# Reductive amination of acetals by anilines in the presence of triethylsilane and iodine

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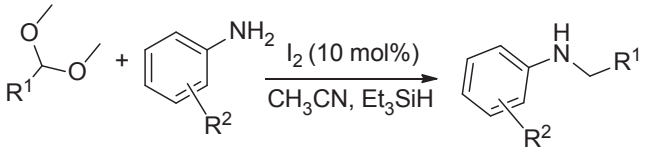
A mild and efficient method for *N*-alkylation of aromatic amines with various acetals such as aryl, alkyl, cyclic and acyclic acetals was developed. A number of aromatic amines bearing electron-donating or electron-withdrawing substituents were directly alkylated by acetals with excellent yields. The method uses a catalytic amount of $I_2$ and triethylsilane as the hydride source without a metal present. Monoalkylation with excellent chemoselectivity was observed.

**Keywords:** acetals, alkylation of amines, secondary amine, triethylsilane

Amines are a very important class of compounds in nature and the chemical industry.[1] They are used in many applications, including numerous active pharmaceuticals,[2] herbicides, agrochemicals,[3] conducting polymers[4] and organic light-emitting diodes.[5] Thus, various procedures for the formation of C–N bonds[6] have been developed. These procedures include Hofmann alkylation,[7] Buchwald–Hartwig[8] and Ullmann reactions,[9] hydroamination of olefins and alkynes,[10] reduction of nitriles,[11] imines[12] and nitro compounds,[13] alkylation of amines using alcohols[14] and reductive amination of carbonyl compounds.[15] However, most of these approaches require noble metal catalysts, organic ligand additives[16] and more than one equivalent of base.[6,17] These additives and expensive metal catalysts render the process uneconomic and hazardous to the environment. Thus, other methods are of particularly great value and are therefore widely sought.

Recently, organosilanes have been successfully applied in reductive amination of carbonyl compounds.[15,18] These compounds offer several advantages over traditional reducing agents such as cyanoborohydride[19] and organotin,[20] which generate toxic byproducts.[21] Silanes are environmentally friendly agents used in many kinds of reactions.[22] Silane-based reduction systems usually contain metals, for example, $IrCl_3$–$Et_3SiH$,[23] TFA–PMHS,[24] $Ti(O^iPr)_4$–PMHS,[25] $AlCl_3$–PMHS,[26] $Re_2O_7$–$Et_3SiH$,[27] $PhSiH_3$–$ReIO_2(PPh_3)_2$,[28] $PhSiH_3$–$Bu_2SnCl_2$[20] and $PhSiH_3$–$MoO_2Cl_2$.[29] Yang and coworkers[30] demonstrated that $Zn(ClO_4)_2{\cdot}6H_2O$ is an essential activator in the reductive amination of carbonyl compounds catalysed by $InCl_3$–$Et_3SiH$.

In addition, one-pot reactions of organic synthesis have advantages over conventional stepwise or indirect reactions. Direct alkylation of amines with acetals is more advantageous over direct alkylation with aldehydes since it obviates the need for deprotecting steps; acetals are extensively used as protecting groups in synthetic chemistry.[31] We report here our findings that acetals can be used efficiently for direct *N*-alkylation of aromatic amines to form secondary arylamines in the presence of $I_2$–$Et_3SiH$ (Scheme 1).




**Scheme 1** Secondary amine formation by direct *N*-alkylation of aromatic amines with acetals catalysed by iodine.

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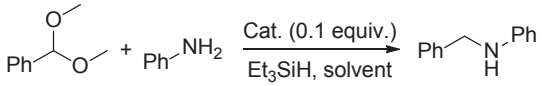
First, we attempted the use of $InCl_3$–$Et_3SiH$ in the *N*-alkylation of aniline with benzyl dimethyl acetal at room temperature. The desired benzyl aniline was obtained at 73% yield (Table 1, entry 1). To improve the efficiency, a series of Lewis acids were screened. The results of this screening indicate that $I_2$–$Et_3SiH$ afforded the highest yield, 93% (Table 1, entries 1–12). Metal-based catalysts such as $Hf(OTf)_4$, $ZrCl_4$, $HfCl_4$, $Bi(OTf)_3$, $BiCl_3$ and $SnCl_2$ led to slightly lower yields (Table 1, 84–87%, entries 2, 4, 6, 9 and 11). The $I_2$–$Et_3SiH$ combination has been used as catalyst for a wide range of reactions.[31,32] However, its application in reductive *N*-alkylation has not been reported.

The effect of solvents on the direct reductive *N*-alkylation reaction was also explored (Table 1, entries 13–21). MeCN was found to provide the best yield (Table 1, entry 8). The yield in ethanol was also satisfactory, higher than those in DMSO,

**Table 1** Optimising the reaction conditions for the one-pot *N*-alkylation of aniline with acetals[a]




| Entry | Catalyst | Solvent | Time/h | Yield/%[b] |
|---|---|---|---|---|
| 1 | $InCl_3$ | $CH_3CN$ | 16 | 73 |
| 2 | $Bi(OTf)_3$ | $CH_3CN$ | 7 | 85 |
| 3 | $FeCl_3$ | $CH_3CN$ | 6 | 71 |
| 4 | $BiCl_3$ | $CH_3CN$ | 16 | 87 |
| 5 | $AlCl_3$ | $CH_3CN$ | 12 | 78 |
| 6 | $SnCl_2$ | $CH_3CN$ | 8 | 85 |
| 7 | CuOTf | $CH_3CN$ | 8 | 63 |
| 8 | $I_2$ | $CH_3CN$ | 5 | 93 |
| 9 | $Hf(OTf)_4$ | $CH_3CN$ | 6 | 84 |
| 10 | $HfCl_4$ | $CH_3CN$ | 5 | 75 |
| 11 | $ZrCl_4$ | $CH_3CN$ | 5 | 87 |
| 12 | $Cu(OTf)_2$ | $CH_3CN$ | 8 | 69 |
| 13 | $I_2$ | DMSO | 7 | 39 |
| 14 | $I_2$ | $CH_3NO_2$ | 6 | 36 |
| 15 | $I_2$ | EtOH | 7 | 77 |
| 16 | $I_2$ | 1,4-Dioxane | 8 | <5 |
| 17 | $I_2$ | THF | 6 | 38 |
| 18 | $I_2$ | $CH_2Cl_2$ | 6 | 32 |
| 19 | $I_2$ | Toluene | 6 | 42 |
| 20 | $I_2$ | $CH_3CN/H_2O(1:1)$ | 6 | 48[c] |
| 21 | $I_2$ | – | 14 | 15 |

[a]Reaction conditions: benzaldehyde dimethyl acetal (1.2 mmol), aniline (1.0 mmol), triethylsilane (2.0 mmol), catalyst (0.10 mmol), solvent (4.0 mL), under argon, room temperature.

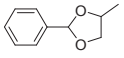
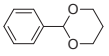
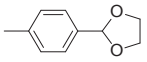
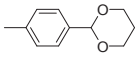
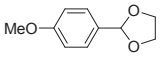
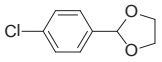
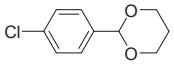
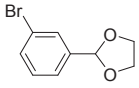
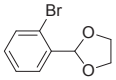
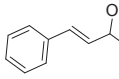
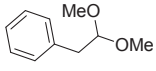
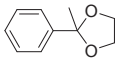
[b]Isolated yields after flash chromatography.

[c]Under reflux.

$MeNO_2$, THF, dioxane, $CH_2Cl_2$, toluene and MeCN–$H_2O$ (Table 1, entries 13–20, 5–48%). However, *N*-alkylation was not effective in the absence of solvent (Table 1, entry 21).

The optimised conditions were found to require 10 mol% $I_2$ and 200 mol% $Et_3SiH$ in MeCN; using these conditions, we then extended the range of acetals used for the direct *N*-alkylation. As shown in Table 2, aniline alkylation was efficiently performed at high yields (60–95%) by using various aryl acetals. We also found that aromatic acetals with electron-donating or weakly electron-withdrawing substituents such as MeO, F, Cl and Br (Table 2, entries 2–6) showed similar reactivity and gave secondary arylamine products at excellent yields (>88%). On the other hand, a strong electron-withdrawing group such as the *p*- or *m*-nitro function did not form products at room temperature; the expected secondary amines were produced in moderate yields by refluxing (Table 2, entries 7 and 8). Compared with the *p*-nitro aromatic acetal, the *m*-nitro aryl acetal afforded a higher yield (73% *vs* 60%) of the desired compound. Thus, electronic variations in aromatic acetals affect the alkylation activity.

**Table 2** Direct *N*-alkylation of aromatic amines with various alkyl and aromatic acetals[a]

| Entry | Acetal ($R^1$) | Time/h | Yield/%[b] |
|---|---|---|---|
| 1 | $C_6H_5$ | 5 | 93 |
| 2 | *p*-$CH_3OC_6H_4$ | 5 | 90 |
| 3 | *p*-$CH_3C_6H_4$ | 5 | 93 |
| 4 | *p*-$FC_6H_4$ | 5 | 90 |
| 5 | *p*-$ClC_6H_4$ | 5 | 88 |
| 6 | *p*-$BrC_6H_4$ | 5 | 97 |
| 7 | *p*-$NO_2C_6H_4$ | 5 | 60[c] |
| 8 | *m*-$NO_2C_6H_4$ | 5 | 73[c] |
| 9 |  | 11 | 74 |
| 10 |  | 5 | 68[c] |
| 11 |  | 5 | 68[c] |
| 12 |  | 5 | 65[c] |
| 13 |  | 5 | 66[c] |
| 14 |  | 5 | 75[c] |
| 15 |  | 5 | 67[c] |
| 16 |  | 5 | 89[c] |
| 17 |  | 5 | 79[c] |
| 18 |  | 5 | 75 |
| 19 |  | 5 | 85[c] |
| 20 |  | 5 | 67[c] |

[a]Reaction conditions: acetal (1.2 mmol), aniline (1.0 mmol), triethylsilane (2.0 mmol), $I_2$ (0.10 mmol), acetonitrile (4.0 mL), under argon, room temperature.
[b]Isolated yield.
[c]Under reflux.

The substrate versatility of this novel protocol was further demonstrated by cyclic acetals, which are more stable than their corresponding acyclic acetals.[31] In most cases, reductive *N*-alkylation of aniline with either five- or six-membered-ring acetals was not observed at room temperature. Under reflux conditions, the expected secondary amines were produced at moderate to high yields (Table 2, entries 9–17, 65–89% yields).

Apart from the aromatic acetals, we also investigated the reactivity of alkyl acetals. Alkylation of aniline with cinnamaldehyde dimethyl acetal was successfully accomplished (75% yield); the double bond was found to be inert under this reductive process (Table 2, entry 18). The reductive system $IrCl_3$–$Et_3SiH$,[23] Pd–$H_2$, or TFA–PMHS,[18] however, is not compatible with substrates containing double bonds in the reductive amination of aldehydes. Reductive alkylation with other alkyl acetals such as dimethyl acetals of phenylacetaldehyde was carried out smoothly under reflux to give the corresponding secondary amines in good yields (Table 2, entry 19). Alkylation with the ketal, 2-methyl-2-phenyl-1,3-dioxolane, was also successful (Table 2, entry 18). Most importantly, none of the cases considered in the present study gave overalkylation products; this observation suggests that the direct alkylation system is highly efficient at producing various secondary aromatic amines.

Furthermore, the reactions of various aromatic amines with benzaldehyde dimethyl acetal were then examined. The results reveal that all anilines with various substituents gave the expected products in good to excellent isolated yields (Table 3, 77–95%). A number of aromatic amines bearing either electron-donating or electron-withdrawing substituents could be smoothly alkylated to give the secondary amines in high yields (Table 3, entries 1–5, 88–95%). Remarkably, a strong withdrawing substituent such as nitro and acyl groups did not decrease the yield (Table 3, entries 6 and 7, >91% yield). In contrast, the catalytic system of $AlCl_3$–PMHS[26] and $NaBH(OAc)_3$[15] catalysed reductive amination of carbonyl compounds, leading to similar products at much lower yields. These results clearly indicate that the electronic effect of substituents in anilines has only a slight impact on the *N*-alkylation by acetals.

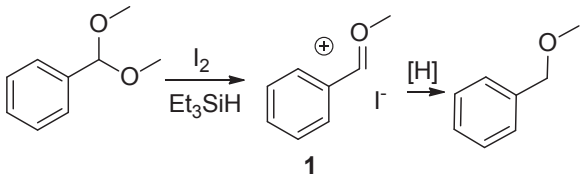
We believe the mechanism involves $I_2$ reacting with $Et_3SiH$ to form HI and $Et_3SiI$, followed by transformation of the acetal into the carboxonium ion **1**, which then reacts with the amine to give the imine. This is then reduced by triethylsilane forming the product. (Scheme 2).[33]

In conclusion, we have demonstrated a mild, metal-free approach for direct reductive *N*-alkylation of aromatic amines with acetals using the $I_2$–$Et_3SiH$ reductive system.

**Table 3** Direct *N*-alkylation of various aromatic amines with acetals[a]

| Entry | Acetal ($R^1$) | Amine ($R^2$) | Time/h | Yield/%[b] |
|---|---|---|---|---|
| 1 | $C_6H_5$ | *p*-$CH_3C_6H_4NH_2$ | 5 | 90 |
| 2 | $C_6H_5$ | *m*-$CH_3C_6H_4NH_2$ | 5 | 95 |
| 3 | $C_6H_5$ | *p*-$CH_3OC_6H_4NH_2$ | 5 | 88 |
| 4 | *p*-$BrC_6H_4$ | *p*-$CH_3OC_6H_4NH_2$ | 5 | 88[c] |
| 5 | $C_6H_5$ | *p*-$ClC_6H_4NH_2$ | 5 | 90 |
| 6 | $C_6H_5$ | *p*-$NO_2C_6H_4NH_2$ | 5 | 91 |
| 7 | $C_6H_5$ | *p*-$COOEtC_6H_4NH_2$ | 5 | 95 |

[a]Reaction conditions: benzaldehyde dimethyl acetal (1.2 mmol), amine (1.0 mmol), triethylsilane (2.0 mmol), $I_2$ (0.10 mmol), acetonitrile (4.0 mL), under argon, room temperature.
[b]Isolated yield.
[c]Under reflux.




**Scheme 2** Reduction of benzaldehyde dimethyl acetal.

This one-pot reaction proceeds at high efficiency to give the corresponding secondary amines, which are extremely useful in the construction of biologically important compounds. The reductive condition is mild enough to tolerate a broad range of functional groups such as Cl, Br, I, F, MeO, $NO_2$ and double bonds.

## Experimental

Reactions were performed under an argon atmosphere at room temperature. The materials were used as purchased. Unless otherwise stated, all solvents and reagents were commercially available and used as purchased without further purification. Reactions were monitored by TLC using gel F 254 plates. The silica gel (300–400 meshes) is used for column chromatography, and the distillation range of petroleum ether is 60–90 °C. NMR spectra were recorded in $CDCl_3$ on either a Varian 400 MHz or Bruker 400 MHz Fourier-transform spectrometer. Chemical shifts are reported in ppm referenced to tetramethylsilane or the $CHCl_3$ solvent residual peak at 7.26 ppm for $^1H$ and 77.23 ppm for $^{13}C$.

Acetal (1.2 mmol), amine (1.0 mmol), triethylsilane (0.319 mL, 2.0 mmol) and $I_2$ (0.025 g, 0.1 mmol) were added to a flask (25 mL), followed by addition of acetonitrile (4.0 mL) under argon. The mixture was stirred at room temperature and monitored by TLC. The solution was then diluted with dichloromethane (5 mL), washed with brine. The aqueous layers was extracted with $CH_2Cl_2$ (3 × 10 mL), the combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to afford the desired product.

*N-Benzylaniline*:[34] Light yellow oily liquid; yield 93% (Table 2, entries 1, 9 and 10), 74% (Table 2, entry 9) and 68% (Table 2, entry 10); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45–7.35 (m, 4H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.26–7.17 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 2H), 4.36 (s, 2H), 4.14 (br s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.8, 127.7, 127.4, 117. 8, 113.1, 48.5.

*N-(4-Methoxybenzyl)aniline*:[34] Light yellow oily liquid; yield 90% (Table 2, entries 2 and 13) and 66% (Table 2, entry 13); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 4.27 (s, 2H), 4.21 (br s, 1H), 3.81 (s, 3H).

*N-(4-Methylbenzyl)aniline*:[35] Light yellow oily liquid; yield 93% (Table 2, entries 3, 11 and 12), 68% (Table 2, entry 11) and 65% (Table 2, entry 12); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.8 Hz, 2H), 7.20–7.13 (m, 4H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 4.28 (s, 2H), 3.98 (br s, 1H), 2.34 (s, 3H).

*N-(4-Fluorobenzyl)aniline*[36]: Light yellow oily liquid; yield 90% (Table 2, entry 4); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 4.31 (s, 2H), 4.07 (br s, 1H).

*N-(4-Chlorobenzyl)aniline*[34]: Light yellow oily liquid; yield 88% (Table 2, entries 5, 14 and 15), 75% (Table 2, entry 14) and 67% (Table 2, entry 15); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 2H), 4.32 (s, 2H), 4.18 (br s, 1H).

*N-(4-Bromobenzyl)aniline*:[36] Light yellow oily liquid; yield 97% (Table 2, entry 6); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.22–7.16 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.31 (s, 2H), 4.15 (br s, 1H).

*N-(4-Nitrobenzyl)aniline*: Yellow solid, m.p. 67–68 °C (lit.[37] 67–69 °C); yield 60% (Table 2, entry 7); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.61 (br s, 1H), 4.48 (s, 2H).

*N-(3-Nitrobenzyl)aniline*: Yellow solid, m.p. 84–85 °C (lit.[38] 84–85 °C); yield 73% (Table 2, entry 8); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 2H), 4.47 (s, 2H), 4.41 (br s, 1H).

*N-(3-Bromobenzyl)aniline*:[39] Light yellow oily liquid; yield 89% (Table 2, entry 16);$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.53 (br s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.24–7.14 (m, 3H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 4.32 (s, 2H).

*N-(2-Bromobenzyl)aniline*:[40] Light yellow oily liquid; yield 79% (Table 2, entry 17); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.22–7.10 (m, 3H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.41 (s, 2H), 4.31 (br s, 1H).

*N-Cinnamylaniline*:[34] Light yellow oily liquid; yield 75% (Table 2, entry 18); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28–7.17 (m, 3H), 6.80–6.58 (m, 4H), 6.45–6.31 (m, 1H), 3.95 (d, *J* = 5.8 Hz, 2H), 3.89 (br s, 1H).

*N-Phenethylaniline*:[36] Light yellow oily liquid; yield 85% (Table 2, entry 19); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.30–7.17 (m, 5H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 3.86 (br s, 1H), 3.42 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.0 Hz, 2H).

*N-(1-Phenylethyl)aniline*:[34] Light yellow oily liquid; yield 67% (Table 2, entry 22); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27–7.21 (m, 1H), 7.15–7.08 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 2H), 4.50 (q, *J* = 6.7 Hz, 1H), 4.21 (br s, 1H), 1.54 (d, *J* = 6.7 Hz, 3H).

*N-Benzyl-4-methylaniline*:[41] Light yellow oily liquid; yield 90% (Table 3, entry 1); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.47–7.35 (m, 4H), 7.34–7.24 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 4.34 (s, 2H), 3.97 (br s, 1H), 2.28 (s, 3H).

*N-Benzyl-3-methylaniline*:[36] Light yellow oily liquid; yield 95% (Table 3, entry 2); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 7.31–7.25 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.51–6.44 (m, 2H), 4.33 (s, 2H), 3.99 (br s, 1H), 2.28 (s, 3H).

*N-Benzyl-4-methoxyaniline*:[34] Light yellow oily liquid; yield 88% (Table 3, entry 3); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.8 Hz, 3H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.31–7.25 (m, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.29 (s, 2H), 4.04 (br s, 1H), 3.75 (s, 3H).

*N-(4-Bromobenzyl)-4-methoxyaniline*:[34] Light yellow oily liquid; yield 88% (Table 3, entry 4); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 4.24 (s, 2H), 3.73 (s, 3H).

*N-Benzyl-4-chloroaniline*:[36] Light yellow oily liquid; yield 90% (Table 3, entry 5); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 4H), 7.27–7.18 (m, 1H), 7.05–7.10 (m, 2H), 6.53–6.50 (m, 2H), 4.26 (s, 2H), 4.17 (br s, 1H).

*N-Benzyl-4-nitroaniline*: Yellow solid, m.p. 146–147 °C (lit.[42] 146–148 °C); yield 91% (Table 3, entry 7); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.15–8.03 (m, 2H), 7.44–7.31 (m, 5H), 6.57 (d, *J* = 7.2 Hz, 2H), 4.86 (br s, 1H), 4.43 (s, 2H).

*Ethyl-4-(benzylamino)benzoate*:[43] White solid, m.p. 90–91 °C; yield 95% (Table 3, entry 8); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.35 (s, 4H), 7.33–7.26 (m, 1H), 6.59 (d, *J* = 8.1 Hz, 2H), 4.54 (br s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.9, 151.8, 138.5, 131.6, 128.9, 127.6, 127.5, 119.1, 111.7, 60.3, 47.8, 14.6.

## Electronic Supplementary Information

Further experimental and spectroscopic details are available through:
stl.publisher. ingentaconnect.com/content/stl/jcr/supp-data.

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