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# $In(OTf)_3$ catalyzed N-benzylation of amines utilizing benzyl alcohols in water

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ABSTRACT

An $In(OTf)_3$-catalyzed N-benzylation of amines utilizing benzyl alcohols through direct C–O bond activation has been reported. The reaction was performed in water without any base, additive, ligand or inert gas protection to afford the chem-selective mono- or bis-alkylated aromatic amines in good to excellent yields.



## 1. Introduction

The direct alkylation especially the benzylation of amines is one of the most practical and important approaches for the formation of C–N bonds. *N*-Benzyl amine motif is featured in a wide variety of pharmacologically and biologically active compounds. For example, 2-(4-(benzo[*d*][1,3]dioxol-5-ylmethyl)piperazin-1-yl) pyrimidine, which is known as Piribedil,[1] is a commonly used drug for the treatment of Parkinson's Disease. Another typical case in point is Antergan[2], which was among the first antihistamine drugs (Fig. 1). Generally, the alkylation of amines is accessible by using conventional alkylating agents, such as alkyl halides, in conjunction with the use of stoichiometric amount of base.[3] Recently, despite the poor electrophilicity of most alcohols, alcohols were regarded as green alkylation reagents in place of alkyl halides due to the fact that water is the only by-product generated in the whole procedure.

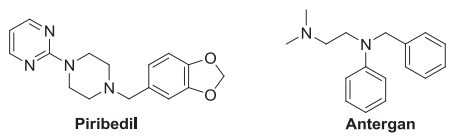


**Fig. 1.** *N*-Benzyl amine motif in drugs.

One popular concept to overcome the poor reactivity of alcohols is to temporarily convert them into the corresponding carbonyl compounds by the metal-catalyzed removal of hydrogen, which is well-known as 'hydrogen-borrowing methodology' or 'hydrogen autotransfer processes' (Scheme 1).[4] Much efforts have been directed towards the development of a transition metal-catalyzed alkylation of amines by alcohols since the pioneer work reported by Grigg[5] and Watanable.[6] Many organometallic species have been explored as catalysts for this process, including Cu,[7] Ru,[8] Rh,[5] Pd,[9] Ir,[10] Fe[11] and so on.[10d,e,12] However, most of these catalytic systems suffered from following limitations such as stoichiometric amounts of base or additive, sensitive catalysts and the substrates scope. On the other hand, benzyl alcohols were rarely used as N-alkylation reagent through $S_N$-type N-alkylation, because aromatic amines were prone to undergoing Friedel–Crafts-type alkylation with alcohols under these conditions.[13] Therefore, how to develop a single and air-tolerant Lewis acid catalyst for the mono- or bis-benzylation of amines through direct C–O activation of benzyl alcohol with high selectivity was challenging and desirable.

Water is an ideal solvent for organic reactions due to its many advantages such as nontoxic, nonflammable, abundantly available and inexpensive. Many organic transformations have been successfully developed in water in terms of 'Green Chemistry'.[14] Besides, indium(III) salt possesses the appealing property of

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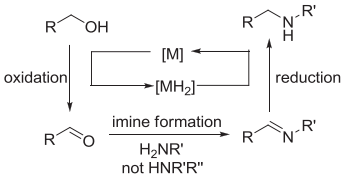
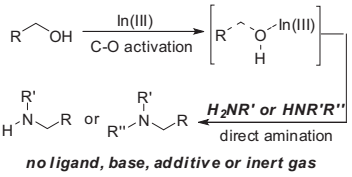



**Scheme 1.** Proposed mechanism for dehydrogenative activation of alcohols and subsequent amination.

enhancing the formation of less stabilized carbocation and its activity would not decrease even when it is dispersed in water.[15] Herein, we reported an indium(III)-catalyzed[16] formation of mono- or bis-alkylated amine through direct C–O bond activation of benzyl alcohol in water without any ligand, additive or inert gas (Scheme 2).

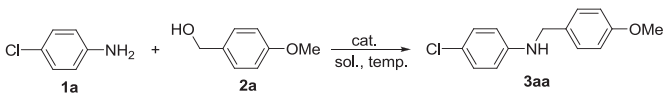



**Scheme 2.** In(OTf)$_3$-catalyzed N-benzylation of amines utilizing benzyl alcohols.

## 2. Results and discussion

We initiated this study by the model reactions of 4-chloroaniline (**1a**) with anisyl alcohol (**2a**) in water under different conditions. As expected, the model reaction did not occur in the absence of catalyst (Table 1, entry 1). Copper and iron species were examined without base and ligand, only very low yields were obtained (Table 1, entries 2–4). To our surprise, In(OTf)$_3$ showed good catalytic activity without the participation of base or additive, affording **3aa** in 68% yield (Table 1, entry 5). Next, various solvents, such as toluene, DMF, and MeOH were investigated. However, no better result was obtained. Water gave the best result while the messy result was observed when the model reaction was carried out in neat conditions. We also examined the effect of base. It was found that base totally inhibited the reaction in our catalytic system (Table 1, entry 9). Moreover, the yield of **3aa** decreased when other indium species, such as $InCl_3$, In(DS)$_3$ and indium powder, were introduced (Table 1, entries 10–12). Both decreasing the loading of catalyst and lowering the temperature led to decrease of the reaction yields (Table 1, entries 13–14). Furthermore, we observed that only 47% yield of **3aa** was isolated when 1 equiv of anisyl alcohol was employed.

**Table 1**
Optimization of reaction conditions[a]

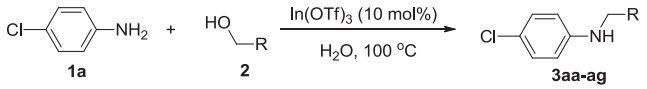



| Entry | Catalyst (mol %) | Solvent | Temp (°C) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | — | $H_2O$ | 100 | — |
| 2 | $Cu(OAc)_2$ (10)[c] | $H_2O$ | 100 | 7 |
| 3 | $CuCl_2 \cdot 2H_2O$ (10) | $H_2O$ | 100 | 25 |
| 4 | Nano-$Fe_3O_4$ (10)[d] | $H_2O$ | 100 | — |
| 5 | In(OTf)$_3$ (10) | $H_2O$ | 100 | 68 |
| 6 | In(OTf)$_3$ (10) | Toluene | 100 | 58 |
| 7 | In(OTf)$_3$(10) | DMF | 100 | 9 |
| 8 | In(OTf)$_3$(10) | — | 100 | Messy |
| 9 | In(OTf)$_3$ (10)/$NaHCO_3$ (50) | $H_2O$ | 100 | — |
| 10 | $InCl_3$ (10) | $H_2O$ | 100 | 45 |
| 11 | In(DS)$_3$ | $H_2O$ | 100 | |
| 12 | In | $H_2O$ | 100 | |
| 13 | In(OTf)$_3$ (5) | $H_2O$ | 100 | 66 |
| 14 | In(OTf)$_3$ (10) | $H_2O$ | 80 | 19 |
| 15 | In(OTf)$_3$ (10)[e] | $H_2O$ | 100 | 47 |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), In(OTf)$_3$ (0.1 mmol), $H_2O$ (5.0 mL).
[b] Isolated yield.
[c] Ref. 7.
[d] Ref. 11b.
[e] **2a** (1.0 mmol) was used.

With the optimized reaction conditions in hand, we further investigated the substrate scope of the reaction utilizing various benzyl alcohols and amines. As shown in Table 2, the benzylations of amines in water catalyzed by In(OTf)$_3$ could be accomplished with relatively good generality. The benzyl alcohols with electron-donating groups (**2a**–**d**) reacted smoothly with **1a**, affording the corresponding products in moderate to good yields (Table 2, entries 1–4). Unfortunately, benzyl alcohol (**2e**) was totally inert under the identical conditions (Table 2, entry 5). Benzo[*d*][1,3]dioxol-5-ylmethanol (**2f**) and ferrocenylmethanol (**2g**) also performed well, giving the desired products in 65% and 78% yields, respectively (Table 2, entries 6 and 7).

**Table 2**
The benzylations of **1a** with **2** catalyzed by In(OTf)$_3$ in water[a]

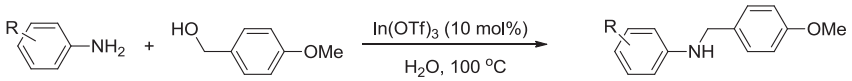



| Entry | 2 | Products | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | **2a** | **3aa** | 6 | 68 |
| 2 | **2b** | **3ab** | 7 | 65 |
| 3 | **2c** | **3ac** | 5 | 63 |
| 4 | **2d** | **3ad** | 6 | 76 |
| 5 | **2e** | **3ae** | 24 | 0 |
| 6 | **2f** | **3af** | 12 | 65 |
| 7 | **2g** | **3ag** | 7 | 78 |

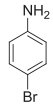
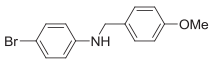
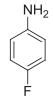
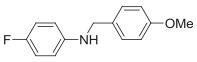
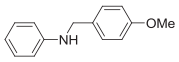
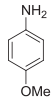
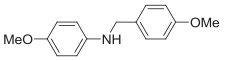
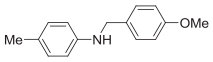
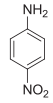
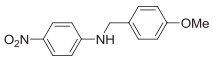
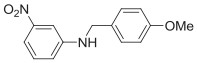
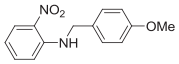
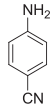
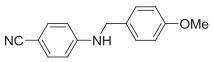
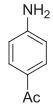
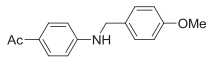
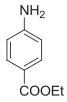
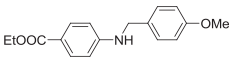
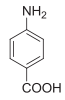
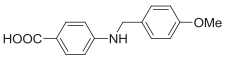
[a] Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), In(OTf)$_3$ (0.1 mmol), $H_2O$ (5.0 mL) at 100 °C.
[b] Isolated yield.

Next, we investigated the substrate scope of amines. The results were summarized in Table 3. Amines with weak electron-withdrawing groups, such as 4-bromoaniline (**1b**) and 4-fluoroaniline (**1c**) were applied to the reactions, which could react smoothly with (4-methoxyphenyl)methanol (**2a**) under the optimal conditions to furnish nucleophilic-substituted products

**Table 3**
The benzylations of **1** with **2a** catalyzed by $In(OTf)_3$ in water[a]




**1** **2a** **3ba-ma**

| Entry | 1 | | Products | | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 |  | **1b** |  | **3ba** | 5 | 71 |
| 2 |  | **1c** |  | **3ca** | 6 | 42 |
| 3 |  | **1d** |  | **3da** | 24 | 42 |
| 4 |  | **1e** |  | **3ea** | 24 | 37 |
| 5 |  | **1f** |  | **3fa** | 24 | 46 |
| 6 |  | **1g** |  | **3ga** | 6 | 87 |
| 7 |  | **1h** |  | **3ha** | 4 | 99 |
| 8 |  | **1i** |  | **3ia** | 5 | 70 |
| 9 |  | **1j** |  | **3ja** | 5 | 96 |
| 10 |  | **1k** |  | **3ka** | 8 | 80 |
| 11 |  | **1l** |  | **3la** | 5 | 97 |
| 12 |  | **1m** |  | **3ma** | 5 | 75 |

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), $In(OTf)_3$ (0.1 mmol), $H_2O$ (5.0 mL) at 100 °C.
[b] Isolated yield.

(**3ba** and **3ca**) in 71% and 42% yields (Table 3, entries 1 and 2). The amines bearing electron-donating groups (**1d**–**f**) could also react with **2a** as well, generating the desired products within 24 h in little lower yields (Table 3, entries 3–5). On the other hand, the presence of a strong electron-withdrawing group such as nitro at the *meta* or *ortho* position of anilines (**1g**–**h**), reacted smoothly with (4-methoxyphenyl)methanol (**2a**) under the standard conditions to afford the corresponding products in 87–99% yields (Table 3, entries 6 and 7). When more bulkier substrate 2-nitro aniline was subjected to the reaction, the yield was decreased to 70% (Table 3, entry 8). Other anilines (**1g**–**l**) bearing electron-donating groups were also investigated, all of them worked well under the optimized conditions (Table 3, entries 9–11). In the case of 4-aminobenzoic acid possessing a free carboxylic acid functionality, it also served as a good substrate under the conditions to give the desired product in 75% yield (Table 3, entry 12).

Then, we examined other aromatic amines analogue under the optimized conditions. As shown in Fig. 2, both benzo[*d*]thiazol-2-amine and 1*H*-benzo[*d*][1,2,3]triazole served as good candidates as well, leading to the N-benzylation product **3na** and **3oa** in 65% and 60% yields, respectively. It was notable that N-dialkylation products (**4aa**, **4ab** and **4ac**) were obtained in moderate to good yields when the amount of the benzyl alcohols was increased from 1.2 to 3.2 equiv.

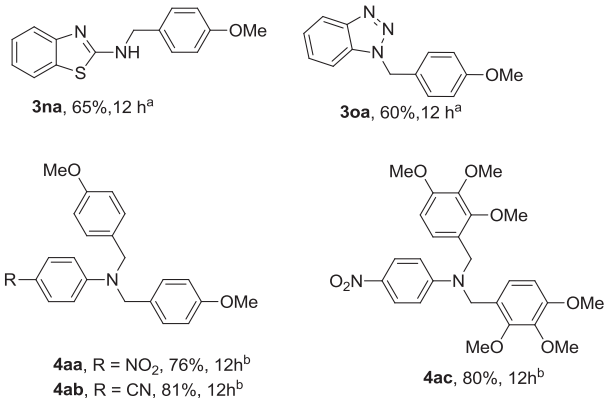
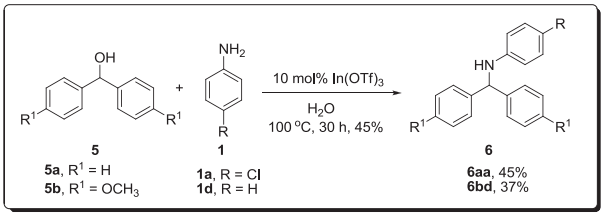


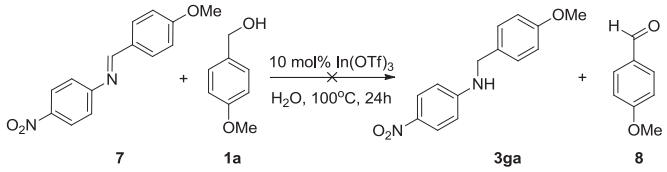

**Fig. 2.** Benzylation of amines with benzyl alcohols. [a]Reaction conditions: amine (1.0 mmol), benzyl alcohol (1.2 mmol), $In(OTf)_3$ (0.1 mmol), $H_2O$ (5.0 mL) at 100 °C. [b]3.2 equiv of alcohol was used.

When diphenylmethanol (**5**) was subjected to the reaction with 4-chloroaniline (**1**) under the identical conditions, it was found that the direct nucleophilic substituted product **6** could also be obtained in low yield (Scheme 3).

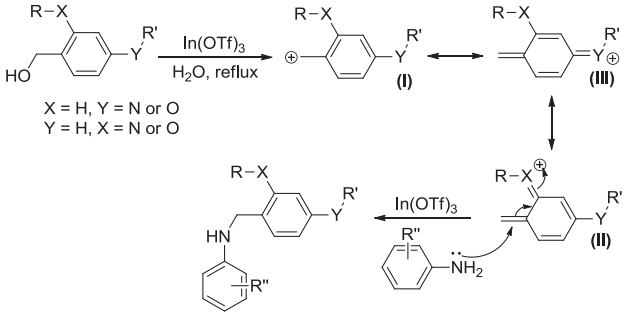



**Scheme 3.**

In order to better understand the mechanism of this reaction, the mixture of (*E*)-*N*-(4-methoxybenzylidene)-4-nitroaniline, which was easily isolated as an intermediate in 'hydrogen autotransfer processes', and **1a** was treated under our optimal conditions. As expected, no *N*-(4-methoxybenzyl)-4-nitroaniline or 4-methoxybenzaldehyde was observed (Scheme 4). This results indicated that the 'hydrogen-borrowing methodology' or 'hydrogen autotransfer processes' was not involved in catalytic system. As shown in Scheme 5, we proposed a plausible mechanism for this reaction. First, the C–O bond was activated by coordination with In(III) and water. Subsequently, C–O bond was cleaved to form a benzyl type carbonium, which was prone to be stabilized by the electron-donating groups in aromatic ring. Finally, the amine attacked the carbonium to give the final product.




**Scheme 4.**




**Scheme 5.** Proposed mechanism.

## 3. Conclusion

We have developed an $In(OTf)_3$-catalyzed direct benzylation of amines ultilizing benzyl alcohols in water. Various amines, benzo[*d*]thiazol-2-amine and 1*H*-benzo[*d*][1,2,3]triazole could react well with benzyl alcohols without any base or additive, affording the corresponding products in moderate to good yields. Mono- or bis-alkylation of amine could be achieved with high selectivity by using various equivalent of benzyl alcohols.

## 4. Experimental section

### 4.1. General

Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Varian INOVA 300 or 400 MHz ($^1H$ NMR) and 75 or 100 MHz ($^{13}C$ NMR) spectrometer using $CDCl_3$ as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with ESI source.

### 4.2. General procedure for the alkylation of indoles, anilines and thiols with enamide

Amine (1.0 mmol), $In(OTf)_3$ (0.1 mmol) and anisyl alcohol (1.2 mmol) were added into a flask. Then the mixture was vigorously stirred at reflux, until amine was completely consumed as indicated by TLC analysis or 24 h. After the completion of reaction, $CH_2Cl_2$ (15 mL×2) was used to extract the product, the organic layer was dried with anhydrous $Na_2SO_4$. Then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other N-benzylation amines.

*4.2.1. N-(4-Methoxybenzyl)-4-chlorobenzenamine (**3aa**).* Yield (168 mg, 68%). $R_f$=0.62 (petroleum ether/ethyl acetate=4:1). Mp: 84–85 °C; IR (KBr): $\nu$=3407, 2918, 1595, 1490, 1235, 815 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.27 (d, *J*=7.8 Hz, 2H), 7.11 (d, *J*=8.6 Hz, 2H), 6.88 (d, *J*=8.5 Hz, 2H), 6.56 (d, *J*=8.7 Hz, 2H), 4.22 (s, 2H), 3.80 ppm (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$=159.2, 146.9, 131.1, 129.2, 128.9, 122.3, 114.3, 114.1, 55.5, 48.1 ppm. HRMS (*m*/*z*): $[M]^+$, calcd for $C_{14}H_{14}ClNO$: 247.0764, found: 247.0763.

*4.2.2. 4-Chloro-N-(3,4-dimethoxybenzyl)aniline (**3ab**).* Yield (180 mg, 65%). $R_f$=0.61 (petroleum ether/ethyl acetate=4:1). Mp: 128–130 °C; IR (KBr): $\nu$=3370, 2937, 2844, 1594, 1504, 1243, 1022, 813 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=3.87 (s, 6H), 4.22 (s, 2H), 6.56 (d, *J*=4.9 Hz, 2H), 6.84–6.88 (m, 3H), 7.11 ppm (d, *J*=5.1 Hz,

2H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$=148.8, 147.7, 147.6, 132.1, 128.5, 119.3, 119.0, 113.8, 111.7, 111.2, 55.5, 55.4, 46.3 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{15}H_{16}ClNO_2$: 277.0870, found: 277.0868.

*4.2.3. N-(2,3,4-Trimethoxybenzyl)-4-chlorobenzenamine (**3ac**).* Yield (193 mg, 63%). $R_f$=0.63 (petroleum ether/ethyl acetate=4:1). Mp: 110–111 °C; IR (KBr): $\nu$=3366, 2936, 1593, 1489, 1090, 809 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=3.84 (s, 3H), 3.88 (s, 3H), 3.92 (s, 3H), 4.03 (br s, H, NH), 4.22 (s, 2H), 6.56 (d, $J$=8.5 Hz, 2H), 6.61 (d, $J$=8.4 Hz, 1H), 6.69 (d, $J$=8.3 Hz, 1H), 7.10 ppm (d, $J$=7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=153.4, 52.0, 146.9, 142.4, 129.2, 124.6, 123.5, 122.1, 114.3, 107.2, 61.3, 61.0, 56.1, 43.6 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{16}H_{18}ClNO_3$: 307.0975, found: 307.0977.

*4.2.4. 4-Chloro-N-(4-morpholinobenzyl)aniline (**3ad**).* Yield (230 mg, 76%). $R_f$=0.64 (petroleum ether/ethyl acetate=4:1). Mp: 186–187 °C; IR (KBr): $\nu$=3357, 2838, 1598, 1504, 1225, 1107, 809 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=3.16 (t, $J$=4.5 Hz, 4H), 3.87 (t, $J$=4.5 Hz, 4H), 4.21 (s, 2H), 6.55 (d, $J$=8.7 Hz, 2H), 6.92 (d, $J$=8.7 Hz, 2H), 7.11 (d, $J$=8.7 Hz, 2H), 7.26 ppm (d, $J$=8.7 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=150.8, 146.9, 130.4, 129.2, 128.7, 122.2, 116.1, 114.1, 67.1, 49.6, 48.0 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{17}H_{19}ClN_2O$: 302.1186, found: 302.1184.

*4.2.5. N-(Benzo[d][1,3]dioxol-5-ylmethyl)-4-chloroaniline (**3af**).* Yield (170 mg, 65%). $R_f$=0.62 (petroleum ether/ethyl acetate=4:1). Mp: 100–102 °C; IR (KBr): $\nu$=3368, 2874, 1597, 1490, 1243, 1103, 808 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=4.20 (s, 2H), 5.95 (s, 2H), 6.57 (d, $J$=7.0 Hz, 2H), 6.79 (m, 3H), 7.11 ppm (d, $J$=6.8 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=148.1, 147.0, 146.6, 132.9, 129.2, 122.4, 120.7, 114.2, 108.5, 108.1, 101.2, 48.4 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{12}ClNO_2$: 261.0557, found: 261.0558.

*4.2.6. N-(1-Ferrocenylmethyl)-4-chloroaniline (**3ag**).* Yield (252 mg, 78%). $R_f$=0.60 (petroleum ether/ethyl acetate=4:1). Mp: 116–117 °C; IR (KBr): 3421, 3086, 2901, 2856, 1595, 1499, 1463, 1400, 1320, 1247, 1102, 815 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=3.92 (br s, 3H, $CH_2$, NH), 4.15–4.23 (m, 9H), 6.57 (d, $J$=7.5 Hz, 2H), 7.13 ppm (d, $J$=7.2 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=147.2, 129.5, 129.2, 122.3, 114.3, 86.4, 69.1, 69.1, 68.9, 68.6, 68.4, 68.2, 43.9 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{17}H_{16}ClFeN$: 325.0321, found: 325.0322.

*4.2.7. N-(4-Methoxybenzyl)-4-bromobenzenamine (**3ba**).* Yield (207 mg, 71%). $R_f$=0.63 (petroleum ether/ethyl acetate=4:1). Mp: 86–88 °C; IR (KBr): $\nu$=3400, 2905, 1530, 1495, 1302, 1022, 811 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=7.23 (d, $J$=7.4 Hz, 2H), 7.14 (d, $J$=8.7 Hz, 2H), 6.86 (d, $J$=8.4 Hz, 2H), 6.50 (d, $J$=8.6 Hz, 2H), 4.14 (s, 2H), 3.70 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=159.2, 146.9, 132.1, 130.8, 129.0, 114.9, 114.3, 109.6, 55.5, 48.2 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{14}BrNO$: 291.0259, found: 291.0258.

*4.2.8. N-(4-Methoxybenzyl)-4-fluorobenzenamine (**3ca**).* Yield (97 mg, 42%). $R_f$=0.61 (petroleum ether/ethyl acetate=4:1). Mp: 70–71 °C; IR (KBr): $\nu$=3407, 2921, 1598, 1508, 1237, 1107, 820 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.28 (d, $J$=8.4 Hz, 2H), 6.88 (dt, $J$=8.5, 4.2 Hz, 4H), 6.62–6.52 (m, 2H, ArH), 4.21 (s, 2H), 3.80 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=159.1, 157.6, 154.5, 144.6, 131.3, 129.0, 116.0, 115.7, 114.2, 113.9, 113.8, 77.7, 77.2, 76.8, 55.5, 48.6 ppm. HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{14}FNO$: 231.1059, found: 231.1052.

*4.2.9. (4-Methoxy-benzyl)-phenyl-amine (**3da**).* Yield (89 mg, 42%). $R_f$=0.59 (petroleum ether/ethyl acetate=4:1). Mp: 75–77 °C; IR (KBr): $\nu$=3410, 2934, 1598, 1491, 1303, 1244, 818 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28 (d, $J$=8.5 Hz, 2H), 7.17 (t, $J$=7.9 Hz, 2H), 6.86 (d, $J$=8.6 Hz, 2H), 6.73 (t, $J$=8.2 Hz, 1H), 6.66 (d, $J$=8.0 Hz, 2H), 4.24 (s, 2H), 3.79 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$=151.8, 148.4, 131.6, 129.5, 129.0, 117.7, 114.2, 113.1, 55.5, 48.0 ppm. HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{15}NO$: 213.1154, found: 213.1150.

*4.2.10. N-(4-Methoxybenzyl)-4-methoxybenzenamine (**3ea**).* Yield (90 mg, 37%). $R_f$=0.62 (petroleum ether/ethyl acetate=4:1). Mp: 96–97 °C; IR (KBr): $\nu$=3379, 2942, 2834, 1603, 1511, 1245, 1028, 818 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.29 (d, $J$=8.3 Hz, 2H), 6.87 (d, $J$=8.4 Hz, 2H), 6.78 (d, $J$=8.7 Hz, 2H), 6.60 (d, $J$=8.7 Hz, 2H), 4.20 (s, 2H), 3.80 (s, 3H), 3.74 ppm (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$=159.0, 152.4, 142.6, 131.8, 129.0, 115.1, 114.4, 114.2, 77.2, 56.0, 55.5, 49.0 ppm. HRMS ($m/z$): [M]$^+$, calcd for $C_{15}H_{17}NO_2$: 243.1259, found: 243.1259.

*4.2.11. (4-Methoxy-benzyl)-p-tolyl-amine (**3fa**).* Yield (104 mg, 46%). $R_f$=0.63 (petroleum ether/ethyl acetate=4:1). Mp: 82–83 °C; IR (KBr): $\nu$=3392, 2936, 1597, 1493, 820 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.28 (d, $J$=8.4 Hz, 2H), 6.98 (d, $J$=8.1 Hz, 2H), 6.87 (d, $J$=8.4 Hz, 2H), 6.57 (d, $J$=8.2 Hz, 2H), 4.23 (s, 2H), 3.81 (s, 3H), 2.23 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=159.0, 145.9, 131.6, 129.9, 129.1, 127.2, 114.2, 113.5, 55.5, 48.5, 20.6 ppm; HRMS ($m/z$): [M]$^+$, calcd for $C_{15}H_{17}NO$: 227.1310, found: 227.1311.

*4.2.12. N-(4-Methoxybenzyl)-4-nitrobenzenamine (**3ga**).* Yield (87%). $R_f$=0.58 (petroleum ether/ethyl acetate=4:1). Mp: 146–147 °C; IR (KBr): $\nu$=3352, 1598, 1512, 1299, 1070, 816 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=7.97 (d, $J$=9.1 Hz, 2H), 7.77 (t, $J$=5.9 Hz, 1H), 7.27 (d, $J$=7.5 Hz, 2H), 6.91 (d, $J$=7.1 Hz, 2H), 6.67 (d, $J$=9.0 Hz, 2H), 4.33 (s, 2H), 3.73 ppm (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$=158.4, 154.4, 135.8, 130.3, 128.6, 126.2, 113.9, 111.2, 55.1, 45.3, 45.2 ppm. HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{14}N_2O_3$: 258.1004, found: 258.1008.

*4.2.13. N-(4-Methoxybenzyl)-3-nitrobenzenamine (**3ha**).* Yield (255 mg, 99%). $R_f$=0.65 (petroleum ether/ethyl acetate=4:1). Mp: 97–98 °C; IR (KBr): $\nu$=3404, 2915, 1620, 1517, 1342, 808 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=7.25–7.32 (m, 5H), 7.03–6.80 (m, 4H), 4.24 (d, $J$=4.1 Hz, 2H), 3.70 ppm (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$=158.3, 149.7, 148.8, 129.9, 128.5, 118.5, 113.8, 109.9, 105.6, 55.0, 45.6 ppm. HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{14}N_2O_3$: 258.1004, found: 258.1003.

*4.2.14. N-(4-Methoxybenzyl)-2-nitrobenzenamine (**3ia**).* Yield (181 mg, 70%). $R_f$=0.61 (petroleum ether/ethyl acetate=4:1). Mp: 97–98 °C; IR (KBr): $\nu$=3382, 2941, 1604, 1498, 1350, 1019, 827 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=8.56 (t, $J$=4.9 Hz, 1H, NH), 8.04 (d, $J$=8.6 Hz, 1H), 7.42 (t, $J$=7.7 Hz, 1H), 7.28 (d, $J$=8.1 Hz, 2H), 6.89 (t, $J$=9.7 Hz, 3H), 6.63 (t, $J$=7.7 Hz, 1H), 4.51 (d, $J$=5.5 Hz, 2H), 3.69 ppm (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$=158.4, 144.9, 136.4, 130.2, 126.2, 115.4, 115.0, 114.0, 113.6, 55.1, 55.0, 45.2 ppm. $^1$HRMS ($m/z$): [M]$^+$, calcd for $C_{14}H_{14}N_2O_3$: 258.1004, found: 258.1005.

*4.2.15. 4-(4-Methoxybenzylamino)benzonitrile (**3ja**).* Yield (228 mg, 96%). $R_f$=0.62 (petroleum ether/ethyl acetate=4:1). Mp: 109–111 °C; IR (KBr): $\nu$=3376, 2851, 2202, 1602, 1513, 820 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=7.42 (d, $J$=7.0 Hz, 2H), 7.26–7.21 (m, 3H), 6.89 (d, $J$=6.7 Hz, 2H), 6.64 (d, $J$=7.0 Hz, 2H), 4.25 (d, $J$=5.0 Hz, 2H), 3.72 ppm (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$=158.3, 152.1, 133.3, 130.7, 128.5, 120.6, 113.8, 112.1, 95.8, 55.1, 55.0, 45.2. HRMS ($m/z$): [M]$^+$, calcd for $C_{15}H_{14}N_2O$: 238.1106, found: 238.1106.

*4.2.16. 1-(4-(4-Methoxybenzylamino)phenyl)ethanone (**3ka**).* Yield (204 mg, 80%). $R_f$=0.65 (petroleum ether/ethyl acetate=4:1). Mp: 116–117 °C; IR (KBr): $\nu$=3341, 2855, 1635, 1584, 1255, 817 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$=7.68 (d, $J$=8.6 Hz, 2H), 7.26 (d, $J$=8.0 Hz, 2H), 6.89 (d, $J$=8.4 Hz, 2H), 6.60 (d, $J$=8.6 Hz, 2H), 4.27 (s, 2H), 3.72 (s, 3H), 2.37 ppm (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$=195.0, 158.2, 152.7, 131.1, 130.4, 128.4, 125.0, 113.8, 111.1, 55.0,

45.2, 25.9 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{16}H_{17}NO_2$: 255.1259, found: 255.1266.

*4.2.17. Ethyl 4-(4-methoxybenzylamino)benzoate (**3la**).* Yield (276 mg, 97%). $R_f$=0.58 (petroleum ether/ethyl acetate=4:1). Mp: 127–128 °C; IR (KBr): $\nu$=3357, 2948, 1679, 1596, 1255, 1014, 825 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$=7.65 (d, $J$=8.7 Hz, 2H), 7.26 (d, $J$=8.5 Hz, 2H), 7.02 (t, $J$=5.6 Hz, 1H), 6.89 (d, $J$=8.6 Hz, 2H), 6.60 (d, $J$=8.7 Hz, 2H), 4.25 (d, $J$=5.8 Hz, 2H), 4.19 (q, $J$=7.1 Hz, 2H), 3.72 (s, 3H), 1.25 ppm (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, DMSO): $\delta$=165.8, 158.2, 152.6, 131.1, 130.9, 128.5, 116.2, 113.8, 111.2, 59.5, 55.0, 45.3, 14.4 ppm; HRMS ($m/z$): $[M]^+$, calcd for $C_{17}H_{19}NO_3$: 285.1365, found: 285.1367.

*4.2.18. 4-(4-Methoxybenzylamino)benzoic acid (**3ma**).* Yield (193 mg, 75%). $R_f$=0.59 (petroleum ether/ethyl acetate=4: 1). Mp: 209–211 °C; IR (KBr): $\nu$=3364, 2846, 1667, 1598, 1511, 1293, 821 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$=11.97 (s, 1H), 7.61 (d, $J$=8.3 Hz, 2H), 7.24 (d, $J$=8.2 Hz, 2H), 6.95 (t, $J$=4.9 Hz, 1H), 6.87 (d, $J$=8.1 Hz, 2H), 6.56 (d, $J$=8.4, 2H), 4.22 (d, 2H), 3.70 ppm (s, 3H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$=167.5, 158.2, 152.4, 131.2, 131.1, 128.5, 117.0, 113.8, 111.2, 55.1, 45.4 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{15}H_{15}NO_3$: 257.1052, found: 257.1056.

*4.2.19. N-(4-Methoxybenzyl)benzo[d]thiazol-2-amine (**3na**).* Yield (176 mg, 65%). $R_f$=0.61 (petroleum ether/ethyl acetate=4:1). Mp: 172–173 °C; IR (KBr): $\nu$=3205, 2925, 2835, 1553, 1445, 1245, 830 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$=8.40 (s, 1H, NH), 7.63 (d, $J$=7.6 Hz, 1H), 7.35 (d, $J$=7.9 Hz, 1H), 7.28 (d, $J$=7.9 Hz, 1H), 7.18 (d, $J$=7.5 Hz, 2H), 6.98 (t, $J$=7.0 Hz, 1H), 6.88 (d, $J$=8.2 Hz, 2H), 4.47 (s, 2H), 3.70 ppm (s, 3H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$=166.0, 158.4, 152.4, 130.8, 130.4, 128.8, 125.5, 120.9, 118.1, 113.8, 55.1, 46.6 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{15}H_{14}N_2OS$: 270.0827, found: 270.0828.

*4.2.20. 1-(4-methoxybenzyl)-1H-benzo[d][1,2,3]triazole (**3oa**).* Yield (143 mg, 60%). $R_f$=0.59 (petroleum ether/ethyl acetate=4:1). Mp: 85–86 °C; IR (KBr): $\nu$=2944, 1600, 1506, 1240, 1018, 830 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=3.77 (s, 3H), 5.78 (s, 2H), 6.86 (d, $J$=8.5 Hz, 2H), 7.25 (d, $J$=9.9 Hz, 2H), 7.31–7.37 (m, 3H), 8.06 ppm (d, $J$=7.9 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$=159.7, 146.3, 132.7, 129.1, 127.3, 126.8, 123.9, 119.9, 114.4, 109.9, 55.3, 51.8 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{14}H_{13}N_3O$: 239.1059, found: 239.1054.

*4.2.21. N,N-Bis(4-methoxybenzyl)-4-nitrobenzenamine (**4aa**).* Yield (287 mg, 76%). $R_f$=0.58 (petroleum ether/ethyl acetate=4: 1). Mp: 94–95 °C; IR (KBr): $\nu$=2932, 2839, 1596, 1502, 1317, 1237, 818 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$=7.97 (d, $J$=9.4 Hz, 2H), 7.15 (d, $J$=8.5 Hz, 4H), 6.89 (d, $J$=8.6 Hz, 4H), 6.79 (d, $J$=9.5 Hz, 2H), 4.74 (s, 4H), 3.70 ppm (s, 6H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$=158.4, 153.4, 136.1, 128.9, 127.8, 125.8, 114.1, 111.5, 55.1, 55.0, 53.4 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{22}H_{22}N_2O_4$: 378.1580, found: 378.1577.

*4.2.22. 4-[Bis-(4-methoxy-benzyl)-amino]-benzonitrile (**4ab**).* Yield (290 mg, 81%). $R_f$=0.63 (petroleum ether/ethyl acetate=4:1). Mp: 87–88 °C; IR (KBr): $\nu$=2933, 2209, 1601, 1512, 1237, 1029, 811 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$=7.45 (d, $J$=8.9 Hz, 2H), 7.13 (d, $J$=8.5 Hz, 4H), 6.87 (d, $J$=8.6 Hz, 4H), 6.73 (d, $J$=9.0 Hz, 2H), 4.67 ppm (s, 4H), 3.70 (s, 6H); $^{13}C$ NMR (75 MHz, DMSO-$d_6$): $\delta$=158.3, 151.2, 133.2, 129.4, 127.8, 120.3, 114.1, 112.4, 96.4, 55.1, 53.2 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{23}H_{22}N_2O_2$: 358.1681, found: 358.1682.

*4.2.23. N,N-Bis(2,3,4-trimethoxybenzyl)-4-nitrobenzenamine (**4ac**).* Yield (398 mg, 80%). $R_f$=0.59 (petroleum ether/ethyl acetate=4:1). Mp: 79–80 °C; IR (KBr): $\nu$=2930, 2211, 1597, 1497, 1271, 1089, 808 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=8.06 (d, $J$=9.4 Hz, 2H), 6.64–6.72 (m, 4H), 6.59 (d, $J$=8.6 Hz, 2H), 4.65 (s, 4H), 3.91 (s, 6H), 3.88 (s, 6H), 3.84 ppm (s, 6H, $OCH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=153.9, 153.5, 151.6, 142.4, 137.5, 126.3, 121.6, 121.4, 111.1, 107.2, 61.0, 60.9, 56.2, 49.8 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{26}H_{30}N_2O_8$: 498.2002, found: 498.2010.

*4.2.24. N-Benzhydryl-4-chlorobenzenamine (**6aa**).* Yield (132 mg, 45%): $R_f$=0.62 (petroleum ether/ethyl acetate=4:1). Mp: 90–91 °C; IR (KBr): $\nu$=3409, 3068, 2844, 1591, 1484, 1305, 1085, 812 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.33–7.27 (m, 10H), 7.04 (d, $J$=8.8 Hz, 2H), 6.45 (d, $J$=8.7 Hz, 2H), 5.45 (s, 1H), 4.24 ppm (s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=146.0, 142.6, 129.1, 129.0, 127.7, 127.6, 122.5, 114.8, 77.7, 77.2, 76.8, 63.3 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{19}H_{16}ClN$: 293.0971, found: 293.0969.

*4.2.25. N-(Bis(4-methoxyphenyl)methyl)aniline (**6bd**).* Yield (118 mg, 37%): $R_f$=0.65 (petroleum ether/ethyl acetate=4:1). liquid, IR (KBr): $\nu$=3409, 3068, 2844, 1591, 1484, 1305, 1085, 812 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=7.24 (d, $J$=8.6 Hz, 4H), 7.10 (t, $J$=7.6 Hz, 2H), 6.84 (d, $J$=8.5 Hz, 4H), 6.67 (t, $J$=7.0 Hz, 1H), 6.53 (d, $J$=8.2 Hz, 2H), 5.40 (s, 1H), 3.76 (s, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=158.4, 147.4, 128.9, 128.5, 117.4, 114.1, 113.4, 61.9, 55.2 ppm. HRMS ($m/z$): $[M]^+$, calcd for $C_{21}H_{21}NO_2$: 319.1572, found: 319.1575.

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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.010.

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