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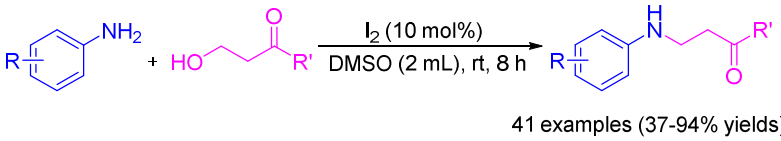
# Iodine-Catalyzed Coupling of *β*-Hydroxyketones with Aromatic Amines to Form *β*-Aminoketones and Benzo[*h*]quinolones

Changqing Miao,[†,‡] Liya Jiang,[†,‡] Lanhui Ren,[*,†] Qingxia Xue,[†] Fang Yan,[†] Weiwei Shi,[†] Xinjian Li,[†] Jiwen Sheng[†] and Shuangshuang Kai[†]

[†]College of Pharmacy, Weifang Medical University, Weifang 261053, P. R. China; E-mail: Ren_lanhui@163.com

[‡]Changqing Miao and Liya Jiang contributed equally to this work




- **Non-metallic catalyst**
- **No oxidant**
- **No experienced unsaturated ketone and Michael addition**

**Abstract:** A iodine-catalyzed coupling of *β*-hydroxyketones with aromatic amines to yield *β*-aminoketones and benzo[*h*]quinolones had been developed. Noble metallic catalysts, oxidants, *α*, *β*-unsaturated ketone intermediates and aza-Michael addition were not involved in this coupling reaction which made it unique when compared to other reactions reported in literatures. Inexpensive iodine catalyst, easy accessible raw materials, mild reaction conditions, good functional group tolerance and excellent selectivity made this coupling reaction be a practical method. This reaction can also be scaled up.

**Keywords:** Iodine, Coupling, *β*-Hydroxyketones, *β*-Aminoketones, Benzo[*h*]quinolones

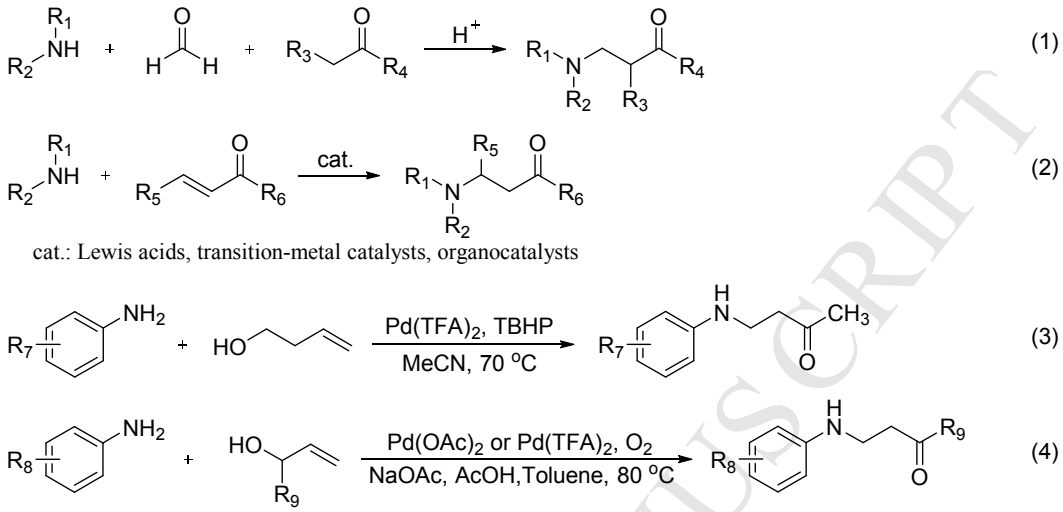
## INTRODUCTION

*β*-Aminoketones are important structures found in many bioactive molecules and pharmaceutical agents, and are very useful intermediates in the synthesis of *β*-aminoacids, *β*-aminoalcohols, 1,3-alkamines, lactams, nikkomycins and neopolyoxines which also find wide applications in fine chemicals and pharmaceuticals.[1] Traditionally, a classical method for the construction of *β*-aminoketones is Mannich reaction (Scheme 1, eq 1),[2] however, the drawbacks such as long reaction times, low yields and harsh conditions limit its application in the synthesis of complex molecules. Aza-Michael addition is another method for the synthesis of *β*-aminoketones using conjugate addition of amines to *α*, *β*-unsaturated ketones with such advantages as simplicity and atom economy (Scheme 1, eq 2).[3-7] A variety of reagents involved stoichiometric or catalytic amounts of Lewis acids,[5] transition-metals,[6] and organic compounds[7] had been reported as catalysts for aza-Michael addition. But the polymerization of labile *α*, *β*-unsaturated carbonyl compounds caused by acidic or basic catalysts limited the application of aza-Michael addition in many fields. To address this challenge, the Pd-catalyzed oxidative amination of homoallylic alcohols[8] or allyl alcohols[9] to afford *β*-aminoketones using TBHP or $O_2$ as oxidants respectively was reported lately (Scheme 1, eq 3 and 4). To our knowledge, non-metal catalyzed coupling of *β*-hydroxyketones with amines to form *β*-aminoketones in one step without oxidants had not been studied.

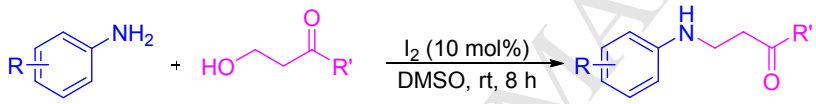
Herein, we disclosed a iodine-catalyzed coupling of *β*-hydroxyketones with aromatic amines to yield *β*-aminoketones and benzo[*h*]quinolones. There are many differences between this

coupling reaction and other reactions reported in literatures (Scheme 1, eq 5), for exemple, non-metal catalyst, no oxidant, no $\alpha$, $\beta$-unsaturated ketone intermediates and aza-Michael addition. This approach has advantages of easy accessible raw materials, mild reaction conditions, good functional group tolerance and excellent selectivity, and can also be scaled up.

**Previous work:**




**This work:**




- **Non-metallic catalyst**
- **No oxidant**
- **No experienced unsaturated ketone and Michael addition**

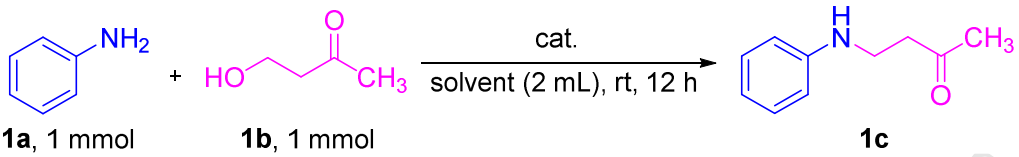
**Scheme 1.** Strategies for the Construction of $\beta$-AminoKetones

## RESULTS AND DISCUSSION

We initiated this study with commercially available aniline (**1a**) and 4-hydroxybutan-2-one (**1b**) as template substrates for the optimization of reaction parameters including catalyst, solvent and reaction time to identify the optimal reactions conditions (Table 1). To our delight, when $I_2$ (10 mol%) was employed as catalyst in THF, the 4-(phenylamino)butan-2-one (**1c**) was obtained in 64% isolated yield (Table 1, entry 1). After detailed examinations of different solvents such as MeCN, ethyl acetate, toluene, EtOH, DMF, DMSO, MeOH, $H_2O$, 1,2-dichloroethane, 1,4-dioxane and solvent-free system (Table 1, entries 2-12), the DMSO was selected for the next optimization study owing to the 93% isolated yield of 4-(phenylamino)butan-2-one (**1c**) (Table 1, entry 8). Next, screening of other iodine compounds such as $H_4NI$, KI, NaI, $ZnI_2$ and $(CH_3)_4NI$ revealed that $I_2$ catalyze the process more efficient than other iodine compounds (Table 1, entries 13-17). As expected, no 4-(phenylamino)butan-2-one (**1c**) could be detected in absence of iodine catalyst (Table 1, entry 18). Then we studied the amount of $I_2$ and found that 10 mol% was the best choice (Table 1, entries 19-22). After the reaction time were studied (Table 1, entries 23-26), we obtained the optimal reactions conditions, viz., 10 mol% $I_2$ as catalyst, 2 mL DMSO as solvent at room temperature for 8 h (Table 1, entry 26). Control reactions were carried out in nitrogen atmosphere also yielded 4-(phenylamino)butan-2-one (**1c**) in 66% and 93% isolated yields respectively (Table

1, entries 1 and 26) which illustrated $O_2$ was not involved in the reaction.

**Table 1. Optimization of Reaction Conditions**




**1a**, 1 mmol **1b**, 1 mmol **1c**

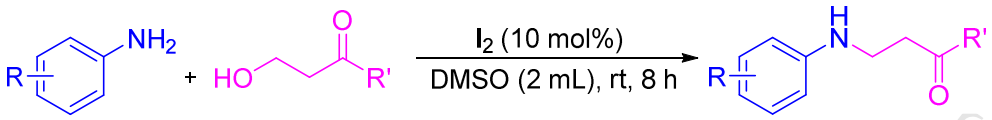
| entry | cat. (mol%) | solvent | yield[a] (%) |
|---|---|---|---|
| 1 | $I_2$ (10) | THF | 64 (66[b]) |
| 2 | $I_2$ (10) | MeCN | 74 |
| 3 | $I_2$ (10) | Ethyl acetate | 34 |
| 4 | $I_2$ (10) | Toluene | 76 |
| 5 | $I_2$ (10) | EtOH | 58 |
| 6 | $I_2$ (10) | - | 63 |
| 7 | $I_2$ (10) | DMF | 90 |
| 8 | $I_2$ (10) | DMSO | 93 |
| 9 | $I_2$ (10) | MeOH | 46 |
| 10 | $I_2$ (10) | $H_2O$ | 22 |
| 11 | $I_2$ (10) | 1,2-Dichloroethane | 68 |
| 12 | $I_2$ (10) | 1,4-Dioxane | 62 |
| 13 | $H_4NI$ (10) | DMSO | 30 |
| 14 | KI (10) | DMSO | trace |
| 15 | NaI (10) | DMSO | 48 |
| 16 | $ZnI_2$ (10) | DMSO | 41 |
| 17 | $(CH_3)_4NI$ (10) | DMSO | 28 |
| 18 | - | DMSO | n.r. |
| 19 | $I_2$ (3) | DMSO | 78 |
| 20 | $I_2$ (5) | DMSO | 81 |
| 21 | $I_2$ (6) | DMSO | 82 |
| 22 | $I_2$ (8) | DMSO | 82 |
| 23[c] | $I_2$ (10) | DMSO | 58 |
| 24[d] | $I_2$ (10) | DMSO | 68 |
| 25[e] | $I_2$ (10) | DMSO | 83 |
| 26[f] | $I_2$ (10) | DMSO | 94 (93[b]) |

[a] Isolated yield, n.r. = no reaction. [b] Reaction was studied in nitrogen atmosphere. [c] Reaction time was 2 h. [d] Reaction time was 4 h. [e] Reaction time was 6 h. [f] Reaction time was 8 h.

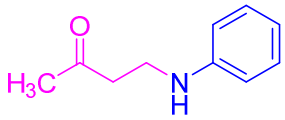
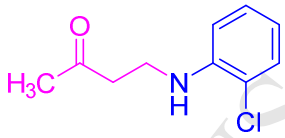
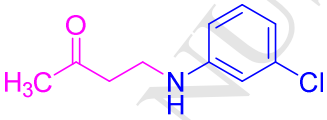
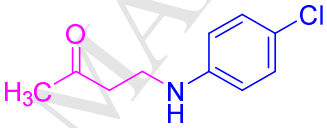
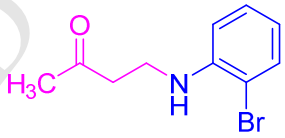
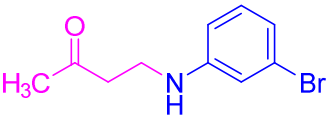
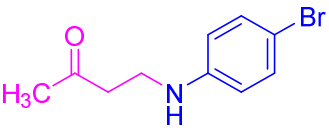
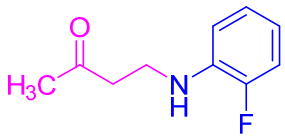
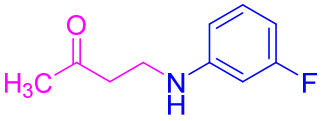
On the basis of the optimized conditions, the generality of the catalyst system was assessed on an array of substituted aromatic amine which have electron-donating and electron-withdrawing groups in the arene. In all cases, the corresponding *β*-aminoketones (monoalkylated products) were obtained in moderate to good yields (Table 2). These results show that the reaction have good functional group tolerance and excellent selectivity which made this reaction be a practical synthetic method. *Para*, *meta* and *ortho* substitution have different impacts on the reaction with the results as yields of *para* substituted aromatic amines were highest, followed by *meta* substituted aromatic amines, *ortho* substituted aromatic amines final (Table 2, **2c**-**12c**, **14c**-**26c**). It

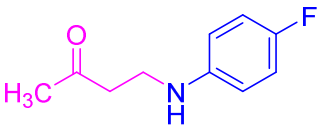
might be due to the steric hindrance of *ortho*-substituent group. The electron-rich aromatic amines provided higher yields than electron-deficient aromatic amines under the standard conditions.

**Table 2. Scope of Substrates of Iodine-catalyzed Coupling of *β*-Hydroxyketones with Aromatic Amines**



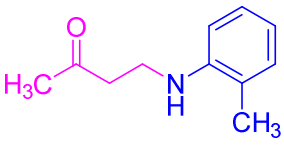
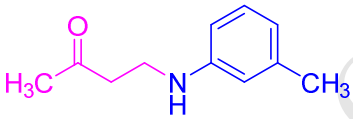
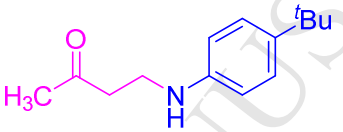
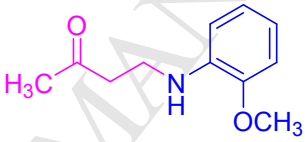
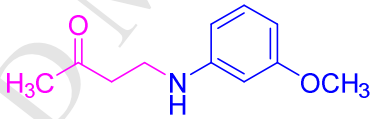
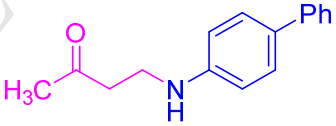
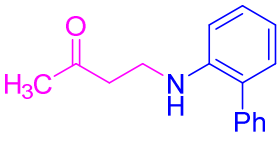
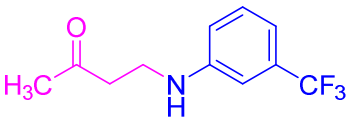
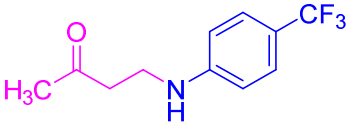
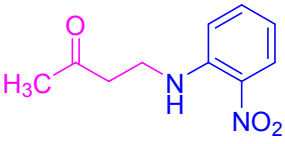

**1a**, 1 mmol **1b**, 1 mmol **1c**

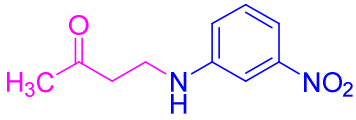
| entry | product | structure | yield[a] (%) |
|---|---|---|---|
| 1 | **1c** |  | 94 |
| 2 | **2c** |  | 73 |
| 3 | **3c** |  | 86 |
| 4 | **4c** |  | 90 |
| 5 | **5c** |  | 71 |
| 6 | **6c** |  | 75 |
| 7 | **7c** |  | 77 |
| 8 | **8c** |  | 40 |
| 9 | **9c** |  | 50 |

| | | | |
|---|---|---|---|
| 10 | **10c** |  | 44 |

[a] Isolated yield. [b] Reaction time was 24 h.

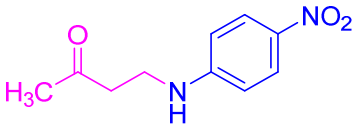
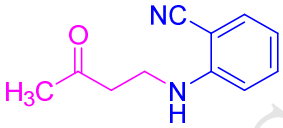
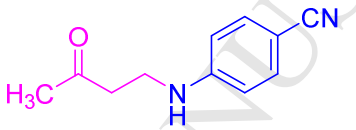
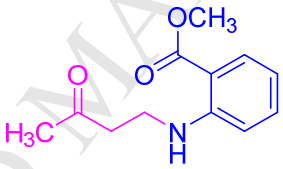
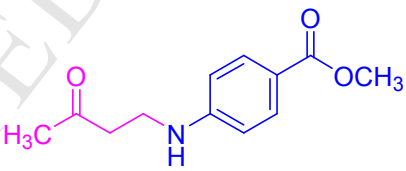
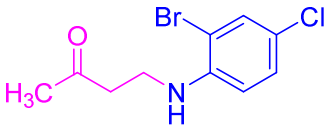
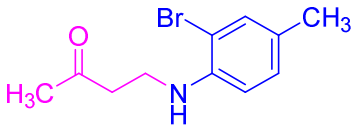
**Table 2.** ***(Contd.)***

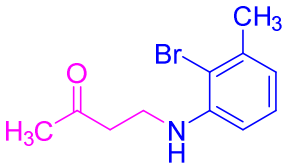
| entry | product | structure | yield[a] (%) |
|---|---|---|---|
| 11 | **11c** |  | 72 |
| 12 | **12c** |  | 79 |
| 13 | **13c** |  | 92 |
| 14 | **14c** |  | 71 |
| 15 | **15c** |  | 74 |
| 16 | **16c** |  | 50 |
| 17 | **17c** |  | 41 |
| 18 | **18c** |  | 42 (70[b]) |
| 19 | **19c** |  | 45 (71[b]) |
| 20 | **20c** |  | 38 (41[b]) |

| | | | |
|---|---|---|---|
| 21 | **21c** |  | 49 (50[b]) |

[a] Isolated yield. [b] Reaction time was 24 h.

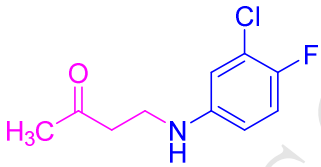
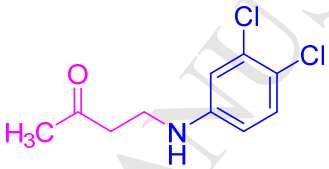
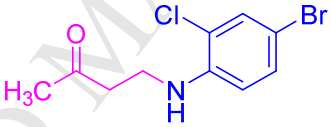
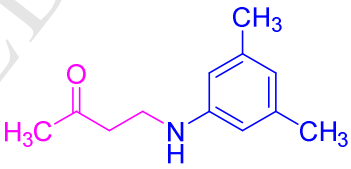
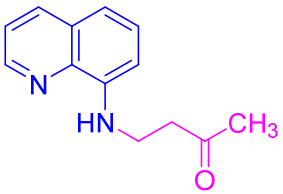
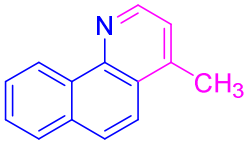
**Table 2.** ***(Contd.)***

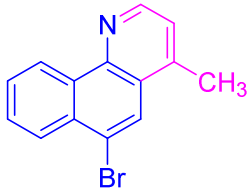
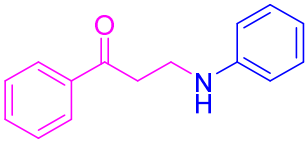
| entry | product | structure | yield[a] (%) |
|---|---|---|---|
| 22 | **22c** |  | 56 (56[b]) |
| 23 | **23c** |  | 78 (79[b]) |
| 24 | **24c** |  | 77 (79[b]) |
| 25 | **25c** |  | 64 (63[b]) |
| 26 | **26c** |  | 87 (89[b]) |
| 27 | **27c** |  | 59 (58[b]) |
| 28 | **28c** |  | 76 |
| 29 | **29c** |  | 84 |

| | | | |
|---|---|---|---|
| 30 | **30c** |  | 90 |

[a] Isolated yield. [b] Reaction time was 24 h.

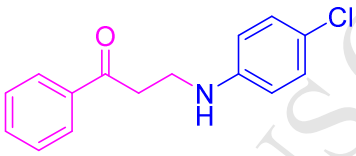
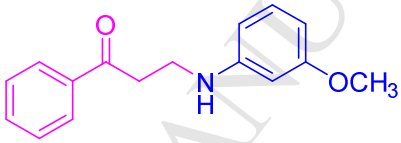
**Table 2.** ***(Contd.)***

| entry | product | structure | yield[a] (%) |
|---|---|---|---|
| 31 | **31c** |  | 80 |
| 32 | **32c** |  | 93 |
| 33 | **33c** |  | 85 |
| 34 | **34c** |  | 86 |
| 35 | **35c** |  | 51 |
| 36 | **36c** |  | 37 |
| 37 | **37c** |  | 51 |

| | | | |
|---|---|---|---|
| 38 | **38c** |  | 50 |
| 39 | **39c** |  | 71[b] |

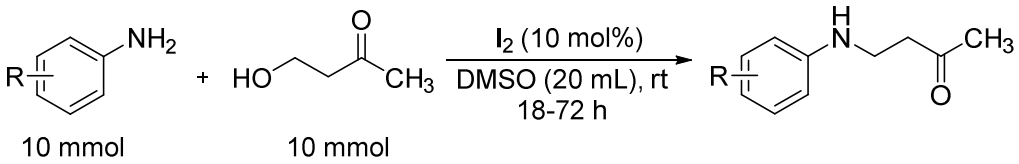
[a] Isolated yield. [b] Reaction time was 24 h.

**Table 2.** ***(Contd.)***

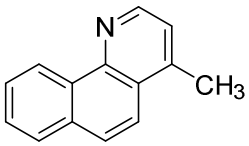
| entry | product | structure | yield[a] (%) |
|---|---|---|---|
| 40 | **40c** |  | 77[b] |
| 41 | **41c** |  | 81[b] |

[a] Isolated yield. [b] Reaction time was 24 h.

The substrates with strong electron-withdrawing group in the aromatic rings which can be utilized for further synthetic transformations, such as -$CF_3$ (Table 2, **18c** and **19c**), -$NO_2$ (Table 2, **20c**-**22c**), -CN (Table 2, **23c** and **24c**), -$COOCH_3$ (Table 2, **25c** and **26c**), -$SO_2CH_3$ (Table 2, **27c**), were tolerated in the reaction in moderate to good yields. We ran experiments with the electron-deficient aromatic amines as substrates for 24 h. The substrates with -$CF_3$ group in the aromatic rings (Table 2, **18c** and **19c**) gave higher yields comparing with the standard conditions. The substrates with -$NO_2$ (Table 2, **20c**-**22c**), -CN (Table 2, **23c** and **24c**), -$COOCH_3$ (Table 2, **25c** and **26c**), -$SO_2CH_3$ (Table 2, **27c**) in the aromatic rings gave similar yields comparing with the standard conditions. The *β*-aminoketones with halo group in the *ortho*-position of NH (Table 2, **2c**, **5c**, **8c**) which can be used for the synthesis of 3-substituted indolines were obtained in good yields. Quinolin-8-amine and 4-hydroxybutan-2-one underwent this protocol to afford product in 51% yields (Table 2, **35c**). The reaction was also compatible with 2° amine to afford the desired product in moderate yield (Table 2, **36c**). Notably, when 1-aminonaphthalenes were utilized as the substrates, the corresponding products benzo[*h*]quinolones were obtained in good yields (Table 2, **37c**, **38c**). Good yields were obtained when 3-hydroxy-1-phenylpropan-1-one was used as substrates (Table 2, **39c**-**41c**).



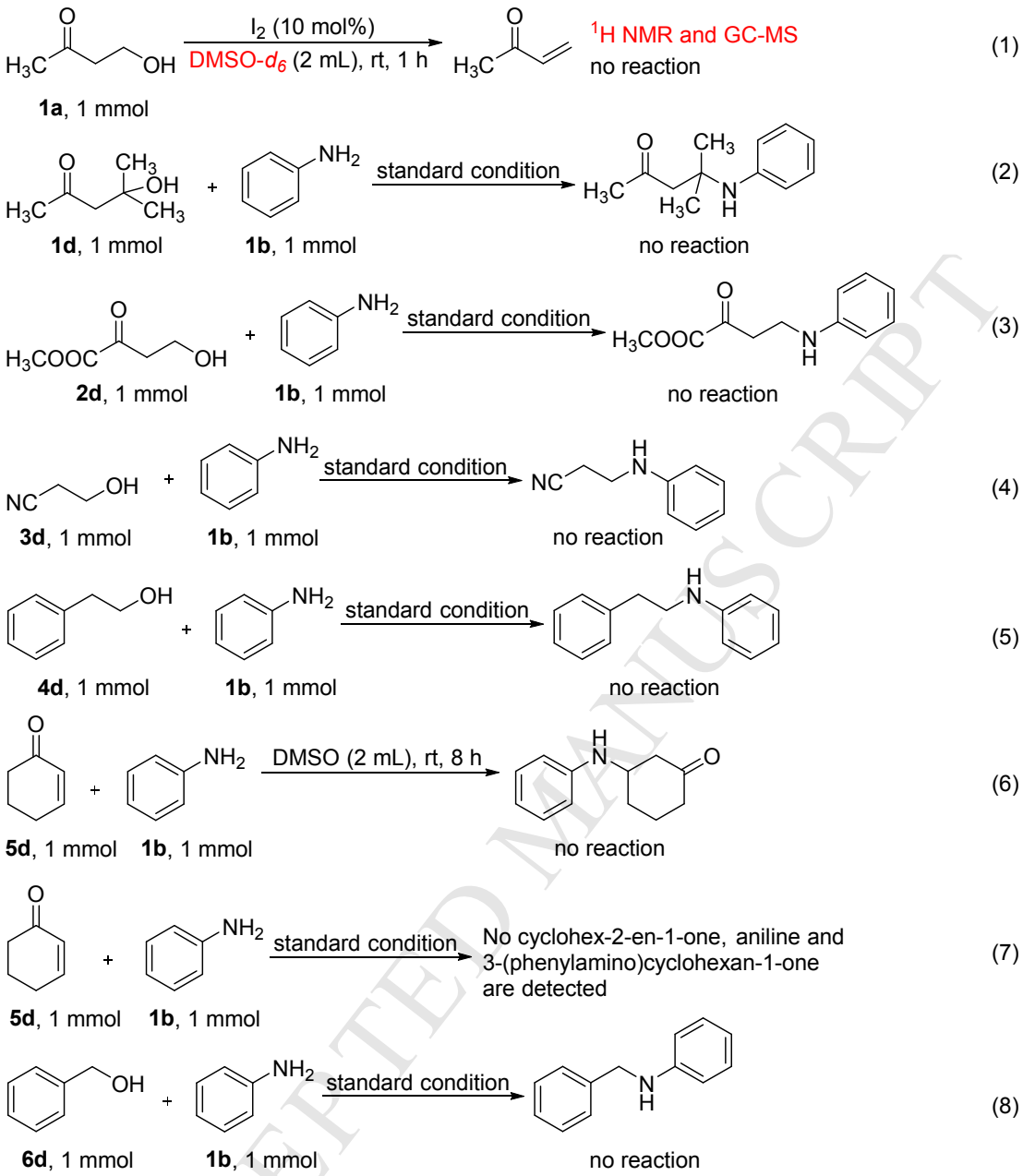

**1c**, R = H, 18 h, 87%
**21c**, R = 3-$NO_2$, 72 h, 48%
**24c**, R = 4-CN, 36 h, 84%
**26c**, R = 4-$COOCH_3$, 36 h, 88%
**29c**, R = 2-Br, 4-$CH_3$, 24 h, 91%
**32c**, R = 3-Cl, 4-Cl, 24 h, 86%




**37c**, 72 h, 51%

**Scheme 2.** Gram Scale Reactions (isolated yield)

The practical applicability of this protocol was demonstrated. We used 4-hydroxybutan-2-one and aromatic amines as the test substrates, working on gram scale at room temperature until complete consumption of starting material as monitored by TLC or 72 h. The desired products were obtained in good isolated yield (Scheme 2). These results suggested that this protocol is a practical process for the preparation of *β*-aminoketones and benzo[*h*]quinolones.




**Scheme 3.** Control Experiments

To gain more insight into the mechanism for the coupling of *β*-hydroxyketones with aromatic amines to form *β*-aminoketones, several control experiments had been conducted (Scheme 3). According to the literature,[10] we hypothesized this coupling reaction experienced proton abstraction, synchronic with the C-O bond rupture of *β*-hydroxyketones by the catalyst iodine to yield *α*, *β*-unsaturated ketones (electron-deficient olefins) and followed by aza-Michael addition with amines to afford *β*-aminoketones. But, when the reaction proceeded with 4-hydroxybutan-2-one (**1a**), $I_2$, DMSO-$d_6$, no reaction occurred (Scheme 3, eq 1) detected by $^1$HNMR (Fig. 1, see the ESI) and GC-MS. Other *β*-hydroxy compounds which also could yield electron-deficient olefins were utilized as the substrates, for example 4-hydroxy-4-methylpentan-2-one (**1d**), methyl 4-hydroxy-2-oxobutanoate (**2d**), 3-hydroxypropanenitrile (**3d**), 2-phenylethan-1-ol (**4d**), no coupling reactions occured (Scheme 3, eq 2-5). The reaction also did not occur when the cyclohex-2-en-1-one and aniline were used as

the substrates without $I_2$ (Scheme 3, eq 6). When the reaction was conducted with cyclohex-2-en-1-one and aniline as the substrates at standard condition, no cyclohex-2-en-1-one, aniline and 3-(phenylamino)cyclohexan-1-one were detected (Scheme 3, eq 7). With the above results, we thought this coupling reaction did not experienced *α*, *β*-unsaturated ketones and aza-Michael addition. According to the literature,[11] $I_2$ may facilitate the generation of carbocation from the activated alcohols. We hypothesized the carbocation is involved in this coupling reaction. But 4-hydroxy-4-methylpentan-2-one (**1d**) and benzyl alcohol (**6d**) which could yield more stable carbocations (3° and benzyl carbocation) were used as the substrates at standard condition, no coupling reactions occured (Scheme 3, eq 2 and 8). It is supposed that the carbocation is not involved in this coupling reaction.

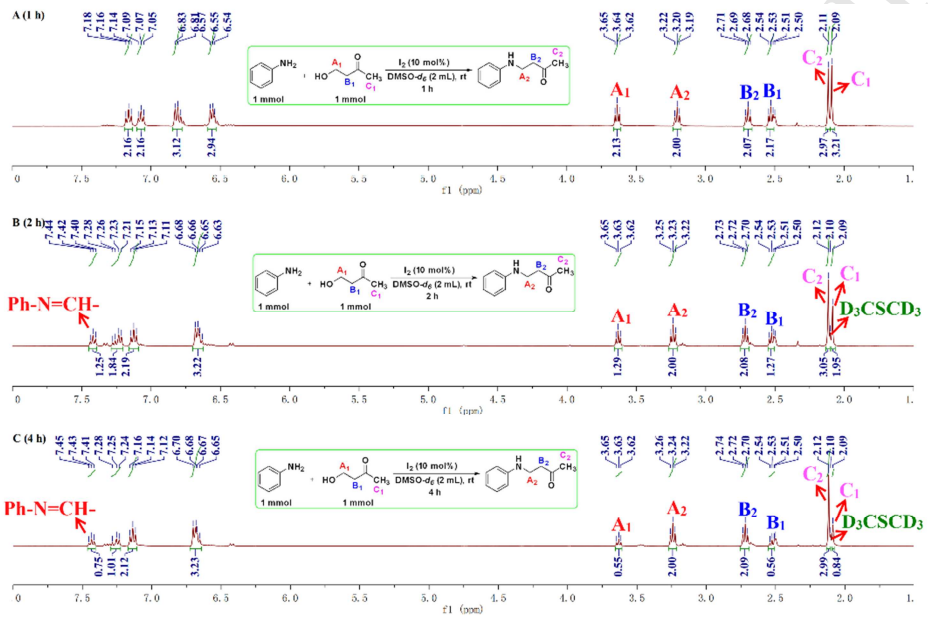



**Figure 1.** $^1$H NMR spectras of the coupling reaction of 4-hydroxybutan-2-one with aniline at various reaction times

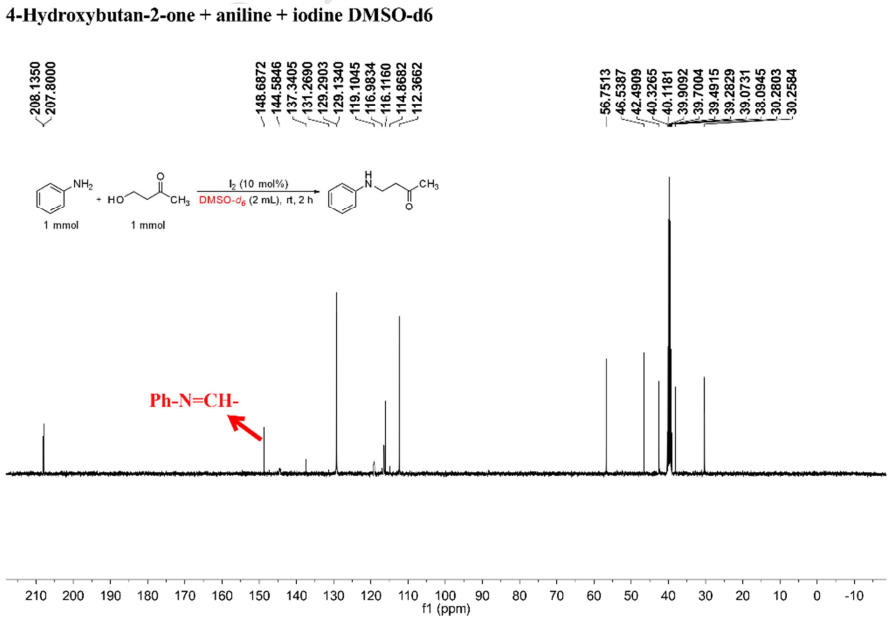
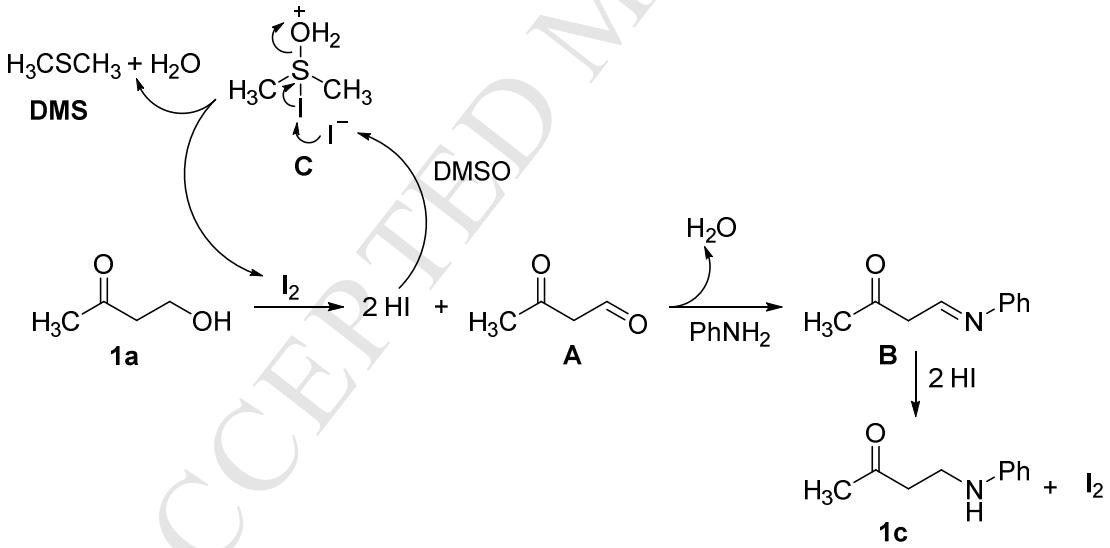



**Figure 2.** $^{13}$C NMR spectra of the coupling reaction of 4-hydroxybutan-2-one with aniline using $I_2$

as catalyst

The $^{1}$H NMR and $^{13}$C NMR were used to measure structural changes during the coupling reaction at standard condition (Figure 1 and 2). The $^{1}$HNMR spectras indicated that the 4-hydroxybutan-2-one (**1a**) decrease and 4-(phenylamino)butan-2-one (**1c**) increase with the extended reaction time. No -$NH_2$ and -OH were detected in the whole coupling process, which were detected obviously in absence of $I_2$ (Fig. 2, see the ESI). We did not obtain the $^{1}$HNMR spectra with prominent feature of olefins and aldehydes. The $^{1}$H NMR spectrums (Figure 1B and 1C) are very different from the spectrums of aniline and the product (**1c**). A resonance characteristic of imine was displayed, which suggested that 4-hydroxybutan-2-one (**1a**) was oxidized to aldehyde, then aldehyde reacted with aniline to generate imine. The $^{13}$C NMR spectrum also demonstrated the generation of imine in our reaction system (Figure 2). $D_3CSCD_3$ was detected which illustrated dimethyl sulfoxide actively participated the coupling reaction.[12]

Based on the above results and previous reports, a tentative mechanism for iodine-catalyzed coupling of *β*-hydroxyketones with aromatic amines to yield *β*-aminoketones was proposed in Scheme 4. Initially, 4-hydroxybutan-2-one (**1a**) was oxidized to aldehyde **A** under the standard condition, synchronic with generation of HI.[13] Next, aldehyde **A** reacted with aniline to form imine **B** quickly which could explain why no -CHO was detected.[8] HI has strong reducing action and decomposed to $H_2$ and $I_2$. Imine **B** was reduced to product (**1c**) by hydrogen. Some party of HI reacted with DMSO to give intermediate **C**.[12] Then, nucleophilic attack of $I^-$ on the iodide atom of intermediate **C** takes place to regenerate $I_2$ releasing DMS and $H_2O$. Further studies aimed at more detailed mechanism are in progress.




**Scheme 4.** Possible Reaction Pathway

## CONCLUSION

In summary, a novel and efficient iodine-catalyzed coupling of *β*-hydroxyketones with aromatic amines to yield *β*-aminoketones and benzo[*h*]quinolones had been developed. Noble metallic catalysts, oxidants, *α, β*-unsaturated ketone intermediates and aza-Michael addition were not involved in this coupling reaction. Many advantages such as inexpensive $I_2$ catalyst, easy accessible raw materials, mild reaction conditions, good functional group tolerance and excellent selectivity made this approach be a practical process for the preparation of *β*-aminoketones and

benzo[*h*]quinolones.

## EXPERIMENTAL SECTION

### General Considerations

All the reagents including aromatic amines, 4-hydroxybutan-2-one, 3-hydroxy-1-phenylpropan-1-one, iodine, iodides, solvents were purchased from commercial sources and were used without further purification. All chemical shift values refer to $\delta_{TMS}$ = 0.00 ppm or $CDCl_3$ ($\delta$ ($^1$H), 7.26 ppm; $\delta$ ($^{13}$C), 77.20 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Analytical TLC plates were viewed by UV light (254 nm).

### General Experimental Procedure

A 25 mL RBF was subsequently charged with 1.0 mmol aromatic amines, 1.0 mmol 4-hydroxybutan-2-one, 10 mol% $I_2$ (25.4 mg), 2 mL DMSO. The resulting mixture was performed at room temperature for 8 h. After reaction was complete, the resulting mixture was poured into water (20 mL) and extracted with ethyl acetate (3×10 mL). The combined organic extracts were washed with brine (3×5 mL), then dried over $Na_2SO_4$ and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether = 1:20-1:4) to afford the desired products.

### Experimental Procedure on Gram Scale

A 100 mL RBF was subsequently charged with 10 mmol aromatic amines, 10 mmol 4-hydroxybutan-2-one, 10 mol% $I_2$ (254 mg), 20 mL DMSO. The resulting mixture was performed at room temperature until complete consumption of starting material as monitored by TLC or 72 h. After reaction was complete, the resulting mixture was poured into water (200 mL). If desired products were isolated as solids from aqueous solutions, desired products were treated through vacuum filtering, washing with water and vacuum drying. If no solid precipitated, the aqueous solutions were extracted with ethyl acetate (3×100 mL). The combined organic extracts were washed with brine (3×50 mL), then dried over $Na_2SO_4$ and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether = 1:20-1:4) to afford the desired products.

### The yields, properties and characterization of new compounds

4-(Phenylamino)butan-2-one **1c** was isolated in 94% yield (153.2 mg). Yellow solid; mp: 81-82 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.19 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 3.99 (s, 1H), 3.42 (t, *J* = 6.1 Hz, 2H), 2.74 (t, *J* = 6.1 Hz, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 208.19, 147.81, 129.42, 117.72, 113.12, 42.70, 38.46, 30.39; Known compound.[8]

4-((2-Chlorophenyl)amino)butan-2-one **2c** was isolated in 73% yield (144.1 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.25 (d, *J* = 9.9 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.65 (dd, *J* = 17.0, 8.2 Hz, 2H), 4.55 (s, 1H), 3.48 (q, *J* = 6.3 Hz, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 2.19 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 207.59, 143.75, 129.49, 127.96, 119.71, 117.61, 111.23, 42.79, 38.24, 30.55. HRMS (ESI) for $C_{10}H_{12}ClNO$, calcd: 197.0607, found: 197.0606.

4-((3-Chlorophenyl)amino)butan-2-one **3c** was isolated in 86% yield (169.8 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.04 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 6.44

(d, *J* = 8.2 Hz, 1H), 4.14 (s, 1H), 3.35 (s, 2H), 2.70 (t, *J* = 5.7 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.99, 149.02, 135.06, 130.33, 117.31, 112.43, 111.41, 42.37, 38.16, 30.32. HRMS (ESI) for $C_{10}H_{12}ClNO$, calcd: 197.0607, found: 197.0604.

4-((4-Chlorophenyl)amino)butan-2-one **4c** was isolated in 90% yield (177.2 mg). Yellow solid; mp: 71-73 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 4.03 (s, 1H), 3.34 (t, *J* = 5.4 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.02, 146.43, 129.15, 122.07, 114.12, 42.41, 38.51, 30.34; Known compound.[8]

4-((2-Bromophenyl)amino)butan-2-one **5c** was isolated in 71% yield (172.3 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.9 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 4.56 (s, 1H), 3.46 (dd, *J* = 11.5, 5.6 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.18 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.55, 144.68, 132.72, 128.62, 118.11, 111.30, 110.21, 42.67, 38.38, 30.50; Known compound.[8]

4-((3-Bromophenyl)amino)butan-2-one **6c** was isolated in 75% yield (181.8 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 4.10 (s, 1H), 3.37 (t, *J* = 6.0 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.99, 149.16, 130.70, 123.48, 120.42, 115.44, 111.94, 42.46, 38.23, 30.45; Known compound.[8]

4-((4-Bromophenyl)amino)butan-2-one **7c** was isolated in 77% yield (187.3 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 4.04 (s, 1H), 3.35 (t, *J* = 6.1 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.03, 146.83, 132.07, 114.65, 109.18, 42.42, 38.43, 30.41; Known compound.[8]

4-((2-Fluorophenyl)amino)butan-2-one **8c** was isolated in 40% yield (72.3 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.03-6.90 (m, 2H), 6.70 (t, *J* = 8.0 Hz, 1H), 6.62 (dd, *J* = 13.2, 8.1 Hz, 1H), 4.17 (s, 1H), 3.43 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 6.3 Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.72, 153.05, 150.68, 136.33 (d, *J* = 11.6 Hz), 124.69 (d, *J* = 3.5 Hz), 116.99 (d, *J* = 7.1 Hz), 114.67 (d, *J* = 18.4 Hz), 112.17 (d, *J* = 3.4 Hz), 42.76, 38.12, 30.40; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -136.12 (dd, *J* = 13.7, 6.2 Hz). Known compound.[8]

4-((3-Fluorophenyl)amino)butan-2-one **9c** was isolated in 50% yield (90.9 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 15.0, 8.1 Hz, 1H), 6.36 (dd, *J* = 17.9, 9.2 Hz, 2H), 6.28 (d, *J* = 11.6 Hz, 1H), 4.15 (s, 1H), 3.38 (t, *J* = 5.9 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.07, 165.52, 163.11, 149.68 (d, *J* = 10.9 Hz), 130.51 (d, *J* = 10.2 Hz), 109.03 (d, *J* = 2.2 Hz), 104.18, 103.96, 99.73, 99.47, 42.50, 38.35, 30.44; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -112.80 (dt, *J* = 10.8, 7.9 Hz). Known compound.[9]

4-((4-Fluorophenyl)amino)butan-2-one **10c** was isolated in 44% yield (79.3 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, *J* = 8.3 Hz, 2H), 6.53 (dd, *J* = 7.8, 3.5 Hz, 2H), 3.88 (s, 1H), 3.35 (t, *J* = 5.8 Hz, 2H), 2.72 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.21, 157.23, 154.90, 144.23, 115.93, 115.71, 114.09 (d, *J* = 7.4 Hz), 42.59, 39.24, 30.40; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -127.72 (tt, *J* = 7.9, 4.0 Hz). Known compound.[8]

4-(*o*-Tolylamino)butan-2-one **11c** was isolated in 72% yield (126.9 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.70-6.59 (m, 2H), 3.90 (s, 1H), 3.47 (t, *J* = 5.9 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.17 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.38, 145.80, 130.45, 127.26, 122.73, 117.34, 109.76, 42.76, 38.48, 30.51, 17.62; Known compound.[6d]

4-(*m*-Tolylamino)butan-2-one **12c** was isolated in 79% yield (140.3 mg). Yellow oil; $^1$H

NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.7 Hz, 2H), 3.41 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 6.2 Hz, 2H), 2.29 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.24, 147.82, 139.16, 129.26, 118.65, 113.93, 110.24, 42.74, 38.47, 30.35, 21.70; Known compound.[6d]

4-((4-(*tert*-Butyl)phenyl)amino)butan-2-one **13c** was isolated in 92% yield (202.2 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 1H), 3.41 (t, *J* = 6.1 Hz, 2H), 2.75 (t, *J* = 6.1 Hz, 2H), 2.17 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.28, 145.46, 140.55, 126.19, 112.90, 42.91, 38.76, 33.97, 31.67, 30.39; Known compound.[8]

4-((2-Methoxyphenyl)amino)butan-2-one **14c** was isolated in 71% yield (136.7 mg). Yellow solid; mp: 40-42 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 6.76 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.57 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.32 (s, 1H), 3.70 (s, 3H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 2.04 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.80, 147.04, 137.67, 121.20, 116.67, 109.73, 109.52, 55.34, 42.82, 38.06, 30.20. HRMS (ESI) for $C_{11}H_{15}NO_2$, calcd: 193.1103, found: 197.1100.

4-((3-Methoxyphenyl)amino)butan-2-one **15c** was isolated in 74% yield (143.1 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.1 Hz, 1H), 6.27 (d, *J* = 8.1 Hz, 1H), 6.21 (d, *J* = 8.1 Hz, 1H), 6.15 (s, 1H), 3.76 (s, 3H), 3.38 (t, *J* = 6.1 Hz, 2H), 2.72 (t, *J* = 6.1 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.19, 160.93, 149.20, 130.12, 106.17, 102.75, 99.01, 55.13, 42.61, 38.38, 30.32. HRMS (ESI) for $C_{11}H_{15}NO_2$, calcd: 193.1103, found: 197.1101.

4-([1,1'-Biphenyl]-4-ylamino)butan-2-one **16c** was isolated in 50% yield (118.2 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.15 (dd, *J* = 13.5, 6.4 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 1H), 3.33 (t, *J* = 6.1 Hz, 2H), 2.63 (t, *J* = 6.1 Hz, 2H), 2.04 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.15, 147.24, 141.24, 130.53, 128.77, 128.07, 126.28 (d, *J* = 14.6 Hz), 113.33, 42.66, 38.44, 30.39. HRMS (ESI) for $C_{16}H_{17}NO$, calcd: 239.1310, found: 239.1313.

4-([1,1'-Biphenyl]-2-ylamino)butan-2-one **17c** was isolated in 41% yield (97.2 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 2H), 7.35-7.25 (m, 3H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 4.12 (s, 1H), 3.35 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 2.06 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.73, 144.61, 139.38, 130.52, 129.38, 129.01, 128.80, 128.22, 127.38, 117.29, 110.45, 42.73, 38.55, 30.38; Known compound.[8]

4-((3-(Trifluoromethyl)phenyl)amino)butan-2-one **18c** was isolated in 42% yield (97.3 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.19 (s, 1H), 3.32 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.07 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.02, 148.11, 132.11, 131.79, 131.48, 131.16, 129.80, 128.53, 125.83, 123.12, 120.42, 116.10, 113.92 (q, *J* = 3.8 Hz), 108.96 (q, *J* = 3.8 Hz), 42.35, 38.17, 30.29; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -62.89. Known compound.[8]

4-((4-(Trifluoromethyl)phenyl)amino)butan-2-one **19c** was isolated in 45% yield (103.8 mg). Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.37 (s, 1H), 3.44 (t, *J* = 6.0 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.97, 150.40, 126.88 (q, *J* = 3.7 Hz), 126.51, 123.83, 112.14, 42.44, 37.99, 30.50; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -61.01. HRMS (ESI) for $C_{11}H_{12}F_3NO$, calcd: 231.0871, found: 231.0872.

4-((2-Nitrophenyl)amino)butan-2-one **20c** was isolated in 38% yield (79.9 mg). Yellow solid; mp: 63-65 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 8.06 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.64 (t, *J* = 7.8 Hz, 1H), 3.59 (q, *J* = 6.5 Hz, 2H), 2.86 (t, *J* = 6.7 Hz, 2H), 2.20 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 206.43, 145.21, 136.42, 132.26, 127.11, 115.63, 113.57, 42.60, 37.45, 30.46. HRMS (ESI) for $C_{10}H_{12}N_2O_3$, calcd: 208.0848, found: 208.0843.

4-((3-Nitrophenyl)amino)butan-2-one **21c** was isolated in 49% yield (101.6 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.38 (s, 1H), 3.39-3.27 (m, 2H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.06 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.94, 149.48, 148.79, 129.88, 119.13, 112.00, 106.24, 42.23, 38.18, 30.39. HRMS (ESI) for $C_{10}H_{12}N_2O_3$, calcd: 208.0848, found: 208.0847.

4-((4-Nitrophenyl)amino)butan-2-one **22c** was isolated in 82% yield (117.3 mg). Yellow solid; mp: 89-91 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 9.2 Hz, 2H), 5.12 (s, 1H), 3.47 (q, *J* = 5.9 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.58, 153.22, 137.76, 126.50, 111.07, 42.14, 37.69, 30.32; Known compound.[8]

2-((3-Oxobutyl)amino)benzonitrile **23c** was isolated in 78% yield (146.7 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 5.8 Hz, 2H), 6.56 (dd, *J* = 8.3, 4.9 Hz, 2H), 4.82 (s, 1H), 3.44-3.33 (m, 2H), 2.70 (d, *J* = 3.7 Hz, 2H), 2.09 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.07, 149.86, 134.19, 132.77, 117.72, 116.52, 110.45, 95.79, 42.19, 37.61, 30.19; Known compound.[8]

4-((3-Oxobutyl)amino)benzonitrile **24c** was isolated in 77% yield (145.2 mg). Yellow solid; mp: 91-93 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.68 (s, 1H), 3.42 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.62, 151.04, 133.81, 120.54, 112.29, 98.71, 42.21, 37.54, 30.38; Known compound.[8]

Methyl 2-((3-oxobutyl)amino)benzoate **25c** was isolated in 64% yield (141.0 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.26 (s, 1H), 6.85 (t, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 8.5 Hz, 1H), 6.09 (t, *J* = 7.5 Hz, 1H), 3.34 (s, 3H), 2.99 (dd, *J* = 12.5, 6.6 Hz, 2H), 2.29 (t, *J* = 6.7 Hz, 2H), 1.68 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.03, 168.93, 150.69, 134.65, 131.76, 114.74, 110.96, 110.21, 51.48, 42.83, 37.33, 30.29; Known compound.[9]

Methyl 4-((3-oxobutyl)amino)benzoate **26c** was isolated in 87% yield (192.1 mg). Yellow solid; mp: 108-110 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 4.57 (s, 1H), 3.81 (s, 3H), 3.42 (dd, *J* = 11.3, 5.5 Hz, 2H), 2.72 (t, *J* = 6.0 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.75, 167.33, 151.60, 131.64, 118.45, 111.55, 51.58, 42.38, 37.69, 30.33; Known compound.[8]

4-((4-(Methylsulfonyl)phenyl)amino)butan-2-one **27c** was isolated in 59% yield (125.7 mg). Colourless solid; mp: 79-81 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 6.0 Hz, 2H), 4.83 (s, 1H), 3.41 (d, *J* = 4.8 Hz, 2H), 2.95 (s, 3H), 2.73 (d, *J* = 5.5 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.62, 152.05, 129.32, 127.02, 111.80, 45.04, 42.13, 37.56, 30.31; Known compound.[8]

4-((2-Bromo-4-chlorophenyl)amino)butan-2-one **28c** was isolated in 76% yield (209.7 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.50 (d, *J* = 8.7 Hz, 1H), 4.54 (s, 1H), 3.36 (s, 2H), 2.72 (t, *J* = 5.7 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.30, 143.41, 131.80, 128.34, 121.48, 111.58, 109.79, 42.27, 38.33, 30.31. HRMS (ESI) for $C_{10}H_{11}BrClNO$, calcd: 274.9713, found: 274.9712.

4-((2-Bromo-4-methylphenyl)amino)butan-2-one **29c** was isolated in 84% yield (215.7 mg).

Colourless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 4.29 (s, 1H), 3.30 (s, 2H), 2.63 (t, *J* = 6.3 Hz, 2H), 2.10 (s, 3H), 2.04 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.53, 142.34, 132.89, 129.04, 127.54, 111.35, 110.00, 42.53, 38.56, 30.29, 20.00. HRMS (ESI) for $C_{11}H_{14}BrNO$, calcd: 255.0259, found:255.0261.

4-((2-Bromo-3-methylphenyl)amino)butan-2-one **30c** was isolated in 90% yield (231.0 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.68 (s, 1H), 3.44 (d, *J* = 5.1 Hz, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.49, 144.70, 138.55, 127.65, 119.19, 112.71, 108.59, 42.52, 38.47, 30.28, 23.79; Known compound.[8]

4-((3-Chloro-4-fluorophenyl)amino)butan-2-one **31c** was isolated in 80% yield (172.7 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 8.9 Hz, 1H), 6.56 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.39 (dt, *J* = 8.7, 3.2 Hz, 1H), 3.30 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.04, 152.19, 149.83, 144.89, 121.10 (d, *J* = 18.3 Hz), 117.05, 116.83, 113.89, 112.47 (d, *J* = 6.3 Hz), 42.32, 38.85, 30.34; $^{19}$F NMR (377 MHz, $CDCl_3$) δ -131.04. Known compound.[8]

4-((3,4-Dichlorophenyl)amino)butan-2-one **32c** was isolated in 93% yield (215.5 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.9 Hz, 1H), 6.62 (s, 1H), 6.39 (d, *J* = 8.7 Hz, 1H), 4.14 (s, 1H), 3.33 (d, *J* = 5.9 Hz, 2H), 2.71 (d, *J* = 3.2 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.93, 147.45, 132.87, 130.74, 119.82, 113.88, 112.88, 42.28, 38.33, 30.40; Known compound.[8]

4-((4-Bromo-2-chlorophenyl)amino)butan-2-one **33c** was isolated in 85% yield (235.6 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.17 (d, *J* = 6.2 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 4.55 (s, 1H), 3.36 (s, 2H), 2.75-2.64 (m, 2H), 2.13 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.27, 142.81, 131.35, 130.56, 119.95, 112.09, 107.63, 42.26, 38.01, 30.28; Known compound.[8]

4-((3,5-Dimethylphenyl)amino)butan-2-one **34c** was isolated in 86% yield (165.1 mg). Colourless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.29 (s, 1H), 6.16 (s, 2H), 3.30 (t, *J* = 6.2 Hz, 2H), 2.63 (t, *J* = 6.1 Hz, 2H), 2.15 (s, 6H), 2.06 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.24, 147.87, 139.01, 119.72, 111.07, 42.80, 38.49, 30.32, 21.57; Known compound.[8]

4-(Quinolin-8-ylamino)butan-2-one **35c** was isolated in 51% yield (109.6 mg). Brown oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.49, 146.93, 144.35, 138.28, 135.94, 128.67, 127.71, 121.43, 114.12, 104.56, 42.77, 37.88, 30.30. HRMS (ESI) for $C_{13}H_{14}N_2O$, calcd: 214.1106, found:214.1110.

4-(Methyl(*p*-tolyl)amino)butan-2-one **36c** was isolated in 37% yield (71.1 mg). Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 2.91 (s, 3H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 208.21, 146.78, 129.89, 126.15, 113.11, 47.76, 40.23, 38.74, 30.65, 20.30; Known compound.[9]

4-Methylbenzo[*h*]quinoline **37c** was isolated in 51% yield (98.1 mg). Brown oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.1 Hz, 1H), 8.74 (d, *J* = 4.5 Hz, 1H), 7.82-7.65 (m, 3H), 7.60 (dt, *J* = 21.4, 7.4 Hz, 2H), 7.21 (s, 1H), 2.60 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.54, 146.27, 144.20, 133.44, 131.98, 128.13, 127.82, 127.47, 127.15, 126.02, 124.88, 123.11, 121.45,

19.17; Known compound.[9]

6-Bromo-4-methylbenzo[*h*]quinoline **38c** was isolated in 50% yield (135.8 mg). Gray oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.29 (dd, *J* = 6.2, 3.1 Hz, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.26 (dd, *J* = 5.7, 3.5 Hz, 1H), 8.09 (s, 1H), 7.74 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.23 (d, *J* = 4.3 Hz, 1H), 2.59 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.74, 145.40, 143.42, 132.75, 131.69, 129.02, 127.90, 127.39, 126.27, 125.16 (d, *J* = 7.1 Hz), 123.45, 122.58, 18.98. HRMS (ESI) for $C_{14}H_{10}BrN$, calcd: 270.9997, found: 270.9992.

Phenyl-3-(phenylamino)propan-1-one **39c** was isolated in 71% yield (160.0 mg). White solid; mp: 93-95 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.12 (s, 1H), 3.63 (t, *J* = 6.1 Hz, 2H), 3.29 (t, *J* = 6.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.49, 147.89, 136.90, 133.53, 129.52, 128.85, 128.21, 117.77, 113.22, 38.87, 37.84. HRMS (ESI) for $C_{15}H_{15}NO$, calcd: 225.1154, found: 225.1164.

3-((4-Chlorophenyl)amino)-1-phenylpropan-1-one **40c** was isolated in 77% yield (200.0 mg). White solid; mp: 126-127 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 4.16 (s, 1H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.27 (t, *J* = 6.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.31, 146.49, 136.79, 133.63, 129.31, 128.88, 128.19, 122.28, 114.28, 38.99, 37.58. HRMS (ESI) for $C_{15}H_{14}ClNO$, calcd: 259.0764, found: 259.0754.

3-((3-Methoxyphenyl)amino)-1-phenylpropan-1-one **41c** was isolated in 81% yield (207.0 mg). White solid; mp: 75-77 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.27 (t, *J* = 7.2 Hz, 2H), 6.20 (s, 1H), 4.16 (s, 1H), 3.77 (s, 3H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.28 (t, *J* = 6.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.47, 161.08, 149.29, 136.88, 133.53, 130.25, 128.84, 128.21, 106.33, 102.84, 99.14, 55.27, 38.83, 37.79. HRMS (ESI) for $C_{16}H_{17}NO_2$, calcd: 255.1259, found: 255.1260.

**Conflict of Interest** The authors declare that they have no conflict of interest.

**Supporting Information Available** $^{1}$H NMR, $^{13}$C NMR and $^{19}$C NMR spectras for all new compounds and control experiments. This material is available free of charge via the internet at http://XXX.XXX.XXX.

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