysts have attracted much attention due to their excellent step-economy and atom-efficiency.[6] To realize the desired C(sp^2)–H bond derivations, a directing group (DG) is usually needed to enhance the reactivity of the substrates and to control the regioselectivity *via* its interaction with the catalyst. In this aspect, the easily obtainable nitroso compounds[7] have aroused intensive interest since the nitroso group has a high affinity to interact with metals,[8] and thus can be used as a powerful DG in TM-catalyzed inert C–H bond functionalizations.[9] Meanwhile, TM-catalyzed decarboxylative C–H functionalization is a highly useful tool for C–C bond formation with high efficiency and sustainability.[10] Among various acid substrates, α-oxocarboxylic acids are ideal acylation reagents through the TM-catalyzed decarboxylative C–C bond formations owing to their easy availability and facile-to-handle nature.[11] In this aspect, Luo,[12a] Wang[12b] and Sun[12c] have independently reported a Pd-catalyzed decarboxylative acylation of *N*-nitrosoanilines with α-oxo-carboxylic acids. While this novel acylation provides a highly valuable and reliable synthesis of *N*-nitroso-2-aminobenzophenone derivatives, it was also noticed, however, that the *N*-nitrosoaniline substrates used therein were pre-prepared *via* nitrosation of anilines by using a combination of sodium nitrite and strong acid as the nitrosation reagent. These strong acidic conditions

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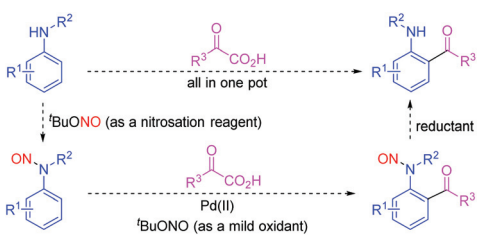
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra of compounds **4a–4hh**, **5a–5r**, **A** and **6**. See DOI: 10.1039/c8ob01846d

may be incompatible with some perishable substrates. In addition, a strong oxidant such as $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ has to be employed in the acylation reactions to regenerate the Pd(II) species, and arguably also to assist the decarboxylation of α-oxocarboxylic acids.[12] Moreover, the *N*-nitroso unit is usually left behind in the 2-aminobenzophenone derivatives thus obtained, and additional step(s) has to be taken for its removal.

To overcome these limitations, we designed a new synthetic approach to *N*-nitroso-2-aminobenzophenones needing neither the pre-nitrosation of the aniline substrates under strong acidic conditions nor the use of a strong oxidant for the decarboxylative acylation *via* an envisioned one-pot three-component reaction of anilines with *tert*-butyl nitrite and α-oxocarboxylic acids. The rationale behind this design is that *tert*-butyl nitrite has been well proven as not only a convenient and mild nitrosation reagent,[13] but also as a sustainable oxidant.[14] It is thus expected that *tert*-butyl nitrite could firstly react with aniline to give *N*-nitrosoaniline, and then act as an oxidant to promote the Pd(II)-catalyzed acylation of *N*-nitrosoaniline with α-oxocarboxylic acid to afford *N*-nitroso-2-aminobenzophenone in one pot. If this could be successful, we would then move forward to search for a suitable reducing system to remove the NO unit of the *in situ* formed *N*-nitroso-2-aminobenzophenones to realize an all-in-one-pot synthesis of 2-aminobenzophenones from commercially available substrates under mild conditions (Scheme 1). To achieve these objectives, the following challenges should be addressed: (i) the nitrosation might also occur with the active intermediates generated *in situ* and (ii) the compatibility of different reaction conditions of our newly designed cascade process is unknown. Herein, we wish to report our results in this regard.

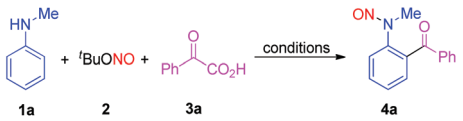
Results and discussion

Our study was initiated by treating a mixture of *N*-methylaniline (**1a**), *tert*-butyl nitrite (**2**) and 2-oxo-2-phenylacetic acid (**3a**) with $Pd(OAc)_2$ in CH_2Cl_2 at 40 °C under air for 20 h. To our delight, the expected cascade reaction took place to give *N*-nitroso-2-aminobenzophenone **4a** in a yield of 75% (Table 1, entry 1). To improve the efficiency, several parameters were screened. First, different catalysts including $Pd(TFA)_2$, $PdCl_2$, $Cu(OAc)_2$ and Ag_2CO_3 were tried, and they were found to be less efficient than $Pd(OAc)_2$ (entries 2–5 *vs.* entry 1). The following study on the solvent effect revealed that DCE was more efficient than CH_2Cl_2, ethyl acetate (EA), THF, CH_3CN and Et_2O in mediating this reaction (entries 6–10). Next, it was observed that reaction temperatures lower or higher than 40 °C gave diminished yields of **4a** (entries 11 and 12). Reducing the loading of ^{t}BuONO from 3 equiv. to 2 equiv. resulted in a remarkable decrease in the yield of **4a** (entry 13), and increasing it to 4 equiv. did not improve the efficiency obviously (entry 14). In addition, further screening showed that the optimum loading of $Pd(OAc)_2$ is 5 mol% (entry 6 *vs.* entries 15 and 16).



Scheme 1 Our designed one-pot synthesis of 2-aminobenzophenones.

Table 1 Optimization study on the formation of **4a**[a]



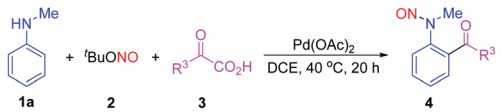
Entry	Catalyst (mol%)	Equiv. of 2	Solvent	*T* (°C)	Yield[b] (%)
1	$Pd(OAc)_2$ (5)	3	CH_2Cl_2	40	75
2	$Pd(TFA)_2$ (5)	3	CH_2Cl_2	40	60
3	$PdCl_2$ (5)	3	CH_2Cl_2	40	0
4	$Cu(OAc)_2$ (5)	3	CH_2Cl_2	40	0
5	Ag_2CO_3 (5)	3	CH_2Cl_2	40	0
6	$Pd(OAc)_2$ (5)	3	DCE	40	88
7	$Pd(OAc)_2$ (5)	3	EA	40	32
8	$Pd(OAc)_2$ (5)	3	THF	40	40
9	$Pd(OAc)_2$ (5)	3	CH_3CN	40	15
10	$Pd(OAc)_2$ (5)	3	Et_2O	40	30
11	$Pd(OAc)_2$ (5)	3	DCE	30	76
12	$Pd(OAc)_2$ (5)	3	DCE	50	86
13	$Pd(OAc)_2$ (5)	2	DCE	40	75
14	$Pd(OAc)_2$ (5)	4	DCE	40	89
15	$Pd(OAc)_2$ (3)	3	DCE	40	79
16	$Pd(OAc)_2$ (10)	3	DCE	40	88

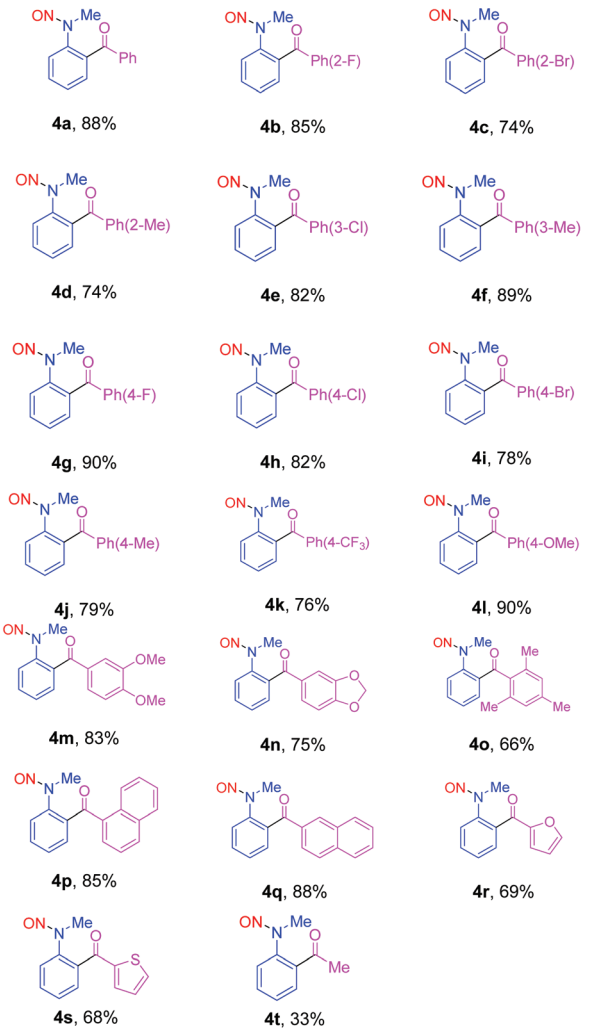
[a] Reaction conditions: **1a** (0.5 mmol), **3a** (1 mmol), 2 mL of solvent, air, 20 h. [b] Isolated yield.

With the optimum conditions established, the suitability of diversely substituted α-oxocarboxylic acids **3** was tested with **1a** and **2** as model substrates. As shown in Table 2, it turned out that this reaction had a good tolerance of various functional groups in that **3** with either a F, Br or Me unit attached on the *ortho*-position, a Cl or Me group on the *meta*-position, or a F, Cl, Br, Me, CF_3 or MeO group on the *para*-position of the 2-phenyl unit reacted with **1a** and **2** smoothly to give **4b–4l** in good to excellent yields. In addition, **3** bearing a bis- or tri-substituted 2-phenyl unit were also suitable for this reaction to afford **4m–4o** in moderate to good yields. Interestingly, the reaction of 2-(naphthalen-1-yl)-2-oxoacetic acid or 2-(naphthalen-2-yl)-2-oxoacetic acid with **1a** and **2** proceeded efficiently to afford **4p** and **4q** in yields of 85% and 88%. Moreover, 2-(furan-2-yl)-2-oxoacetic acid and 2-oxo-2-(thiophen-2-yl)acetic acid participated in this reaction smoothly to give heteroaromatic ketones **4r** and **4s** in yields of 69% and 68%, respectively. Finally, 2-oxopropanoic acid as an aliphatic unit substituted substrate could also take part in this reaction, albeit the yield of the corresponding product **4t** is lower.

Next, the suitability of a number of diversely substituted aniline derivatives **1** for this reaction was studied by using **2**

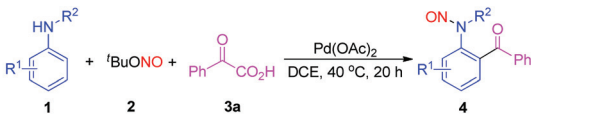
Table 2 Substrate scope for the preparation of **4** (I)[a,b]

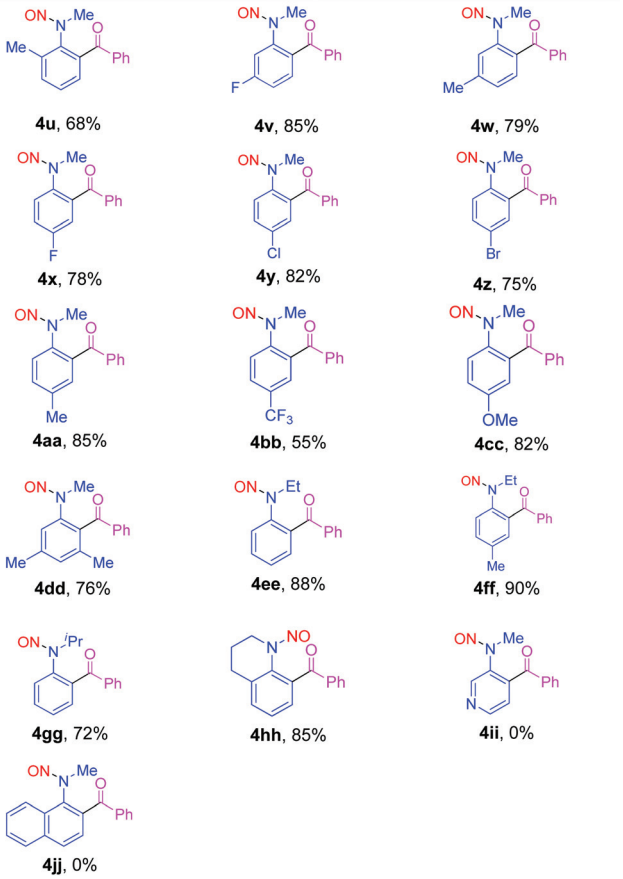




[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.5 mmol), **3** (1 mmol), $Pd(OAc)_2$ (0.025 mmol), DCE (2 mL), 40 °C, 20 h. [b] Isolated yield.

Table 3 Substrate scope for the preparation of **4** (II)[a,b]





[a] Reaction conditions: **1** (0.5 mmol), **2** (1.5 mmol), **3a** (1 mmol), $Pd(OAc)_2$ (0.025 mmol), DCE (2 mL), 40 °C, 20 h. [b] Isolated yield.

and **3a** as model substrates, and the results are listed in Table 3. We were pleased to find that all the aniline derivatives tested herein took part in this cascade reaction smoothly to give the corresponding *N*-nitrosoaniline products **4u–4hh** in moderate to good yields. Interestingly, different substituents such as Me, MeO, F, Cl, Br and CF_3 attached on different positions of the phenyl ring of **1** were well compatible with the reaction conditions, making subsequent structural elaboration of the phenyl skeleton possible. In comparison, substrates bearing an *ortho*-substituent showed lower efficiency as demonstrated in the formation of **4u**, most likely due to steric hindrance. In addition, this reaction showed an excellent regioselectivity for *meta*-Me or *meta*-F substituted anilines, which underwent acylation at the less sterically encumbered site to give **4v** or **4w**, and the formation of other possible regioisomers was not observed. It is also worth stressing that **1** bearing an electron-donating group (EDG) on the *para*-position of the phenyl ring afforded the corresponding products in higher yields than those with an electron-withdrawing group (EWG) as representatively demonstrated in the formation of **4aa** and **4cc** *vs.* **4bb**. Moreover, this reaction is compatible with a bis-substituted aniline substrate to give **4dd** in a yield of 76%. Interestingly, **1** with a *N*-ethyl unit could also react with **2** and **3a** to give **4ee** and **4ff** in excellent yields. On the other hand, **1** with a *N*-isopropyl group showed reduced efficiency compared with its *N*-methyl/ethyl counterparts, presumably due to increased steric hindrance (**4gg**). Notably, an 8-acylated tetrahydroquinoline derivative could also be easily obtained as shown in the formation of **4hh**. This is an interesting application of this novel method as 8-acylquinoline derivatives are valuable synthetic intermediates used in the preparation of

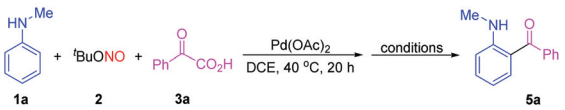
organic functional materials.[15] Finally, *N*-methylpyridin-3-amine and *N*-methylnaphthalen-1-amine have also been tried as the amine substrates to react with **2** and **3a**. From these reactions, the formation of the expected acylation products, *N*-(4-benzoyl pyridin-3-yl)-*N*-methylnitrous amide (**4ii**) and *N*-(2-benzoyl naphthalen-1-yl)-*N*-methylnitrous amide (**4jj**), was not observed.

Thus far, we have established a novel synthesis of *N*-nitroso-2-aminobenzophenones **4** *via* the cascade reactions of anilines **1**, *tert*-butyl nitrite **2** and α-oxocarboxylic acids **3** with the elimination of the pre-nitrosation of aniline substrates under strong acidic conditions and the use of a strong oxidant in the decarboxylative acylation process as encountered in preceding procedures. As a further aspect, we continued our study to explore the possibility of developing an all-in-one-pot synthesis of 2-aminobenzophenones **5** directly from **1**, **2** and **3** by searching for a compatible reducing system to remove the NO unit left behind in the *in situ* generated **4** without isolation and purification of the involved intermediates. We believed that the successful establishment of this envisioned synthesis would lead to a significant reduction of the time and labor cost in the previously reported preparation of 2-aminobenzophenone derivatives. For this purpose, the resulting mixture from the reaction of **1a** with **2** and **3a** was treated with zinc powder at 60 °C for 10 h. Unfortunately, the formation of the desired (2-(methylamino)phenyl)(phenyl) methanone (**5a**) was not observed (Table 4, entry 1). With the replacement of zinc with iron, a similar result was observed (entry 2). Next, a combination of zinc powder with NH_4Cl was used as the reducing system. Under this circumstance, **5a** was obtained in a yield of 32% (entry 3). When a combination of iron with NH_4Cl was used, to our pleasure, the yield of **5a** increased to 62% (entry 4). Next, NH_4Cl was replaced with HOAc as the additive to give **5a** in a lower yield of 51% (entry 5). Further screening on the effect of temperature showed that the reaction could afford **5a** in a yield of 67% when it was carried out at 80 °C (entry 6). Finally, we have also varied the loadings of iron powder and NH_4Cl. It turned out that the optimum loadings are 4 equiv. for iron powder and 3 equiv. for NH_4Cl (entries 8–11 *vs.* entry 6).

With the optimum reaction conditions in hand, the generality of this convenient all-in-one-pot synthesis of **5** was studied. Thus, various anilines **1** and α-oxocarboxylic acids **3** were reacted with **2**, respectively. It was concluded that diversely substituted **1** and **3** could participate in this one-pot multi-step cascade reaction smoothly to afford 2-aminobenzophenones **5a–5r** in reasonably good yields as shown in Table 5. It is also worth noting herein that a wide range of functional groups tolerated the reaction conditions very well, indicating that this is not only a convenient approach but also a general synthetic approach toward 2-aminobenzophenones from simple starting materials.

As a preliminary investigation into the reaction mechanism for the formation of **4**, we performed several control reactions.

Table 4 Optimization study for the synthesis of **5a**[a]

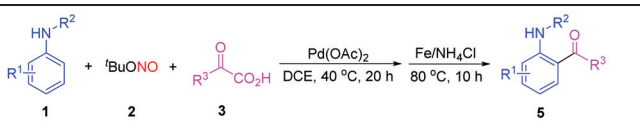


1a 2 3a 5a

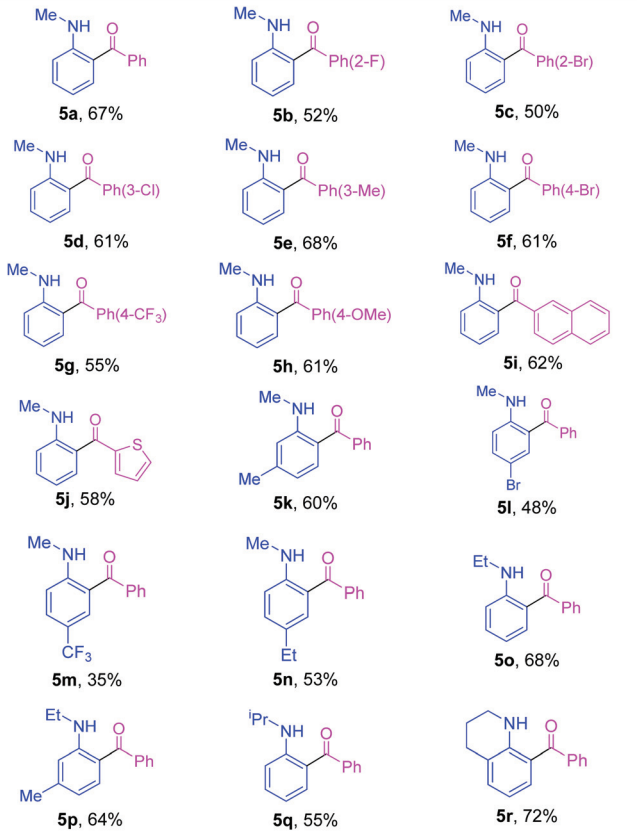
Entry	Reductant (equiv.)	Additive (equiv.)	*T* (°C)	Yield[b] (%)
1	Zn (4)		60	0
2	Fe (4)		60	0
3	Zn (4)	NH_4Cl (3)	60	32
4	Fe (4)	NH_4Cl (3)	60	62
5	Fe (4)	HOAc (3)	60	51
6	Fe (4)	NH_4Cl (3)	80	67
7	Fe (4)	NH_4Cl (3)	100	66
8	Fe (3)	NH_4Cl (3)	80	60
9	Fe (5)	NH_4Cl (3)	80	65
10	Fe (4)	NH_4Cl (2)	80	62
11	Fe (4)	NH_4Cl (4)	80	66

[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.5 mmol), **3a** (1 mmol), $Pd(OAc)_2$ (0.025 mmol), 2 mL of DCE, 40 °C, 20 h; then reductant, additive, 10 h. [b] Isolated yield.

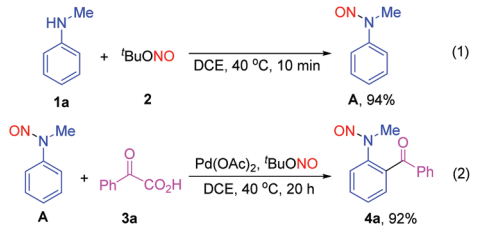
Table 5 Substrate scope for the preparation of **5**[a,b]



1 2 3 5



[a] Reaction conditions: **1** (0.5 mmol), **2** (1.5 mmol), **3** (1 mmol), $Pd(OAc)_2$ (0.025 mmol), 2 mL of DCE, 40 °C, 20 h; then iron powder (2 mmol), NH_4Cl (1.5 mmol), 80 °C, 10 h. [b] Isolated yield.

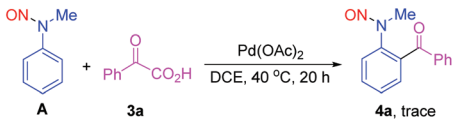


Scheme 2 Control experiment (I).

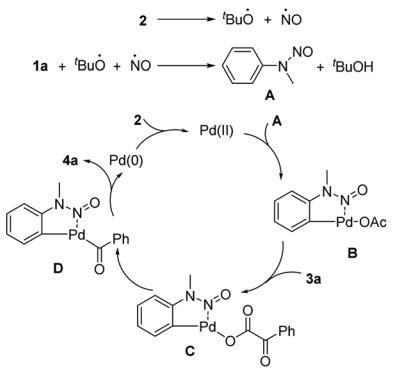
First, **1a** was treated with **2** in DCE at 40 °C for 10 min. From this reaction, *N*-methyl-*N*-phenylnitrous amide (**A**) was obtained in a yield of 94% (Scheme 2, eqn (1)). Next, **A** was treated with **3a** in the presence of $Pd(OAc)_2$ and *tert*-butyl nitrite in DCE at 40 °C for 20 h to afford **4a** in a yield of 92% (Scheme 2, eqn (2)). These results tell that **A** should be a key intermediate in the formation of **4a** from the reaction of **1a** with **2** and **3a**.

Second, a mixture of **A** and **3a** was treated with $Pd(OAc)_2$ in DCE at 40 °C for 20 h in the absence of *tert*-butyl nitrite. From this reaction, only a trace amount of **4a** was formed (Scheme 3). This result demonstrates that the presence of *tert*-butyl nitrite as an oxidant is crucial for the Pd(II)-catalyzed $C(sp^2)$–H acylation.

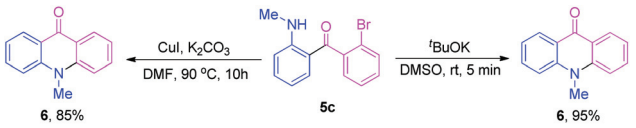
Based on the above observations and literature reports,[12] a plausible mechanism to account for the formation of **4a** is proposed in Scheme 4. Firstly, the homolysis of *tert*-butyl nitrite (**2**) under the reaction conditions gives a *tert*-butoxyl radical and a NO radical, which then react with **1a** to give intermediate **A**. Next, the *in situ* generated **A** undergoes an *ortho*-palladation with $Pd(OAc)_2$ under the assistance of the NO moiety to provide a five-membered palladacycle **B**. Subsequently, **B**



Scheme 3 Control experiment (II).



Scheme 4 Plausible catalytic cycle accounting for the formation of **4a**.



Scheme 5 Synthesis of an acridinone derivative **6** from **5c**.

Scheme 6 Gram-scale synthesis of **4a** and **5a**.

reacts with **3a** to afford intermediate **C**. The following oxidative decarboxylation of complex **C** affords intermediate **D**. Next, a reductive elimination occurs with **D** to provide **4a** and release the Pd(0) species, which is then oxidized by **2** to regenerate the active Pd(II) catalyst for the next catalytic cycle.

Furthermore, it is well known that acridinone derivatives are highly valuable in synthetic and medicinal chemistry.[16] To demonstrate the usability of the 2-aminobenzophenone product obtained above, **5c** was treated with ^{t}BuOK in DMSO at room temperature for 5 min. From this reaction, the corresponding acridinone derivative **6** was obtained in a yield of 95%. In addition, the preparation of **6** has also been tried through Cu(I)-catalyzed coupling. It turned out that treatment of **5c** with CuI and K_2CO_3 in DMF afforded **6** in a yield of 85% (shown in Scheme 5).

Finally, to test whether these newly developed synthetic protocols are suitable for large-scale synthetic missions, the preparations of **4a** and **5a** were carried out in an enlarged scale of 5 mmol. It turned out that under the optimum reaction conditions described above, the corresponding cascade reactions of **1a** with **2** and **3a** proceeded smoothly to afford **4a** and **5a** in yields of 85% and 65%, respectively (Scheme 6).

Conclusions

In summary, an efficient and regioselective synthesis of *N*-nitroso-2-aminobenzophenones through the one-pot three-component cascade reactions of anilines with *tert*-butyl nitrite and α-oxocarboxylic acids under the catalysis of $Pd(OAc)_2$ has been established. To our knowledge, this is the first example in which *N*-nitroso-2-aminobenzophenones were synthesized directly from anilines and α-oxocarboxylic acids in a highly regioselective manner by using *tert*-butyl nitrite as both a nitrosation reagent and an oxidant. Moreover, direct treatment of the resulting mixture from the acylation reactions with Fe/NH_4Cl led to a highly practical and all-in-one-pot preparation of 2-aminobenzophenones *via* the removal of the NO unit that is left behind in the *in situ* generated *N*-nitroso-2-aminobenzophenones without isolation and purification of any involved intermediates. Compared with literature

methods, these novel protocols have notable features such as simple starting materials, mild reaction conditions, high efficiency and excellent regioselectivity.

Experimental section

All commercial reagents and solvents were used without further purification. Melting points were recorded with a micro-melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), m (multiplet), *etc*. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and the components were visualized by observation under UV light (254 and 365 nm).

A typical procedure for the synthesis of 4a and the spectroscopic data of 4a–4hh

To a reaction tube equipped with a stir bar were sequentially added *N*-methylaniline (**1a**, 0.5 mmol), *tert*-butyl nitrite (**2**, 1.5 mmol), DCE (2 mL), $Pd(OAc)_2$ (0.025 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 1 mmol) with stirring. The solution was stirred at 40 °C for 20 h. Upon completion of the reaction, the reaction mixture was diluted with brine (5 mL) and extracted with EtOAc (8 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (10 : 1) to give **4a** in a yield of 88%. **4b–4hh** were obtained in a similar manner.

***N*-(2-Benzoylphenyl)-*N*-methylnitrous amide (4a).**[12c] Yellowish oil (105 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.24 (s, 3H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.66–7.71 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.6, 123.2, 128.1, 128.5, 129.6, 130.3, 131.6, 133.5, 134.2, 136.9, 140.6, 195.2.

***N*-(2-(2-Fluorobenzoyl)phenyl)-*N*-methylnitrous amide (4b).**[12c] Yellowish oil (110 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.27 (s, 3H), 7.02–7.06 (m, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.49–7.52 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.68–7.72 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.3, 116.3 (d, $^2J_{C-F}$ = 21.9 Hz), 122.9, 124.6 (d, $^4J_{C-F}$ = 3.3 Hz), 126.2 (d, $^2J_{C-F}$ = 11.0 Hz), 128.2, 130.1, 131.5, 132.1, 134.6 (d, $^3J_{C-F}$ = 8.7 Hz), 135.4, 140.5, 160.8 (d, $^1J_{C-F}$ = 254.9 Hz), 191.5.

***N*-(2-(2-Bromobenzoyl)phenyl)-*N*-methylnitrous amide (4c).**[12c] Yellowish oil (118 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 7.29–7.36 (m, 2H), 7.39–7.43 (m, 2H), 7.54 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.57–7.60 (m, 1H), 7.68–7.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 120.4, 124.4, 127.4, 128.7, 131.3, 131.8, 132.5, 133.0, 133.87, 133.90, 139.3, 141.2, 194.3.

***N*-Methyl-*N*-(2-(2-methylbenzoyl)phenyl)nitrous amide (4d).**[12c] Yellowish oil (94 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.04 (s, 3H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.22–7.28 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.55–7.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 34.3, 123.3, 125.1, 128.3, 129.7, 130.9, 131.8, 131.9, 132.0, 135.7, 137.3, 139.6, 140.8, 196.8.

***N*-(2-(3-Chlorobenzoyl)phenyl)-*N*-methylnitrous amide (4e).**[12c] Yellowish oil (112 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (s, 3H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.42–7.49 (m, 2H), 7.51–7.55 (m, 2H), 7.59–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 122.8, 127.7, 128.0, 129.4, 129.9, 130.2, 131.9, 133.3, 133.5, 134.8, 138.6, 140.6, 193.7.

***N*-Methyl-*N*-(2-(3-methylbenzoyl)phenyl)nitrous amide (4f).**[12c] Yellowish oil (113 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.25 (s, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.44–7.49 (m, 2H), 7.52–7.56 (m, 2H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.68 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 34.6, 123.3, 127.0, 128.0, 128.3, 130.0, 130.2, 131.5, 134.3, 134.4, 136.9, 138.4, 140.7, 195.3.

***N*-(2-(4-Fluorobenzoyl)phenyl)-*N*-methylnitrous amide (4g).**[12c] Yellowish oil (116 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.28 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.43–7.46 (m, 1H), 7.51 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.55–7.62 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.4, 115.8 (d, $^2J_{C-F}$ = 21.9 Hz), 123.1, 128.0, 130.0, 131.7, 132.3 (d, $^3J_{C-F}$ = 8.9 Hz), 133.3 (d, $^4J_{C-F}$ = 3.3 Hz), 134.0, 140.5, 165.9 (d, $^1J_{C-F}$ = 254.9 Hz), 193.6.

***N*-(2-(4-Chlorobenzoyl)phenyl)-*N*-methylnitrous amide (4h).**[12c] Yellowish oil (112 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.27–7.29 (m, 2H), 7.34–7.36 (m, 1H), 7.43–7.46 (m, 1H), 7.51 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.55–7.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 122.9, 128.0, 128.9, 130.1, 130.9, 131.8, 133.7, 135.3, 139.8, 140.5, 193.9.

***N*-(2-(4-Bromobenzoyl)phenyl)-*N*-methylnitrous amide (4i).**[12c] Yellowish oil (124 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.53–7.62 (m, 6H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 122.9, 128.0, 128.6, 130.1, 131.0, 131.8, 131.9, 133.7, 135.7, 140.5, 194.1.

***N*-Methyl-*N*-(2-(4-methylbenzoyl)phenyl)nitrous amide (4j).**[12c] Yellowish oil (100 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.17 (s, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43–7.47 (m, 1H), 7.52–7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 34.6, 123.4, 128.1, 129.2, 129.8, 130.1, 131.4, 134.3, 134.5, 140.6, 144.4, 194.9.

***N*-Methyl-*N*-(2-(4-(trifluoromethyl)benzoyl)phenyl)nitrous amide (4k).**[12c] Yellowish oil (117 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.52–7.54 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.63 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.0, 122.6, 123.5 (q, $^1J_{C-F}$ = 271.3 Hz), 125.5 (q, $^3J_{C-F}$ = 3.7 Hz), 128.0, 129.7, 130.2, 132.1, 133.3, 134.4 (q, $^2J_{C-F}$ = 32.7 Hz), 139.9, 140.6, 193.9.

***N*-(2-(4-Methoxybenzoyl)phenyl)-*N*-methylnitrous amide (4l).**[12c] Yellowish oil (121 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18

(s, 3H), 3.77 (s, 3H), 6.79–6.82 (m, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.51 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.57 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.62–7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 55.5, 113.8, 123.6, 128.1, 129.6, 130.0, 131.2, 132.2, 134.8, 140.5, 163.9, 193.9.

***N*-(2-(3,4-Dimethoxybenzoyl)phenyl)-*N*-methylnitrous amide (4m).**[12a] Yellowish oil (124 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 6.71 (d, J = 8.4 Hz, 1H), 7.13 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.37–7.39 (m, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.51 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.56–7.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 56.0, 56.1, 109.9, 111.1, 123.7, 125.5, 128.0, 129.7, 130.0, 131.2, 134.7, 140.5, 149.2, 153.8, 193.9.

***N*-(2-(Benzo[*d*][1,3]dioxole-5-carbonyl)phenyl)-*N*-methylnitrous amide (4n).** Yellowish oil (107 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.28 (s, 3H), 6.03 (s, 2H), 6.76 (d, J = 8.4 Hz, 1H), 7.23 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.43 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.51 (td, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.57 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.64 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7, 102.0, 107.8, 109.0, 123.5, 126.9, 128.0, 129.9, 131.3, 131.5, 134.6, 140.5, 148.3, 152.3, 193.4. HRMS calcd for $C_{15}H_{12}N_2O_4Na$: 307.0689 $[M + Na]^+$, found: 307.0701.

***N*-Methyl-*N*-(2-(2,4,6-trimethylbenzoyl)phenyl)nitrous amide (4o).**[12c] Yellowish oil (93 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.01 (s, 6H), 2.22 (s, 3H), 3.25 (s, 3H), 6.78 (s, 2H), 7.33 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.42 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.56 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.60 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0, 21.2, 35.7, 127.0, 129.0, 129.4, 132.1, 133.4, 135.0, 135.4, 136.3, 139.5, 141.1, 198.6.

***N*-(2-(1-Naphthoyl)phenyl)-*N*-methylnitrous amide (4p).**[12a] Yellowish oil (123 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (s, 3H), 7.34–7.38 (m, 1H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.52–7.62 (m, 4H), 7.67–7.74 (m, 2H), 7.88 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6, 123.8, 124.0, 125.8, 126.7, 128.2, 128.3, 128.5, 130.3, 130.9, 131.1, 132.1, 133.5, 133.8, 134.9, 136.2, 141.1, 196.5.

***N*-(2-(2-Naphthoyl)phenyl)-*N*-methylnitrous amide (4q).**[12a] Yellowish oil (128 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (s, 3H), 7.48–7.62 (m, 4H), 7.69–7.74 (m, 2H), 7.84–7.88 (m, 4H), 8.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.5, 123.3, 124.7, 126.9, 127.9, 128.1, 128.6, 128.8, 129.6, 130.3, 131.6, 132.0, 132.3, 134.2, 134.4, 135.7, 140.8, 195.1.

***N*-(2-(Furan-2-carbonyl)phenyl)-*N*-methylnitrous amide (4r).**[12c] Yellowish oil (79 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.30 (s, 3H), 6.45 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 7.02 (d, J = 4.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.46 (dd, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.60 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6, 112.6, 120.5, 123.6, 128.1, 130.1, 131.9, 133.4, 140.6, 147.5, 152.1, 181.9.

***N*-Methyl-*N*-(2-(thiophene-2-carbonyl)phenyl)nitrous amide (4s).**[12c] Yellowish oil (84 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.27 (s, 3H), 7.00 (dd, J_1 = 4.8 Hz, J_2 = 3.6 Hz, 1H), 7.35 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.46 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.58–7.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9, 124.0, 128.1, 128.2, 129.8, 131.6, 134.3, 135.2, 135.3, 140.4, 143.7, 187.1.

***N*-(2-Acetylphenyl)-*N*-methylnitrous amide (4t).**[12a] Brown oil (29 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.44 (s, 3H), 7.37 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.52 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.64 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.73 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.3, 111.2, 113.8, 117.6, 132.7, 135.1, 152.0, 200.8.

***N*-(2-Benzoyl-6-methylphenyl)-*N*-methylnitrous amide (4u).**[12c] Yellowish oil (86 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.27 (s, 3H), 7.28–7.45 (m, 3H), 7.49 (t, J = 8.0 Hz, 1H), 7.54–7.59 (m, 2H), 7.76 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 36.6, 127.4, 128.4, 128.9, 130.2, 133.60, 133.62, 136.0, 136.9, 137.9, 139.5, 195.8.

***N*-(2-Benzoyl-5-fluorophenyl)-*N*-methylnitrous amide (4v).**[12a] Yellow oil (110 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 7.18 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.25 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.64–7.71 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.1, 110.4 (d, $^2J_{C-F}$ = 24.0 Hz), 114.9 (d, $^2J_{C-F}$ = 21.1 Hz), 128.6, 129.5, 130.1 (d, $^4J_{C-F}$ = 3.7 Hz), 132.4 (d, $^3J_{C-F}$ = 9.4 Hz), 133.5, 136.9, 142.5 (d, $^3J_{C-F}$ = 10.2 Hz), 163.9 (d, $^1J_{C-F}$ = 251.7 Hz), 194.1.

***N*-(2-Benzoyl-5-methylphenyl)-*N*-methylnitrous amide (4w).**[12c] Yellowish oil (100 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.23 (s, 3H), 7.24 (s, 1H), 7.33–7.41 (m, 3H), 7.51–7.55 (m, 2H), 7.69–7.71 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5, 34.7, 124.0, 128.5, 128.8, 129.6, 130.4, 131.5, 133.3, 137.2, 140.8, 142.5, 195.3.

***N*-(2-Benzoyl-4-fluorophenyl)-*N*-methylnitrous amide (4x).**[12c] Yellowish oil (101 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 7.33–7.46 (m, 5H), 7.58 (t, J = 7.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 117.2 (d, $^2J_{C-F}$ = 24.0 Hz), 118.5 (d, $^2J_{C-F}$ = 22.6 Hz), 125.5 (d, $^3J_{C-F}$ = 8.0 Hz), 128.7, 129.6, 133.8, 136.2, 136.3 (d, $^3J_{C-F}$ = 6.5 Hz), 136.9 (d, $^4J_{C-F}$ = 3.7 Hz), 161.5 (d, $^1J_{C-F}$ = 249.4 Hz), 193.7.

***N*-(2-Benzoyl-4-chlorophenyl)-*N*-methylnitrous amide (4y).**[12c] Yellowish oil (112 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (s, 3H), 7.30–7.36 (m, 3H), 7.47–7.53 (m, 2H), 7.57 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.4, 124.3, 128.7, 129.6, 130.1, 131.5, 133.8, 134.0, 135.4, 136.3, 139.1, 193.7.

***N*-(2-Benzoyl-4-bromophenyl)-*N*-methylnitrous amide (4z).**[12c] Yellowish oil (119 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.21 (s, 3H), 7.31 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 2.0 Hz, 1H), 7.78 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 121.7, 124.5, 128.7, 129.6, 133.0, 133.8, 134.5, 135.6, 136.3, 139.6, 193.5.

***N*-(2-Benzoyl-4-methylphenyl)-*N*-methylnitrous amide (4aa).**[12c] Yellowish oil (108 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.22 (s, 3H), 7.33 (d, J = 8.0 Hz, 1H), 7.39–7.44 (m, 3H), 7.48 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.72 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1, 34.7, 123.2, 128.5, 129.6, 130.6, 132.2, 133.4, 134.2, 137.0, 138.3, 138.4, 195.5.

***N*-(2-Benzoyl-4-(trifluoromethyl)phenyl)-*N*-methylnitrous amide (4bb).**[12c] Yellowish oil (85 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 3H), 7.40–7.44 (m, 2H), 7.55–7.59 (m, 2H), 7.69–7.71 (m, 2H), 7.89 (s, 1H), 7.93 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.7, 122.7, 123.3 (q, $^1J_{C-F}$ = 270.2 Hz), 127.4 (q, $^3J_{C-F}$ = 3.2 Hz), 128.4 (q, $^3J_{C-F}$ = 3.3 Hz), 128.8, 129.5, 130.0 (q, $^2J_{C-F}$ = 32.9 Hz), 133.9, 134.1, 136.2, 143.2, 193.6.

***N*-(2-Benzoyl-4-methoxyphenyl)-*N*-methylnitrous amide (4cc).**[12c] Yellowish oil (111 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.19 (s, 3H), 3.88 (s, 3H), 7.11 (d, J = 2.4 Hz, 1H), 7.17 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.1, 55.9, 114.8, 117.3, 125.3, 128.5, 129.6, 133.5, 133.8, 135.8, 136.8, 159.2, 195.0.

***N*-(2-Benzoyl-3,5-dimethylphenyl)-*N*-methylnitrous amide (4dd).** Yellow oil (102 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.47 (s, 3H), 3.17 (s, 3H), 7.05 (s, 1H), 7.20 (s, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.3, 34.9, 121.9, 128.7, 129.2, 131.5, 132.0, 133.7, 137.40, 137.42, 140.0, 140.5, 196.6. HRMS calcd for $C_{16}H_{17}N_2O_2$: 269.1285 $[M + H]^+$, found: 269.1283.

***N*-(2-Benzoylphenyl)-*N*-ethylnitrous amide (4ee).**[12c] Yellowish oil (112 mg, 88%), a mixture of two isomers, the ratio of which being about 5 : 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 0.6H), 3.78 (q, J = 7.2 Hz, 2H), 4.48 (q, J = 7.2 Hz, 0.4H), 7.06 (d, J = 8.0 Hz, 0.2H), 7.19–7.41 (m, 4H), 7.44–7.48 (m, 2.2H), 7.51–7.55 (m, 1H), 7.57–7.61 (m, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.6 Hz, 0.4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.4, 14.2, 41.7, 49.7, 123.4, 126.9, 127.9, 128.4, 128.5, 128.6, 129.5, 129.8, 130.1, 130.3, 131.4, 131.6, 133.4, 133.5, 134.8, 135.8, 136.1, 137.0, 137.3, 140.0, 194.5, 195.3.

***N*-(2-Benzoyl-4-methylphenyl)-*N*-ethylnitrous amide (4ff).** Yellowish oil (120 mg, 90%), a mixture of two isomers, the ratio of which being about 4.3 : 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J = 7.6 Hz, 3H), 1.47 (t, J = 7.2 Hz, 0.71H), 2.42 (s, 0.69H), 2.47 (s, 3H), 3.82 (q, J = 7.2 Hz, 2H), 4.52 (q, J = 7.2 Hz, 0.46H), 7.01 (d, J = 8.0 Hz, 0.22H), 7.32 (d, J = 8.0 Hz, 1H), 7.38–7.47 (m, 4.68H), 7.52–7.59 (m, 1.36H), 7.72–7.74 (m, 2H), 7.79–7.81 (m, 0.47H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.4, 14.2, 21.0, 21.2, 41.8, 49.7, 123.6, 126.8, 128.3, 128.4, 129.8, 130.0, 130.3, 130.5, 131.9, 132.1, 133.3, 133.4, 134.8, 137.0, 137.2, 138.3, 195.5. HRMS calcd for $C_{16}H_{16}N_2O_2Na$: 291.1104 $[M + Na]^+$, found: 291.1105.

***N*-(2-Benzoylphenyl)-*N*-isopropylnitrous amide (4gg).**[12c] Yellowish oil (96 mg, 72%), a mixture of two isomers, the ratio of which being about 5 : 4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, J = 6.8 Hz, 4.8H), 1.50 (t, J = 6.8 Hz, 6H), 4.56–4.63 (m, 1H), 4.75–4.82 (m, 0.8H), 7.03 (d, J = 7.6 Hz, 1H), 7.32–7.40 (m, 6.6H), 7.44–7.58 (m, 5.2H), 7.69–7.72 (m, 3.6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 22.4, 48.9, 57.9, 126.5, 127.4, 128.1, 128.3, 128.4, 128.6, 129.7, 129.9, 130.28, 130.34, 130.8, 131.4, 133.4, 133.5, 136.2, 136.6, 137.0, 137.1, 137.3, 138.5, 194.6, 195.4.

(1-Nitroso-1,2,3,4-tetrahydroquinolin-8-yl)(phenyl)methanone (4hh).[12a] Yellowish oil (113 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (quint, J = 6.4 Hz, 2H), 2.85 (t, J = 6.0 Hz, 2H), 3.71 (t, J = 6.4 Hz, 2H), 7.34–7.44 (m, 5H), 7.49 (t, J = 7.6 Hz, 1H), 7.70–7.72 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.3, 27.7, 43.3, 126.1, 128.37, 128.43, 129.1, 129.8, 130.5, 131.1, 132.8, 135.0, 137.3, 194.9.

A typical procedure for the synthesis of 5a and the spectroscopic data of 5a–5r

To a reaction tube equipped with a stir bar were sequentially added *N*-methylaniline (**1a**, 0.5 mmol), *tert*-butyl nitrite (**2**, 1.5 mmol), DCE (2 mL), $Pd(OAc)_2$ (0.025 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 1 mmol) with stirring. The solution was stirred at 40 °C for 20 h. Then, iron powder (2 mmol) and NH_4Cl (1.5 mmol) were added to the resulting mixture. The tube was sealed and the reaction mixture was stirred at 80 °C for 10 h. After being cooled to room temperature, it was diluted with brine (5 mL) and EtOAc (8 mL), and then filtered and separated. The aqueous phase was extracted with EtOAc (5 mL × 2). All the organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (30 : 1) to give **5a** in a yield of 67%. **5b–5r** were obtained in a similar manner.

(2-(Methylamino)phenyl)(phenyl)methanone (5a).[9c] Yellow solid (71 mg, 67%), mp 71–72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.00 (d, J = 4.8 Hz, 3H), 6.57 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 7.43–7.55 (m, 5H), 7.63 (d, J = 7.8 Hz, 2H), 8.58 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5, 111.1, 113.7, 117.3, 128.1, 129.0, 130.7, 135.1, 135.5, 140.6, 152.8, 199.4.

(2-Fluorophenyl)(2-(methylamino)phenyl)methanone (5b).[9c] Yellow oil (60 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (d, J = 4.4 Hz, 3H), 6.43–6.47 (m, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.04–7.09 (m, 1H), 7.15 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.18–7.29 (m, 1H), 7.31–7.40 (m, 3H), 8.80 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.4, 111.2, 114.0, 116.0 (d, $^2J_{C-F}$ = 21.9 Hz), 117.4, 124.1 (d, $^4J_{C-F}$ = 3.3 Hz), 129.0 (d, $^2J_{C-F}$ = 16.5 Hz), 129.6 (d, $^4J_{C-F}$ = 3.3 Hz), 131.4 (d, $^3J_{C-F}$ = 7.7 Hz), 135.4, 135.8, 152.8, 158.9 (d, $^1J_{C-F}$ = 247.2 Hz), 195.3.

(2-Bromophenyl)(2-(methylamino)phenyl)methanone (5c). Yellow solid (72 mg, 50%), mp 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (d, J = 4.8 Hz, 3H), 6.39 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 7.08 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.16–7.22 (m, 2H), 7.27–7.33 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 8.84 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4, 111.3, 114.1, 116.4, 119.4, 127.1, 128.4, 130.3, 132.9, 135.6, 136.0, 142.1, 153.1, 197.9. HRMS calcd for $C_{14}H_{13}BrNO$: 290.0175 $[M + H]^+$, found: 290.0175.

(3-Chlorophenyl)(2-(methylamino)phenyl)methanone (5d). Yellow oil (75 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (d, J = 4.8 Hz, 3H), 6.57 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 6.78–6.80 (m, 1H), 7.38–7.51 (m, 5H), 7.59 (t, J = 1.6 Hz, 1H), 8.58 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 111.3, 113.8, 116.7, 127.0, 128.8, 129.4, 130.6, 134.2, 135.3, 135.5, 142.3, 152.9,

197.5. HRMS calcd for $C_{14}H_{12}ClNONa$: 268.0500 $[M + Na]^+$, found: 268.0511.

(2-(Methylamino)phenyl)(*m*-tolyl)methanone (5e).[9c] Yellow oil (77 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.86 (d, J = 5.2 Hz, 3H), 6.42–6.46 (m, 1H), 6.65 (d, J = 8.4 Hz, 1H), 7.21–7.24 (m, 2H), 7.26–7.32 (m, 3H), 7.39 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.44 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.4, 29.5, 111.1, 113.6, 117.4, 126.2, 127.9, 129.4, 131.4, 135.0, 135.6, 137.9, 140.7, 152.7, 199.6.

(4-Bromophenyl)(2-(methylamino)phenyl)methanone (5f).[9c] Yellow solid (88 mg, 61%), mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (d, J = 5.2 Hz, 3H), 6.44–6.48 (m, 1H), 6.67–6.69 (m, 1H), 7.18–7.35 (m, 2H), 7.39 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.51 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 8.43 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 111.3, 113.8, 116.8, 125.3, 130.6, 131.3, 135.2, 135.3, 139.4, 152.8, 198.0.

(2-(Methylamino)phenyl)(4-(trifluoromethyl)phenyl)methanone (5g).[9c] Yellow solid (77 mg, 55%), mp 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (d, J = 5.2 Hz, 3H), 6.42–6.47 (m, 1H), 6.69 (d, J = 8.4 Hz, 1H), 7.29 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.32–7.36 (m, 1H), 7.57–7.64 (m, 4H), 8.57 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4, 111.4, 113.9, 116.5, 123.9 (q, $^1J_{C-F}$ = 270.8 Hz), 125.1 (q, $^3J_{C-F}$ = 3.6 Hz), 129.0, 132.2 (q, $^2J_{C-F}$ = 32.5 Hz), 135.3, 135.7, 143.9, 153.0, 197.8.

(4-Methoxyphenyl)(2-(methylamino)phenyl)methanone (5h).[9c] Yellow solid (73 mg, 61%), mp 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (d, J = 5.2 Hz, 3H), 3.78 (s, 3H), 6.45–6.49 (m, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.85 (dt, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 7.28–7.32 (m, 1H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.55 (dt, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 8.12–8.13 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 55.4, 111.0, 113.3, 113.6, 117.9, 131.6, 132.9, 134.6, 135.0, 152.3, 162.1, 198.2.

(2-(Methylamino)phenyl)(naphthalen-2-yl)methanone (5i).[17] Yellow solid (81 mg, 62%), mp 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (d, J = 5.2 Hz, 3H), 6.42–6.46 (m, 1H), 6.67 (d, J = 8.4 Hz, 1H), 7.31 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.40–7.47 (m, 3H), 7.63 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.77–7.81 (m, 3H), 7.97 (s, 1H), 8.43–8.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5, 111.2, 113.8, 117.6, 125.9, 126.7, 127.6, 127.8, 128.0, 129.0, 129.7, 132.4, 134.4, 135.1, 135.6, 137.9, 152.8, 199.2.

(2-(Methylamino)phenyl)(thiophen-2-yl)methanone (5j). Yellow oil (63 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (d, J = 5.2 Hz, 3H), 6.53 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 7.00–7.02 (m, 1H), 7.30–7.34 (m, 1H), 7.44 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.52 (dd, J_1 = 4.8 Hz, J_2 = 0.8 Hz, 1H), 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.83 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.6, 111.2, 114.0, 118.1, 127.5, 132.3, 133.4, 133.6, 134.7, 145.1, 151.9, 189.6. HRMS calcd for $C_{12}H_{12}NOS$: 218.0634 $[M + H]^+$, found: 218.0634.

(4-Methyl-2-(methylamino)phenyl)(phenyl)methanone (5k). Yellow oil (67 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.99 (d, J = 5.2 Hz, 3H), 6.39 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.59 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.44–7.48 (m, 2H), 7.49–7.54 (m, 1H), 7.59–7.62 (m, 2H), 8.66 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 29.4, 111.2, 115.1, 115.2, 128.0, 128.8, 130.4, 135.7, 140.9, 146.2, 153.0, 198.8. HRMS calcd for $C_{15}H_{16}NO$: 226.1226 $[M + H]^+$, found: 226.1225.

(5-Bromo-2-(methylamino)phenyl)(phenyl)methanone (5l).[9c] Yellow solid (69 mg, 48%), mp 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (d, J = 5.2 Hz, 3H), 6.59 (d, J = 9.2 Hz, 1H), 7.37–7.41 (m, 3H), 7.44–7.52 (m, 4H), 8.41 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.6, 104.9, 113.2, 118.6, 128.3, 129.0, 131.2, 137.0, 137.6, 139.8, 151.5, 198.3.

(2-(Methylamino)-5-(trifluoromethyl)phenyl)(phenyl)methanone (5m).[9c] Yellow oil (49 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (d, J = 5.2 Hz, 3H), 6.81 (d, J = 8.8 Hz, 1H), 7.46–7.50 (m, 2H), 7.53–7.61 (m, 4H), 7.75 (d, J = 1.6 Hz, 1H), 8.83 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 111.4, 115.5 (q, $^2J_{C-F}$ = 32.9 Hz), 116.2, 124.5 (q, $^1J_{C-F}$ = 269.1 Hz), 128.4, 129.0, 131.2 (q, $^3J_{C-F}$ = 3.3 Hz), 131.4, 132.7 (q, $^3J_{C-F}$ = 4.4 Hz), 139.6, 154.3, 198.8.

(5-Ethyl-2-(methylamino)phenyl)(phenyl)methanone (5n). Yellow oil (63 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, J = 7.6 Hz, 3H), 2.40 (q, J = 7.6 Hz, 2H), 2.89 (d, J = 5.2 Hz, 3H), 6.65 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.19–7.22 (m, 2H), 7.36–7.40 (m, 2H), 7.42–7.46 (m, 1H), 7.52–7.54 (m, 2H), 8.28–8.29 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9, 27.7, 29.6, 111.3, 117.1, 128.0, 129.0, 129.2, 130.6, 134.0, 135.1, 140.7, 151.1, 199.2. HRMS calcd for $C_{16}H_{18}NO$: 240.1383 $[M + H]^+$, found: 240.1383.

(2-(Ethylamino)phenyl)(phenyl)methanone (5o).[9c] Yellow oil (76 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3H), 3.18–3.25 (m, 2H), 6.43 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.27–7.31 (m, 1H), 7.33–7.43 (m, 4H), 7.50–7.52 (m, 2H), 8.44 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 37.4, 111.5, 113.5, 117.0, 128.1, 129.0, 130.7, 135.0, 135.6, 140.7, 151.9, 199.3.

(2-(Ethylamino)-4-methylphenyl)(phenyl)methanone (5p). Yellow oil (76 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 5.2 Hz, 3H), 2.17 (s, 3H), 3.10–3.17 (m, 2H), 6.18 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 6.41 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.24–7.28 (m, 2H), 7.30–7.34 (m, 1H), 7.40–7.43 (m, 2H), 8.45 (brs, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.5, 22.3, 37.3, 111.6, 114.8, 115.1, 128.0, 128.9, 130.4, 135.7, 140.9, 146.1, 152.1, 198.8. HRMS calcd for $C_{16}H_{18}NO$: 240.1383 $[M + H]^+$, found: 240.1382.

(2-(Isopropylamino)phenyl)(phenyl)methanone (5q). Yellow oil (66 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, J = 6.4 Hz, 6H), 3.67–3.76 (m, 1H), 6.38–6.42 (m, 1H), 6.71 (d, J = 8.4 Hz, 1H), 7.17–7.30 (m, 1H), 7.33–7.44 (m, 4H), 7.50–7.53 (m, 2H), 8.53 (d, J = 6.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.8, 43.4, 112.0, 113.2, 116.9, 128.0, 129.0, 130.7, 135.0, 135.8, 140.7, 151.1, 199.3. HRMS calcd for $C_{16}H_{18}NO$: 240.1383 $[M + H]^+$, found: 240.1383.

Phenyl(1,2,3,4-tetrahydroquinolin-8-yl)methanone (5r). Yellow oil (85 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84–1.90 (m, 2H), 2.74 (t, J = 6.4 Hz, 2H), 3.38–3.41 (m, 2H), 6.27–6.31 (m, 1H), 6.97 (d, J = 6.8 Hz, 1H), 7.16–7.21 (m, 1H), 7.32–7.42 (m, 3H), 7.48–7.51 (m, 2H), 8.72 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 27.9, 41.2, 112.8, 115.8, 122.6, 128.0, 128.8, 130.4, 133.5, 134.0, 141.0, 149.3, 199.2. HRMS calcd for $C_{16}H_{16}NO$: 238.1226 $[M + H]^+$, found: 238.1225.

Procedures for the synthesis of 6 and the spectroscopic data of 6

To a reaction tube equipped with a stir bar were added (2-bromophenyl)(2-(methylamino)phenyl)methanone (**5c**, 0.5 mmol), DMSO (2 mL) and ^{t}BuOK (0.5 mmol). The mixture was stirred at room temperature. Upon completion of the reaction as monitored by TLC, ethyl acetate (5 mL) and water (5 mL) were added, and the layers were separated. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4 : 1) as the eluent to give **6** in a yield of 95% (99 mg).

To a reaction tube equipped with a stir bar were added (2-bromophenyl)(2-(methylamino)phenyl)methanone (**5c**, 0.5 mmol), DMF (2 mL), CuI (0.1 mmol) and K_2CO_3 (0.5 mmol). The mixture was stirred at 90 °C for 10 h. Upon completion of the reaction as monitored by TLC, ethyl acetate (5 mL) and water (5 mL) were added, and the layers were separated. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4 : 1) as the eluent to give **6** in a yield of 85% (89 mg).

10-Methylacridin-9(10*H*)-one (6).[18] Yellowish solid, mp 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.29 (t, J = 7.2 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.70–7.74 (m, 2H), 8.57 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.6, 114.7, 121.2, 122.5, 127.8, 133.8, 142.6, 178.1.

Gram-scale synthesis of 4a and 5a

To a reaction tube equipped with a stir bar were sequentially added *N*-methylaniline (**1a**, 5 mmol), *tert*-butyl nitrite (**2**, 15 mmol), DCE (15 mL), $Pd(OAc)_2$ (0.25 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 10 mmol) with stirring. The solution was stirred at 40 °C for 20 h. Upon completion of the reaction, the reaction mixture was diluted with brine (20 mL) and extracted with EtOAc (30 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (10 : 1) to give **4a** in a yield of 85%.

To a reaction tube equipped with a stir bar were sequentially added *N*-methylaniline (**1a**, 5 mmol), *tert*-butyl nitrite (**2**, 15 mmol), DCE (15 mL), $Pd(OAc)_2$ (0.25 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 10 mmol) with stirring. The solution was stirred at 40 °C for 20 h. Then, iron powder (20 mmol) and NH_4Cl (15 mmol) were added to the resulting mixture. The tube was sealed and the reaction mixture was stirred at 80 °C for 10 h. After being cooled to room temperature, it was diluted with brine (30 mL) and EtOAc (50 mL), and then filtered and separated. The aqueous phase was extracted with EtOAc (50 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (30 : 1) to give **5a** in a yield of 65%.

Mechanistic studies

Control experiment (I). To a reaction tube equipped with a stir bar were sequentially added *N*-methylaniline (**1a**, 0.5 mmol), *tert*-butyl nitrite (**2**, 1 mmol) and DCE (2 mL) with stirring. The solution was stirred at 40 °C for 10 min. It was then concentrated under vacuum. The crude product was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (10 : 1) to give *N*-methyl-*N*-phenylnitrous amide (**A**) in a yield of 94%.

N-Methyl-N-phenylnitrous amide (A).[17] Brown oil (64 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (d, J = 0.8 Hz, 3H), 7.34–7.38 (m, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, 119.2, 127.3, 129.5, 142.3.

To a reaction tube equipped with a stir bar were sequentially added *N*-methyl-*N*-phenylnitrous amide (**A**, 0.5 mmol), *tert*-butyl nitrite (**2**, 1 mmol), DCE (2 mL), $Pd(OAc)_2$ (0.025 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 1 mmol) with stirring. The solution was stirred at 40 °C for 20 h. Upon completion, it was diluted with brine (5 mL) and extracted with EtOAc (8 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (10 : 1) to give **4a** in a yield of 92%.

Control experiment (II). To a reaction tube equipped with a stir bar were sequentially added *N*-methyl-*N*-phenylnitrous amide (**A**, 0.5 mmol), DCE (2 mL), $Pd(OAc)_2$ (0.025 mmol) and 2-oxo-2-phenylacetic acid (**3a**, 1.0 mmol) with stirring. The solution was then stirred at 40 °C for 20 h. Subsequent treatment of the resulting mixture showed that the desired *N*-nitroso-2-aminobenzophenone product **4a** was formed only in a trace amount.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (NSFC) (Grant No. 21572047), Program for Innovative Research Team in Science and Technology in Universities of Henan Province (15IRTSTHN003), Program for Science and Technology Innovation Talents in Universities of Henan Province (15HASTIT005), and Plan for Scientific Innovation Talents of Henan Province (184200510012) for financial support.

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