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Metal-Free Intermolecular Coupling of Arenes with Secondary Amides: Chemoselective Synthesis of Aromatic Ketimines and Ketones, and *N*-Deacylation of Secondary Amides

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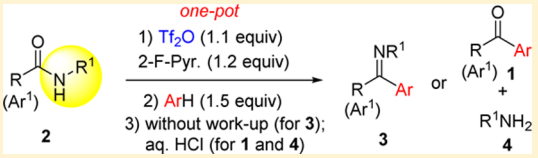
Supporting Information

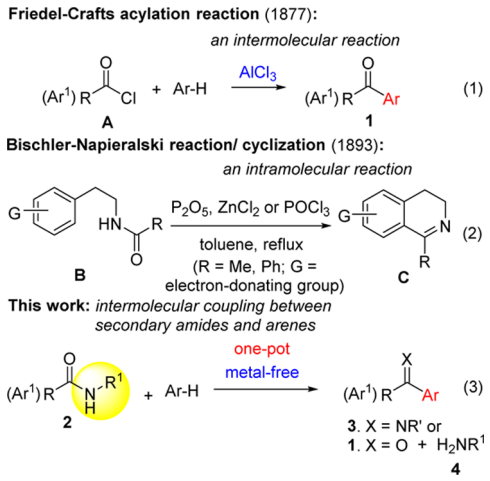
ABSTRACT: The direct transformation of common secondary amides into aromatic ketimines and aromatic ketones with C−C bond formation is described. The reaction can also be used for *N*-deacylation of secondary amides to release amines. This method consists of *in situ* amide activation with triflic anhydride and intermolecular capture of the resulting highly electrophilic nitrilium intermediate with an arene. The reaction is applicable to various kinds of secondary amides (electrophiles), but only electron-rich and moderately electron-rich arenes can be used as nucleophiles. Thanks to the use of bench stable arenes instead of reactive and basic organometallics as nucleophiles, the reaction proceeded with high chemoselectivity at the secondary amido group in the presence of a series of sensitive functional groups such as aldehyde, ketone, ester, cyano, nitro, and tertiary amido groups. The reaction can be viewed as a Friedel−Crafts-type reaction using secondary amides as acylating agents or as an intermolecular version of the Bischler−Napieralski reaction.



INTRODUCTION

With the urgent need for a "greener" and sustainable chemistry,[1] development of chemoselective synthetic methods employing bench stable and readily available starting materials has attracted considerable attention over the past decades. Those efforts have resulted in many powerful methodologies utilizing arenes, alkenes, and alkynes as C_{sp2} and C_{sp} nucleophiles as exampled by the Heck reaction[2] and A^3-coupling.[3] On the other hand, the intermolecular Friedel−Crafts reaction[4] (eq 1 in Scheme 1) and the intramolecular Bischler−Napieralski reaction (Bischler−Napieralski cyclization)[5] (eq 2 in Scheme 1) are two classical reactions utilizing arenes as nucleophiles. In particular, for the Bischler−Napieralski reaction, highly stable aryl and secondary amide groups serve as nucleophilic and electrophilic partners, respectively. However, in the Friedel−Crafts reaction, reactive acyl chlorides are employed as electrophiles, while the Bischler−Napieralski reaction is restricted to intramolecular reaction. Because of the wide use of the Friedel−Crafts reaction in the pharmaceutical industry for the production of aromatic ketones, it is highly demanding to substitute acyl chlorides by unactivated substrates.[6] In this regard, although the Friedel−Crafts reactions using carboxylic acids,[7] esters,[8] and tertiary amides[9] as acylating agents have been documented, very few examples employing secondary amides as substrates have been reported. Early studies by Hurd and Webb involved only one example.[10] The method for the synthesis of 7-indolylimines reported by Black and co-workers is limited to only one special and highly electron-rich arene (4,6-dimethoxy-2,3-diphenylindole).[11] Using phosphoryl chloride as the coupling reagent (referred to as Vilsmeier conditions),[11] those reactions required harsh conditions and used a large excess of reagents, and are of low functional group tolerance. More recently, two novel methods using specially designed secondary amides have been reported. The first one was developed by Tepe and Anderson, which involves the use of inherently activated (by ring strain)

Scheme 1



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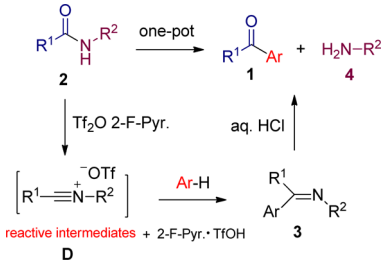
β-lactams as substrates.[12] The second one was reported by Klumpp and co-workers, which is based on some specific amides capable of generating dication intermediates by action of superacid.[13] It is not surprising that both methods are restricted to some specific amides. In view of multiple roles played by secondary amides in organic synthesis and medicinal chemistry,[14] including as intermediates for resolution[15] and as directing groups in C−H functionalization,[16] the development of a general method for the chemoselective intermolecular coupling of arenes with common secondary amides is highly desirable. Such a reaction could also serve as an *N*-deacylation[17] method for secondary amides. However, this task is challenging because, on one hand, amides are the most stable class of carbonyl compounds,[18,19] and on the other hand, a secondary amide contains an acidic proton, which renders the nucleophilic addition of an organometallic reagent more difficult.[20,21]

As a continuation of our endeavor on the development of C−C bond forming methods[19b,20b,c,e,21] based on the amide activation with triflic anhydride (Tf_2O),[22] we report herein a mild and versatile Tf_2O-mediated intermolecular coupling of arenes with secondary amides. This method allows the direct and chemoselective transformation of common secondary amides into aromatic ketimines and ketones, and *N*-deacylation of secondary amides to give amines (eq 3 in Scheme 1).

RESULTS AND DISCUSSION

Our plan was to merge the key features of both the Friedel−Crafts reaction and the Bischler−Napieralski reaction and develop a general and chemoselective intermolecular coupling of arenes with secondary amides. Very recently, we have developed a versatile and direct method for the intermolecular coupling of alkenes with secondary amides to give enimines or enones.[21a] In that method, nitrilium ion intermediate **D** (Scheme 2) was proven to be the pivotal reactive species. In

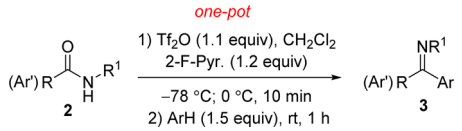
Scheme 2

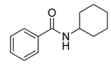
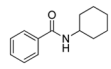
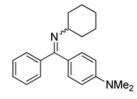
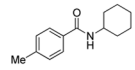
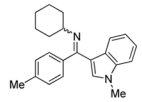
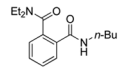
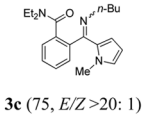
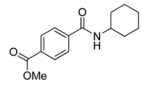
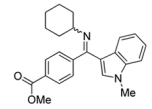
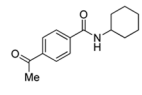
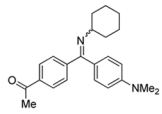
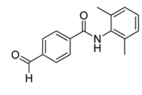
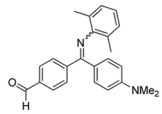
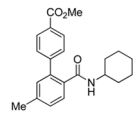
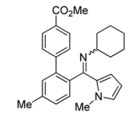


light of those results, we envisioned that arenes could be used as nucleophiles to react with nitrilium ion intermediates **D** to yield the corresponding aromatic ketimines **3** or aromatic ketones **1** and amines **4** after acidic hydrolysis (Scheme 2). Thus, for the current investigation, the conditions established therein[21a] were adopted.

In the event, secondary *N*-cyclohexylbenzamide (**2a**) was successively treated with 1.2 equiv of 2-fluoropyridine (2-F-Pyr.),[23] 1.1 equiv of triflic anhydride (Tf_2O) in CH_2Cl_2 at −78 °C, and 3.0 equiv of toluene, and the mixture was stirred at room temperature for 2 h. Unfortunately, the desired coupling product was not observed even after heating at 40 °C for 2 h (Table 1, entry 1). The same disappointing results were obtained when subjecting acetamide **2b** to react with either anisole or 1,2-dimethoxybenzene (Table 1, entries 2 and 3). To our delight, the reaction of 1.5 equiv of electron-rich *N*,*N*-

Table 1. Intermolecular Cross-Coupling of Arenes with Secondary Amides To Give Ketimines 3



Entry	Substrate	ArH	Product (% yield)[a,b]
1.	 **2a**		**2a** recovered
2.	 **2b**		**2b** recovered
3.	 **2b**		**2b** recovered
4.	 **2a**		 **3a** (88, E/Z^c = 92: 8)
5.	 **2c**		 **3b** (91, E/Z = 75: 25)
6.	 **2d**		 **3c** (75, E/Z >20: 1)
7.	 **2e**		 **3d** (86, E/Z = 87: 13)
8.	 **2f**		 **3e** (76, E/Z = 88:12)
9.	 **2g**		 **3f** (86, E/Z = 60: 40)
10.	 **2h**		 **3g** (82, E/Z >20:1)

[a]Isolated yield. [b]Reaction conditions: (1) Amide (1.0 mmol), 2-fluoropyridine (1.2 mmol), CH_2Cl_2 (4 mL), −78 °C, Tf_2O (1.1 mmol), then 0 °C, 10 min; (2) Arene (1.5 mmol), rt, 1 h. [c]E/Z ratio of imine determined by ^{1}H NMR; E/Z stereochemistry not determined.

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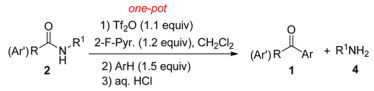
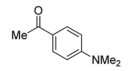
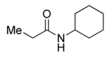
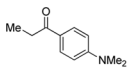
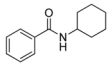
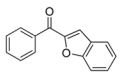
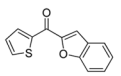
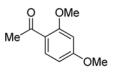
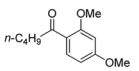
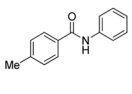
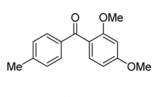
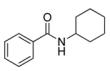
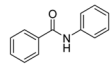
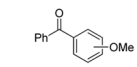
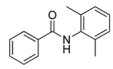
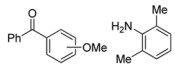
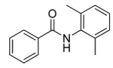
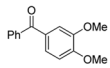
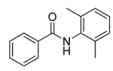
Table 2. Intermolecular Coupling of Arenes with Secondary Amides To Give Aromatic Ketones 2



Entry	Substrate	ArH	Product (% yield)[a,b]
1.	 **2b**		 **1a** (90)
2.	 **2i**		 **1b** (92)
3.	 **2b**		 **1c** (84)
4.	 **2a**		 **1d** (80)[c]
5.	 **2j**		 **1e** (81)[c]
6.	 **2k**		 **1f** (77)[c]
7.	 **2b**		 **1g** (74)[c]
8.	 **2l**		 **1h** (79)[c]
9.	 **2m**		 **1i** (88),[d] **4a** (83)
10.	 **2a**		**2a** recovered

Entry	Substrate	ArH	Product (% yield)[a,b]
11.	 **2n**		 **1j** (89, *p*:*o* = 8.5:1)[d]
12.	 **2o**		 **1j** (94, *p*:*o* = 4.6:1),[d] **4b** (87)
13.	 **2o**		 **1k** (97),[d] **4b** (90)
14.	 **2o**		**5** (87)[c]
15.	**2p**		**1l** (91)
16.	**2p**		**1m** (75)[d]
17.	**2q**		**1n** (75)
18.	**2e**		**1o** (65)
19.	**2r**		**1a** (87), **4c** (85)

[a]Isolated yield. [b]Reaction conditions: (1) Amide (1.0 mmol), 2-fluoropyridine (1.2 mmol), CH_2Cl_2 (4 mL), −78 °C, Tf_2O (1.1 mmol), then 0 °C, 10 min; (2) Arene (1.5 mmol), rt, 1 h; (3) aq. HCl (3 M, 5 mL), reflux, 2 h. [c]The reaction run at 40 °C. [d]Hydrolytic conditions: aq. HCl (3 M, 5 mL) in EtOH, reflux, 2−12 h.

dimethylaniline with benzamide **2a** proceeded smoothly (rt, 1 h) to give regioselectively diaryl ketimine **3a** in 88% yield as a 92:8 *E*/*Z* geometric mixture (Table 1, entry 4). It is worth mentioning that a simplified purification protocol could be used to isolate the product, which consists of directly concentrating the reaction mixture without workup and subjecting the residue to flash chromatographic purification. Encouraged by this result, reaction of other arenes and functional group tolerance of the method were investigated. Reaction of amide **2c** with *N*-methylindole produced ketimine **3b** in 91% yield as a 75:25 *E*/

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Z geometric mixture (Table 1, entry 5). Interestingly, the reaction of diamide **2d** (entry 6) showed a preference for secondary amido over tertiary amido group, which afforded amido imine **3c** in 75% yield with excellent geometric selectivity (ratio of *E*/*Z* isomers > 20:1). Significantly, reaction of amido ester **2e** with *N*-methylindole took place chemoselectively at the amido group to yield imino ester **3d** in excellent yield and stereoselectivity (entry 7, 86% yield, *dr* (*E*/*Z*) = 87:13). More importantly, the reaction of keto amide **2f** and amido aldehyde **2g** with *N*,*N*-dimethylaniline occurred chemoselectively at the least reactive amido group to give the corresponding imino ketone **3e** and imino aldehyde **3f** in 76% and 86% yield, respectively (entries 8 and 9). As we have mentioned earlier, because secondary amides constitute a class of valuable directing groups in both modern catalytic[16a−d] and classical stoichiometric[16e] C−H functionalization, transformation of the resulting C−H functionalization products is imperative. To demonstrate the value of the current method in this regard, transformation of the amide **2h**, a C−H functionalization product prepared by Daugulis' method[16d] was envisaged. For this purpose, amide **2h** was subjected to react with *N*-methylindole. Pleasantly, the desired ketimine **3g** was isolated in 82% yield (entry 10).

After establishing an efficient method for the direct transformation of secondary amides into aromatic ketimines, we turned our attention to extend this methodology to synthesize aromatic ketones. This should be readily realizable by *in situ* acidic hydrolysis of aromatic ketimines. Indeed, after activation-coupling of *N*-*c*-hexyl acetamide **2b** with *N*,*N*-dimethylaniline (0 °C, 10 min), the resulting mixture was treated with a solution of 3 M HCl at 40 °C for 2 h, which yielded *N*,*N*-dimethyl *p*-acetylaniline **1a** in 90% yield (Table 2, entry 1). Similarly, propionylation of *N*,*N*-dimethylaniline with propionamide **2i** (entry 2), acetylation of pyrrole with acetamide **2b** (entry 3), and benzoylations of furan and benzofuran with *N*-*c*-hexyl benzamide **2a** (entry 4) and *N*-methyl benzamide **2j** (entry 5) afforded, respectively, and regioselectively, 1-(4-(dimethylamino)phenyl)propan-1-one (**1b**) (yield: 92%), 2-acetylpyrrole **1c** (yield: 84%), 2-benzoylfuran **1d** (yield: 80%), and 2-benzoylbenzofuran **1e** (yield: 81%) in good yields. Electron-rich heteroarene *N*-butylthiophene-2-carboxamide **2k** reacted smoothly with benzofuran to give benzofuran-2-yl(thiophen-2-yl)methanone **1f** in 77% yield (Table 2, entry 6). It is worth mentioning that **1b** has served as an intermediate in the synthesis of trichostatin A,[24] a histone deacetylase inhibitor (HDACi).

Although less electron-rich arenes such as anisole and 1,2-dimethoxybenzene failed to undergo cross-coupling reaction with secondary amides (cf. Table 1, entries 1−3), to extend the scope of the method, further efforts have been made. To this end, we first examined the alkoylation of 1,3-dimethoxybenzene. To our surprise, reaction of 1,3-dimethoxybenzene with acetamide **2b** proceeded smoothly to give regioselectively the desired acetylated product **1g** in 74% yield (Table 2, entry 7). As exampled by *N*-methylpentanamide (**2l**) and 4-methyl-*N*-phenylbenzamide (**2m**), extension of this method to other alkoyl and *N*-aryl amides proved to be successful (Table 2, entries 8 and 9), which afforded 1-(2,4-dimethoxyphenyl)-pentan-1-one (**1h**) in 79% yield and (2,4-dimethoxyphenyl)(*p*-tolyl)methanone (**1i**) in 88% yield, respectively. The significant difference in reactivity between 1,2-dimethoxybenzene (Table 1, entry 3) and 1,3-dimethoxybenzene (Table 2, entries 7−9) may be attributed to the matched directing effect of the two methoxyl groups in 1,3-dimethoxybenzene, which renders the latter more nucleophilic.

A closer inspection of the results outlined in entries 7−9 allowed us to assume that *N*-phenyl amides resulted in a higher yield as compared to *N*-alkyl amides. To confirm this assumption, we surveyed the benzoylation reaction of anisole with three benzamides bearing different *N*-substituents, **2a**, **2n**, and **2o**. Attempted benzoylation of anisole with *N*-cyclohexylbenzamide **2a** failed to yield the desired product; instead, the starting amide was recovered after workup (Table 2, entry 10). This result is consistent with that outlined in Table 1, entry 2. To our delight, the reaction of anisole with *N*-phenyl benzamide **2n** produced the desired benzoylated product **1j** in excellent yield (89%) as a mixture of *p*- and *o*-regioisomers (ratio = 8.5:1) (Table 2, entry 11). An even higher yield (94%, *p*- and *o*-regioisomers ratio = 4.6:1) was obtained by reacting anisole with *N*-(2,6-dimethylphenyl)benzamide (**2o**), an amide that we have previously used for the coupling of amides with alkenes[21a] (Table 2, entry 12). Furthermore, the reaction of 1,2-dimethoxybenzene with amide **2o** afforded the benzoylated product **1k** in 97% yield as a single regioisomer (Table 2, entry 13). Encouraged by these results, we next attempted the benzoylation of toluene. However, instead of the desired benzoylation product, reaction of toluene (3.0 equiv) with *N*-(2,6-dimethylphenyl)benzamide (**2o**) at 40 °C for 2 h resulted in the formation of amidine derivative **5** in 87% yield as a single geometric isomer (Table 2, entry 14). It is worthwhile noting that such amidine derivatives have previously been synthesized by Wang.[25] The fact that amidine derivative **5** was resulted from the addition of amide **2o** to the **2o**-derived nitrilium intermediate **D-2o** (cf. Scheme 2) (a self-condensation) implies that, in competition with the amide substrate, toluene is too weak as a nucleophile to react with the nitrilium intermediate **D-2o**.

The results outlined in entries 15−19 (Table 2) show that, akin to the formation of ketimines (cf. Table 1, entries 6−10), the intermolecular coupling reactions of arenes with secondary amides to yield aromatic ketones **1** also displayed good functional group tolerance and good chemoselectivity at the amido group. Comparing the result outlined in entry 5 (Table 1) with those in entries 15−19 (Table 2) shows that not only electron-rich amides such as **2c** but also benzamides bearing electron-deficient groups such as nitro, cyano, and ester at the *para* position served well as the aroylation agents in reacting with arenes.

Finally, in view of the importance of *N*-deacylation reaction in organic synthesis and medicinal chemistry,[17] and the mildness of the current method, it is expectable that this method could be applicable for mild *N*-deacylation of amides as well. Thus, a simple acid−base extraction procedure was established which was used for the isolation of amines **4a** (yield: 83%) (Table 2, entry 9), **4b** (yield: 87%) (entry 12), and **4c** (yield: 87%) (entry 19).

CONCLUSION

In summary, a method for the intermolecular coupling of common secondary amides with arenes has been developed, which affords a flexible access to aromatic ketimines and aromatic ketones. Moreover, the reaction can be used as a mild and high-yielding method for *N*-deacylation of amides. Both aliphatic and aromatic amides bearing either electron-withdrawing or electron-donating groups can be used. The *N*-substituent can be a primary, a secondary alkyl group or an

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aromatic group. Electron-rich arenes and heteroarenes such as 1,3-dimethoxybenzene, *N*,*N*-dimethylaniline, pyrrole, *N*-methylpyrrole, *N*-methylindole, furan, and benzofuran can react with all kinds of secondary amides. Moderately electron-rich arenes such as anisole and 1,2-dimethoxybenzene reacted only with *N*-aryl secondary amides to give the corresponding aromatic ketones in 94−97% yields. The method is unsuitable for non-electron-rich arenes such as toluene, which yielded the self-condensation product (an amidine derivative). The method displayed excellent functional group tolerance and chemoselectivity, which allows the reaction to take place at the secondary amido group in the presence of a series of sensitive functional groups including aldehyde, ketone, ester, tertiary amide, nitro, cyano, and OTBDPS. Except for anisole, which reacted to give a mixture of *p*- and *o*-benzoylated products in a ratio of 8.5:1 and 4.6:1, the reactions of all other arenes examined produced only one regioisomer in each case. The method was used to transform a C−H functionalization product prepared by the method of Daugulis to the corresponding aromatic ketimine. In view of the fact that many aromatic ketimines[26] and aromatic ketones[27] either are bioactive compounds or serve as pivotal building blocks in the synthesis of natural products and medicinal agents,[24,26,27] the present method would find applications in this regard.

EXPERIMENTAL SECTION

For general experimental methods, see ref 21c.

General Procedure for the Direct Coupling of Arenes with Secondary Amides 2 To Yield Aromatic Ketimines 3, Aromatic Ketones 1, and Amines 4. Into a dry 10 mL round-bottom flask equipped with a magnetic stirring bar were added successively a secondary amide (1.0 mmol), 4 mL of anhydrous CH_2Cl_2, and 2-fluoropyridine (103 uL, 1.2 mmol) under an argon atmosphere. After being cooled to −78 °C, trifluoromethanesulfonic anhydride (Tf_2O) (185 uL, 1.1 mmol) was added dropwise via a syringe, and the reaction was stirred for 10 min at 0 °C. To the resulting mixture was added an arene (1.5 mmol) dropwise at 0 °C. The mixture was allowed to warm-up to room temperature and stirred for 2 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (FC) on silica gel (preneutralized with 2% Et_3N in *n*-hexane) to afford the desired aromatic ketimine **3**.

Alternately, after concentration, to the residue were added 5 mL of EtOH and 5 mL of an aqueous solution of HCl (3.0 M). The resulting mixture was heated to reflux until completion of the reaction as monitored by TLC analysis. After being cooled to room temperature, 10 mL of CH_2Cl_2 was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired aromatic ketone **1**. To isolate the corresponding amine, the aqueous layer was basified with an aqueous solution of 15% NaOH (6 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired amine **4**.

4-[(Cyclohexylimino)(phenyl)methyl]-*N*,*N*-dimethylaniline (3a). Following the general procedure, the reaction of amide **2a** (203 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), aromatic ketimine **3a** (270 mg, yield: 88%) as a 92:8 inseparable mixture of *E*/*Z* isomers. For the major isomer: Yellow oil. IR (film) ν_{max}: 3063, 2933, 2860, 1580, 1546, 1349, 1289, 1243, 1153, 1030, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97−1.60 (m, 4H), 1.74−1.86 (m, 4H), 1.96−2.09 (m, 2H), 3.14 (s, 6H), 3.36 (tt, *J* = 11.4, 4.0 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.57−7.72 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 24.6 (2C), 31.6 (2C), 40.1 (2C), 59.5, 111.7 (2C), 116.5, 127.9 (2C), 129.1 (2C), 131.0, 131.7 (2C), 134.6, 155.6, 174.0. MS (ESI) *m*/*z*: 307 (M + H^+, 100%); HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{21}H_{27}N_2$ [M + H]$^+$: 307.2169; found: 307.2163.

***N*-[(1-Methyl-1*H*-indol-2-yl)(*p*-tolyl)methylene]cyclohexanamine (3b).** Following the general procedure, the reaction of amide **2c** (217 mg, 1.0 mmol) with *N*-methylindole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/1), the aromatic ketimine **3b** (300 mg, yield: 91%) as a 75:25 inseparable mixture of *E*/*Z* isomers. For the major isomer: White solid. mp: 106−108 °C; IR (film) ν_{max}: 3046, 2922, 2851, 1659, 1598, 1467, 1384, 802, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13−1.37 (m, 3H), 1.52−1.69 (m, 5H), 1.72−1.82 (m, 2H), 3.42 (s, 3H), 3.21−3.30 (m, 1H), 3.63 (s, 3H), 6.69 (s, 1H), 7.12−7.25 (m, 7H), 8.46 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 24.4 (2C), 25.9, 32.8, 34.6 (2C), 60.0, 108.9, 118.1, 120.9, 122.4, 123.3, 126.5, 127.6 (2C), 128.7 (2C), 133.0, 135.6, 137.3, 137.8, 161.8. MS (ESI) *m*/*z*: 331 (M + H^+, 100%); HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{23}H_{27}N_2$ [M + H]$^+$: 331.2169; found: 331.2177.

(*Z*)-2-[(*n*-Butylimino)(1-methyl-1*H*-pyrrol-2-yl)methyl]-*N*,*N*-diethylbenzamide (3c). Following the general procedure, the reaction of amide **2d** (276 mg, 1.0 mmol) with *N*-methylpyrrole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/3), the aromatic ketimine **3c** (254 mg, yield: 75%, *E*/*Z* > 20:1). Yellow oil. IR (film) ν_{max}: 2967, 2934, 2855, 1628, 1399, 1375, 1088, 1051, 923, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 1.34−1.46 (m, 2H), 1.58−1.71 (m, 2H), 2.63−2.76 (m, 1H), 2.93−3.14 (m, 2H), 3.20−3.39 (m, 2H), 3.52−3.64 (m, 1H), 3.93 (s, 3H), 5.71 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.89−5.93 (m, 1H), 6.60−6.64 (m, 1H), 7.23−7.31 (m, 2H), 7.34−7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 13.7, 14.0, 20.7, 33.6, 37.1, 38.0, 42.7, 53.5, 106.4, 115.3, 125.7, 127.0, 127.6, 128.2, 128.5, 132.1, 135.8, 136.1, 158.9, 169.1. HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{21}H_{29}N_3ONa$ [M + Na]$^+$: 362.2203; found: 362.2216.

Methyl 4-[(Cyclohexylimino)(1-methyl-1*H*-indol-3-yl)-methyl]benzoate (3d). Following the general procedure, the reaction of amide **2e** (261 mg, 1.0 mmol) with *N*-methylindole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/1), the aromatic ketimine **3d** (284 mg, yield: 86%) as an 87:13 inseparable mixture of *E*/*Z* isomers. For the major isomer: White solid. mp: 127−128 °C; IR (film) ν_{max}: 3050, 2922, 2847, 1724, 1598, 1536, 1467, 1385, 1276, 1230, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06−1.40 (m, 4H), 1.50−1.83 (m, 6H), 3.08−3.18 (m, 1H), 3.65 (s, 3H), 3.95 (s, 3H), 6.61 (s, 1H), 7.17−7.30 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 7.8 Hz, 2H), 8.48 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3 (2C), 25.8, 32.9, 34.5 (2C), 52.1, 60.3, 109.0, 117.3, 121.1, 122.7, 123.3, 126.3, 127.7 (2C), 129.4 (2C), 129.6, 132.9, 137.8, 143.3, 160.6, 166.8. MS (ESI) *m*/*z*: 375 (M + H^+, 100%); HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{24}H_{27}N_2O_2$ [M + H]$^+$: 375.2067; found: 375.2071.

1-{4-[(Cyclohexylimino)[4-(dimethylamino)phenyl]methyl]-phenyl}ethanone (3e). Following the general procedure, the reaction of amide **2f** (245 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the aromatic ketimine **3e** (264 mg, yield: 76%) as a 88:12 inseparable mixture of *E*/*Z* isomers. For the major isomer: Yellow oil. IR (film) ν_{max}: 3078, 3029, 2927, 2857, 1687, 1595, 1521, 1364, 1268, 826 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05−1.30 (m, 3H), 1.51−1.80 (m, 7H), 2.66 (s, 3H), 2.96 (s, 6H), 3.00−3.08 (m, 1H), 6.58−6.62 (m, 2H), 7.23−7.78 (m, 2H), 7.39−7.44 (m, 2H), 8.00−8.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.4, 25.6, 26.6, 34.1, 40.2, 61.2, 111.2 (2C), 127.6, 128.0 (2C), 128.2 (2C), 129.4 (2C), 136.3, 143.3, 151.5, 164.1, 197.7. HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{23}H_{29}N_2O$ [M + H]$^+$: 349.2274; found: 349.2271.

4-{[4-(Dimethylamino)phenyl][(2,6-dimethylphenyl)imino]-methyl}benzaldehyde (3f). Following the general procedure, the reaction of amide **2g** (253 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/

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n-hexane = 1/10), the aromatic ketimine **3f** (306 mg, yield: 86%) as a 60:40 inseparable mixture of *E*/*Z* isomers. For the mixture of two isomers: Yellow solid. mp: 142−143 °C; IR (film) ν_{max}: 3049, 2921, 2844, 1700, 1598, 1582, 1361, 1201, 1137 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 2.4H), 2.05 (s, 3.6H), 2.93 (s, 2.4H), 3.04 (s, 3.6H), 6.44−6.48 (m, 0.8H), 6.67−6.97 (m, 5H), 7.27−7.31 (m, 1.2H), 7.65−7.69 (m, 1.2H), 7.71−7.75 (m, 1.2H), 7.90−7.95 (m, 1.6H), 9.94 (s, 0.6H), 10.10 (s, 0.4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.3, 18.6, 39.9, 40.2, 110.6, 111.1, 122.5, 123.0, 125.6, 126.0, 126.1, 127.6, 127.8, 128.8, 128.9, 129.3, 130.1, 130.5, 135.8, 137.0, 143.7, 146.8, 148.9, 149.2, 150.7, 152.2, 165.3, 166.0, 191.7, 192.1. HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{24}H_{25}N_2O$ $[M + H]^+$: 357.1961; found: 357.1959.

(*Z*)-Methyl 2′-[(Cyclohexylimino)(1-methyl-1*H*-pyrrol-2-yl)-methyl]-5′-methyl-[1,1′-biphenyl]-4-carboxylate (3g). Following the general procedure, the reaction of amide **2h** (351 mg, 1.0 mmol) with *N*-methylpyrrole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the aromatic ketimine **3g** (339 mg, yield: 82%, *E*/*Z* > 20:1). Pale yellow solid. mp: 151−152 °C; IR (film) ν_{max}: 2913, 2851, 1727, 1603, 1420, 1279, 1093, 1014, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.65−0.74 (m, 1H), 0.94−1.20 (m, 4H), 1.24−1.65 (m, 5H), 2.44 (s, 3H), 2.84−2.92 (m, 1H), 3.81 (s, 3H), 3.89 (s, 3H), 5.91 (dd, *J* = 3.8, 1.8 Hz, 1H), 5.98 (dd, *J* = 3.8, 2.6 Hz, 1H), 6.62 (t, *J* = 2.1 Hz, 1H), 7.11−7.16 (m, 1H), 7.18−7.23 (m, 2H), 7.28−7.33 (m, 2H), 7.89−7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 24.1, 24.3, 25.8, 33.4, 34.0, 37.7, 52.0, 60.7, 106.7, 116.1, 127.3, 128.1, 128.5, 128.6 (2C), 128.8, 129.2 (2C), 129.9, 133.2, 133.4, 138.1, 139.3, 145.9, 157.7, 167.0. MS (ESI) *m*/*z*: 374 (M + H^+, 100%); HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{27}H_{31}N_2O_2$ $[M + H]^+$: 415.2380; found: 415.2384.

1-[4-(Dimethylamino]phenylethanone (1a). Following the general procedure, the deamination reaction of amide **2b** (141 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1a**[28c] (146 mg, yield: 90%). White solid. mp: 104−105 °C; IR (film) ν_{max}: 2902, 2823, 1658, 1612, 1358, 1230, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.05 (s, 6H), 6.65 (d, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 9.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 40.0 (2C), 110.5 (2C), 125.3, 130.5 (2C), 153.3, 196.3. MS (ESI) *m*/*z*: 186 (M + Na^+, 100%).

1-[4-(Dimethylamino)phenyl]propan-1-one (1b). Following the general procedure, the deamination reaction of amide **2i** (155 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1b**[24] (163 mg, yield: 92%). White solid. mp: 94−95 °C; IR (film) ν_{max}: 2959, 2917, 2847, 1658, 1611, 1191, 1079, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.3 Hz, 3H), 2.91 (q, *J* = 7.3 Hz, 2H), 3.05 (s, 6H), 6.66 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.8, 31.0, 40.0, 110.6 (2C), 125.0, 130.1 (2C), 153.2, 199.2. MS (ESI) *m*/*z*: 200 (M + Na^+, 100%).

2-Acetylpyrrole (1c). Following the general procedure, the deamination reaction of amide **2b** (141 mg, 1.0 mmol) with pyrrole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1c**[28i] (92 mg, yield: 84%). White solid. mp: 88−89 °C; IR (film) ν_{max}: 3276, 3114, 1646, 1447, 1428, 1402, 1129, 772, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 6.26−6.29 (m, 1H), 6.91−6.94 (m, 1H), 7.03−7.07 (m, 1H), 9.90 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 110.6, 116.9, 124.8, 132.2, 188.1. MS (ESI) *m*/*z*: 132 (M + Na^+, 100%).

Furan-2-yl-phenylmethanone (1d). Following the general procedure, the deamination reaction of amide **2a** (203 mg, 1.0 mmol) with furan gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1d**[28d] (138 mg, yield: 80%). Colorless oil. IR (film) ν_{max}: 3134, 3058, 1648, 1465, 1390, 1298, 956, 870, 727, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 3.7, 1.7 Hz, 1H), 7.23 (dd, *J* = 3.7, 0.7 Hz, 1H), 7.46−7.61 (m, 3H), 7.70 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.94−7.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.1, 120.5, 128.3 (2C), 129.2 (2C), 132.5, 137.1, 147.2, 152.2, 182.4. MS (ESI) *m*/*z*: 195 (M + Na^+, 100%).

Benzofuran-2-yl(phenyl)methanone (1e). Following the general procedure, the deamination reaction of amide **2j** (135 mg, 1.0 mmol) with 2,3-benzofuran gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1e**[28b] (180 mg, yield: 81%). White solid. mp: 90−91 °C; IR (film) ν_{max}: 3059, 2959, 2851, 1651, 1613, 1545, 1444, 1329, 1278, 1184, 971, 753, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 1H), 7.46−7.56 (m, 4H), 7.60−7.66 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.5, 116.5, 123.3, 123.9, 126.9, 128.3, 128.5 (2C), 129.4 (2C), 132.8, 137.2, 152.2, 155.9, 184.3. MS (ESI) *m*/*z*: 245 (M + Na^+, 100%).

(1*H*-Inden-2-yl)-phenylmethanone (1f). Following the general procedure, the deamination reaction of amide **2k** (183 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aryl ketone **1f**[28a] (175 mg, yield: 77%). White solid. mp: 65−66 °C; IR (film) ν_{max}: 3034, 2959, 2926, 2851, 1622, 1552, 1411, 1356, 1239, 1180, 953, 773, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−7.27 (m, 1H), 7.31−7.37 (m, 1H), 7.47−7.54 (m, 1H), 7.62−7.66 (m, 1H), 7.71−7.78 (m, 3H), 8.31−8.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.4, 114.5, 123.2, 124.0, 127.0, 128.1, 128.3, 134.4, 134.6, 142.3, 152.5, 155.8, 175.0. MS (ESI) *m*/*z*: 251 (M + Na^+, 100%).

1-(2,4-Dimethoxyphenyl)ethanone (1g). Following the general procedure, the deamination reaction of amide **2b** (141 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1g**[28e] (133 mg, yield: 74%). Colorless oil. IR (film) ν_{max}: 3003, 2965, 2943, 2840, 1664, 1599, 1466, 1358, 1268, 1163, 1029, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 3.85 (s, 3H), 3.89 (s, 3H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.8, 55.4, 55.4, 98.2, 105.0, 121.0, 132.6, 161.0, 164.5, 197.7. MS (ESI) *m*/*z*: 203 (M + Na^+, 100%).

1-(2,4-Dimethoxyphenyl)pentan-1-one (1h). Following the general procedure, the deamination reaction of amide **2l** (115 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the aromatic ketone **1h** (175 mg, yield: 79%). White wax. IR (film) ν_{max}: 3083, 2963, 2930, 2872, 1665, 1575, 1466, 1262, 1163, 1029, 836, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.31−1.42 (m, 2H), 1.61−1.70 (m, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 3.85 (s, 3H), 3.88 (s, 3H), 6.45 (d, *J* = 2.2 Hz, 1H), 6.52 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 26.7, 43.3, 55.4, 55.5, 98.4, 105.0, 121.5, 132.5, 160.5, 164.1, 201.0. HRMS (ESI-TOF) *m*/*z*: Calcd for $C_{13}H_{18}O_3Na$ $[M + Na]^+$: 245.1148; found: 245.1149.

(2,4-Dimethoxyphenyl)(*p*-tolyl)methanone (1i). Following the general procedure, the deamination reaction of amide **2m** (211 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the known aromatic ketone **1i** (225 mg, yield: 88%) and aniline hydrochloride **4a** (107 mg, yield: 83%). **1i**: Colorless oil. IR (film) ν_{max}: 3007, 2937, 2847, 1655, 1604, 1575, 1284, 1217, 1159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.71 (s, 3H), 3.86 (s, 3H), 6.50−6.56 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 56.5, 56.5, 98.8, 104.4, 121.8, 128.7 (2C), 129.9 (2C), 131.9, 136.0, 143.1, 159.4, 163.0, 195.3. MS (ESI) *m*/*z*: 279 (M + Na^+, 100%).

(4-Methoxyphenyl)(phenyl)methanone + (2-Methoxy-phenyl)(phenyl)methanone (1j). Following the general procedure, the deamination reaction of amide **2n** (197 mg, 1.0 mmol) or **2o** (225 mg, 1.0 mmol) amide with anisole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/10), the known aromatic ketone **1j**[28d] (189 mg, yield: 89%, *p*:*o* = 8.5:1 from **2n**, or 199 mg, yield: 94%, *p*:*o* = 4.6:1 from **2o**) as an inseparable mixture of two regioisomers and 2,6-dimethylaniline **4b** (105 mg, yield: 87% from **2o**). **1j** for the mixture of two regioisomers: Colorless oil. IR (film) ν_{max}: 3062, 2959, 2921, 2831, 1656, 1601, 1258, 695

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cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 0.55H), 3.88 (s, 2.45H), 6.61−7.85 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 55.6, 111.4, 113.5, 117.9, 120.4, 121.6, 128.1 (2C), 128.2, 128.8, 129.5, 129.7 (2C), 129.8, 130.1, 131.9, 132.5, 132.9, 137.8, 138.2, 157.3, 163.2, 195.5, 196.4. MS (ESI) m/z: 235 (M + Na^+, 100%).

(3,4-Dimethoxyphenyl)(phenyl)methanone (1k). Following the general procedure, the deamination reaction of amide **2o** (225 mg, 1.0 mmol) with 1,2-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the known aromatic ketone **1k**[28f] (235 mg, yield: 97%) and 2,6-dimethylaniline **4b** (109 mg, yield: 90%). **1k**: Colorless oil. IR (film) ν_{max}: 3068, 3007, 2965, 2933, 1646, 1591, 1511, 1268, 1130, 1027, 723 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.96 (s, 3H), 6.89 (d, J = 8.3 Hz, 1H), 7.38 (dd, J = 8.3, 1.6 Hz, 1H), 7.45−7.51 (m, 3H), 7.54−7.59 (m, 1H), 7.74−7.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.0, 56.0, 109.6, 112.0, 125.4, 128.1 (2C), 129.6 (2C), 130.1, 131.8, 138.2, 148.9, 152.9, 195.5. MS (ESI) m/z: 265 (M + Na^+, 100%).

(1-Methyl-1*H*-pyrrol-2-yl)(4-nitrophenyl)methanone (1l). Following the general procedure, the deamination reaction of amide **2p** (248 mg, 1.0 mmol) with *N*-methylpyrrole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the known aromatic ketone **1l**[28h] (210 mg, yield: 91%). Yellow solid. mp: 151−152 °C; IR (film) ν_{max}: 3092, 2955, 2839, 1627, 1596, 1515, 1409, 1349, 1251, 848, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H), 6.20 (dd, J = 4.0, 2.4 Hz, 1H), 6.69 (dd, J = 4.0, 1.5 Hz, 1H), 6.98−7.02 (m, 1H), 7.92 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 108.8, 123.3 (2C), 123.6, 129.8 (2C), 132.7, 145.3, 149.2, 183.6. MS (ESI) m/z: 253 (M + Na^+, 100%).

(1-Methyl-1*H*-indol-2-yl)(4-nitrophenyl)methanone (1m). Following the general procedure, the deamination reaction of amide **2p** (248 mg, 1.0 mmol) with *N*-methylindole gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the known aryl ketone **1m**[28g] (210 mg, yield: 75%). Yellow solid. mp: 183−184 °C; IR (film) ν_{max}: 2914, 1620, 1597, 1524, 1463, 1370, 1345, 1234, 844, 744, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.34−7.43 (m, 3H), 7.49 (s, 1H), 7.92 (d, J = 8.5 Hz, 2H), 8.32 (d, J = 8.5 Hz, 2H), 8.36−8.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.7, 109.8, 115.3, 122.6, 123.2, 123.6 (2C), 124.2, 126.8, 129.3 (2C), 137.7, 138.1, 146.3, 149.1, 188.3. MS (ESI) m/z: 303 (M + Na^+, 100%).

4-(2,4-Dimethoxybenzoyl)benzonitrile (1n). Following the general procedure, the deamination reaction of amide **2q** (202 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the aromatic ketone **1n** (200 mg, yield: 75%). White solid. mp: 108−110 °C; IR (film) ν_{max}: 2916, 2847, 2228, 1656, 1600, 1574, 1502, 1462, 1418, 1309, 1275, 939, 854, 835, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.89 (s, 3H), 6.49 (d, J = 2.2 Hz, 1H), 6.59 (dd, J = 8.6, 2.2 Hz, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 55.6, 98.6, 105.3, 115.1, 118.3, 120.2, 129.5 (2C), 131.8 (2C), 132.8, 142.9, 159.9, 164.4, 193.8. MS (ESI) m/z: 290 (M + Na^+, 100%); HRMS (ESI-TOF) m/z: Calcd for $C_{16}H_{13}NO_3Na$ $[M + Na]^+$: 290.0788; found: 290.0794.

Methyl 4-(2,4-Dimethoxybenzoyl)benzoate (1o). Following the general procedure, the deamination reaction of amide **2e** (261 mg, 1.0 mmol) with 1,3-dimethoxybenzene gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/5), the aromatic ketone **1o** (195 mg, yield: 65%). White solid. mp: 99−101 °C; IR (film) ν_{max}: 3005, 2947, 2843, 1724, 1657, 1598, 1436, 1311, 1245, 1106, 821, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.88 (s, 3H), 3.95 (s, 3H), 6.50 (d, J = 2.2 Hz, 1H), 6.58 (dd, J = 8.5, 2.2 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 55.4, 55.5, 98.7, 104.9, 120.9, 129.2 (2C), 129.2 (2C), 132.6, 132.9, 142.8, 159.9, 164.0, 166.5, 194.8. MS (ESI) m/z: 323 (M + Na^+, 100%). HRMS (ESI-TOF) m/z: Calcd for $C_{17}H_{16}O_5Na$ $[M + Na]^+$: 323.0890; found: 323.0888.

(*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methylbutan-2-amine (4c). Following the general procedure, the deamination reaction of amide **2r** (383 mg, 1.0 mmol) with *N*,*N*-dimethylaniline gave, after flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane = 1/1), the known aromatic ketone **1a** (141 mg, yield: 87%) and amine **4c**[28j] (290 mg, yield: 85%). **4c**: Colorless oil. IR (film) ν_{max}: 3388, 3074, 2962, 2930, 2859, 1425, 1114, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H), 1.06 (s, 9H), 1.53 (br s, 2H), 1.58−1.67 (m, 1H), 2.61−2.67 (m, 1H), 3.48 (dd, J = 9.9, 7.8 Hz, 1H), 3.68 (dd, J = 9.9, 4.1 Hz, 1H), 7.35−7.45 (m, 6H), 7.64−7.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 19.2, 19.5, 26.9 (2C), 30.4, 58.4, 67.3, 127.7 (4C), 129.6 (2C), 133.6, 133.6, 135.6 (4C). MS (ESI) m/z: 342 (M + Na^+, 100%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01647.

^1H and ^{13}C NMR spectra of all products (PDF)

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Notes

The authors declare no competing financial interest.

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