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An efficient homogeneous gold(I) catalyst for N-alkylation of amines with alcohols by hydrogen autotransfer

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ABSTRACT

A new and highly efficient homogeneous [Ph_3PAuCl]/AgOTf catalytic system was developed in N-alkylation reaction of primary amines with alcohols through a hydrogen autotransfer process. This Au(I) catalytic system shows excellent selectivity for mono-alkylation of primary amines with benzyl alcohol under moderate temperature of 100 °C (only secondary amines as product). The possible mechanism of this hydrogen autotransfer reaction with the catalytic system was proposed.

1. Introduction

Amines play an important role in organic synthesis due to their wide use as synthetic intermediates for the production of pharmacophores, fine chemicals, agrochemicals, bioactive compounds, polymers, and dyes.[1] With the rapid development of green synthetic chemistry, synthesis of amines from alcohols as green reagents have attracted considerable interests.[2] However, this process has been largely restricted to multistep synthesis due to the weak activity of the hydroxyl group. Thus the hydroxyl group was generally transformed into a more reactive substituent, such as halide, carbonyl group, and then afford the corresponding amine product by N-alkylation of alkyl halides[1d,3] and reductive amination of carbonyl compounds,[4] respectively (Scheme 1, pathway 1 and 2). In addition, these organic transformations inevitably lead to stoichiometric amounts of waste salt (pathway 1) or low selectivity for mono-alkylation (pathway 2) of primary amines.[1a,5]

Recently the direct catalytic N-alkylation of amines with alcohols, commonly known as 'the borrowing hydrogen' or hydrogen autotransfer reactions,[6] has received considerable attention. This attention arises from its one-step process and environmentally friendly byproduct (only H_2O as a byproduct) (Scheme 1, pathway 3). Several attempts have been carried out to perform this transformation catalyzed by transition-metal complexes, including complexes of iridium,[7] rhodium,[8] ruthenium,[7a,9] and other transition metals.[10] Although these catalysts exhibited good activity in transfer hydrogenation reactions, they also have some disadvantages. For example, amine alkylation reactions with Ruthenium and Rhodium complexes as catalysts require high reaction temperature (>150 °C).[11] Ag/Al_2O_3 as a heterogeneous catalyst shows poor selectivity for mono-alkylation of primary amines with benzyl alcohol.[12] Thus, the development of an efficient, alternative catalytic system for N-alkylation of amines with alcohols is highly desirable.

Gold-catalyzed organic transformations[13] have received considerable attention in organic synthesis since Bond et al.[14] reported the hydrogenation of olefins over supported gold catalysts in 1973. In comparison with other transition-metal catalysts, investigations of gold-catalyzed transfer hydrogenation were very scarce. There have been a few successful attempts for heterogeneous gold catalyst, showing excellent activity for N-alkylation of amines with alcohols.[1a] However, homogeneous gold catalyst for this hydrogen autotransfer reaction was scarcely reported. Herein we report a successful example of homogeneous gold(I) complex catalyzing the hydrogen autotransfer of amines with alcohols under relatively mild conditions.

2. Results and discussion

2.1. N-alkylation of aniline with benzyl alcohol: optimization of the reaction conditions

Our investigation started with the reaction of aniline (**1a**) with benzyl alcohol (**2a**) using a catalyst system consisting of Ph_3PAuCl

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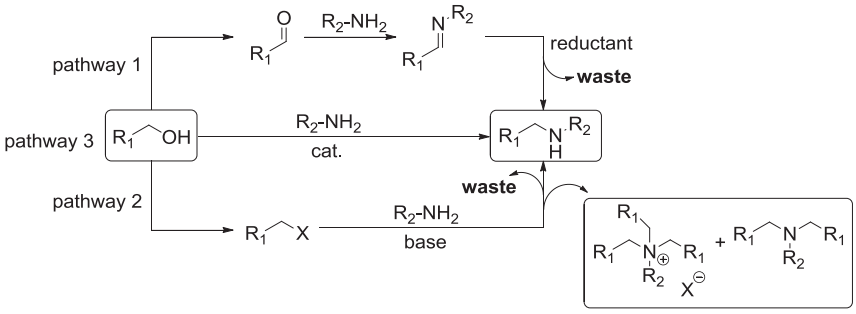
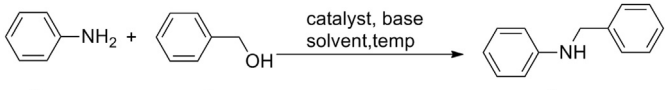
0040-4020/



Scheme 1. Strategies for synthesis of amine with alcohol-based.

(5 mol %), *t*-BuOK (1.0 equiv), and 1,4-dioxane (2 mL) at 100 °C for 48 h. The desired product **3aa** could be obtained in 25% yield (Table 1, entry 1). Addition of additive was studied to improve the catalyst activity. The yield was not obviously changed by the addition of Cs_2CO_3 in a ratio of 1:1 with Ph_3PAuCl (Table 1, entry 2), whereas catalytic activity was considerably promoted by the addition of AgOTf (Table 1, entry 3, 48% yield). AgOTf alone showed lower reactivity with 14% yield (Table 1, entry 4). Thus the combination of Ph_3PAuCl and AgOTf was more efficient to this reaction, which could be ascribed to the major reactive role of $Ph_3PAuOTf$, generated from Ph_3PAuCl and AgOTf.[15] Decreasing temperature would result in a reduction of catalytic activity of Au(I). No desired product was obtained at 60 °C (Table 1, entry 5), and the yield was only 9% when reaction temperature increases to 80 °C (Table 1, entry 6). In order to optimize the reaction condition, the catalyst loading was screened from 3 mol % to 15 mol %. The results indicated that yield of **3aa** was enhancing with an increased amount of catalyst. The yield of **3aa** was only 37% (Table 1, entry 7) when the catalyst loading was 3 mol %. By further increasing the catalyst loading to 10 mol %, the yield of **3aa** was improved dramatically, and reached 78% (Table 1, entries 8 and 9). But the yield was increased by only 4% when the catalyst amount was increased from 10 to 15 mol % (Table 1, entries 9–11). So 10 mol % was chosen as the optimized catalyst loading in consideration of economical efficiency and effectiveness. In addition, the addition of the base was assumed to further facilitate the initial alcohol dehydrogenation. The influence of the base was also investigated, such as NaOH, KOH, K_2CO_3, and $K_3PO_4{\cdot}3H_2O$ (Table 1, entries 12–15). But these bases couldn't afford the desired product in higher yield than that of *t*-BuOK. Investigations into the optimum solvent for this reaction suggested that 1,4-dioxane is the best choice (Table 1, entries 9, 16–19). Various other solvents such as $PhCH_3$, THF, MeCN, $ClCH_2CH_2Cl$ show low catalytic activities and afford no more than 18% yield of product.

Table 1
Optimization of the reaction conditions of gold(I) complex catalyzed N-alkylation of aniline (**1a**) with benzyl alcohol (**2a**)[a]



1a **2a** **3aa**

Entry	Cat. (mol %)	Base	Solvent	*T* (°C)	Yield/%[b]
1	Ph_3PAuCl (5%)	*t*-BuOK	1,4-Dioxane	100	25
2	Ph_3PAuCl (5%)+Cs_2CO_3 (5%)	*t*-BuOK	1,4-Dioxane	100	26
3	Ph_3PAuCl (5%)/AgOTf (5%)	*t*-BuOK	1,4-Dioxane	100	48
4	AgOTf (5%)	*t*-BuOK	1,4-Dioxane	100	14
5	Ph_3PAuCl (5%)/AgOTf (5%)	*t*-BuOK	1,4-Dioxane	60	n.d.
6	Ph_3PAuCl (5%)/AgOTf (5%)	*t*-BuOK	1,4-Dioxane	80	9
7	Ph_3PAuCl (3%)/AgOTf (3%)	*t*-BuOK	1,4-Dioxane	100	37
8	Ph_3PAuCl (8%)/AgOTf (8%)	*t*-BuOK	1,4-Dioxane	100	59
9	Ph_3PAuCl (10%)/AgOTf (10%)	*t*-BuOK	1,4-Dioxane	100	78
10	Ph_3PAuCl (12%)/AgOTf (12%)	*t*-BuOK	1,4-Dioxane	100	81
11	Ph_3PAuCl (15%)/AgOTf (15%)	*t*-BuOK	1,4-Dioxane	100	82
12	Ph_3PAuCl (10%)/AgOTf (10%)	NaOH	1,4-Dioxane	100	16
13	Ph_3PAuCl (10%)/AgOTf (10%)	KOH	1,4-Dioxane	100	25
14	Ph_3PAuCl (10%)/AgOTf (10%)	K_2CO_3	1,4-Dioxane	100	6
15	Ph_3PAuCl (10%)/AgOTf (10%)	$K_3PO_4{\cdot}3H_2O$	1,4-Dioxane	100	8
16	Ph_3PAuCl (10%)/AgOTf (10%)	*t*-BuOK	$PhCH_3$	100	18
17	Ph_3PAuCl (10%)/AgOTf (10%)	*t*-BuOK	THF	Reflux	0
18	Ph_3PAuCl (10%)/AgOTf (10%)	*t*-BuOK	MeCN	Reflux	8
19	Ph_3PAuCl (10%)/AgOTf (10%)	*t*-BuOK	$ClCH_2CH_2Cl$	Reflux	5

[a] The reaction was carried out with aniline (1.0 mmol), benzyl alcohol (1.2 mmol), catalyst (10 mol %), and base (1.0 equiv) in 2 mL solvent for 48 h.
[b] Isolated yield.

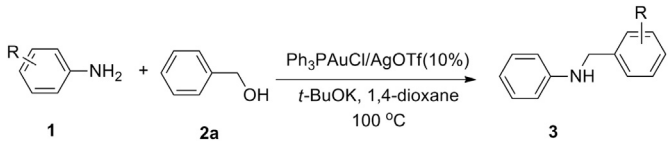
2.2. N-alkylation of various amines with benzyl alcohol

With the optimized conditions established, we investigated the generality of aniline derivatives with benzyl alcohol (**2a**) in Au(I) catalytic system (Table 2). Electron-donating substituents have a positive effect on the reactivity of anilines with benzyl alcohol. Anilines substituted with electron-donating group $-CH_3$ at the *ortho*, *para* position, $-OCH_3$ at the *para* position give high yields of corresponding mono-alkylation of primary aromatic amines (Table 2, entries 1–3). The substituted anilines bearing electron-withdrawing substituents were smoothly alkylated with **1a** in moderate to good yields (Table 2, entries 4–7). It is noteworthy that halo-substituted anilines show good reactivity in the reaction while a small amount of *N*-benzylaniline (**3aa**) as a dehalogenation byproduct was obtained. The generation of dehalogenation byproduct could be accounted for the catalytic reduction of the desired product **3** with the intermediate Au–H species. However, no reaction was observed if anilines bearing strong electron-withdrawing substituents such as $-NO_2$, $-OCCH_3$ or $-F_3C$ were used as substrates (Table 2, entry 8). Unexpectedly, *N*-phenylacetamide as substrate afford 63% yield of *N*-benzylaniline (entry 9), which could be caused by the hydrolysis of acetanilide in the alkaline solution. Hetero-amine and naphthylamine also show good reactivity in this reaction and give good yields (Table 2, entries 10, 11).

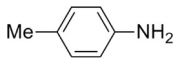
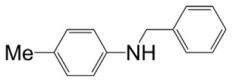
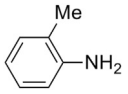
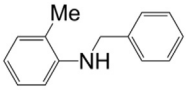
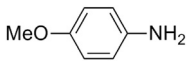
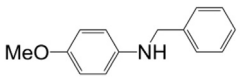
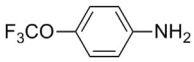
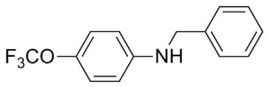
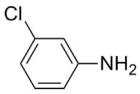
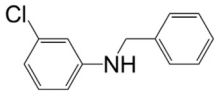
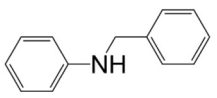
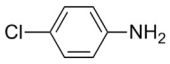
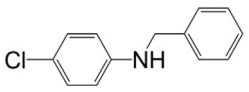
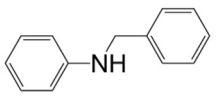
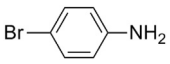
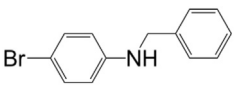
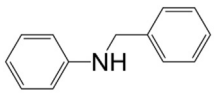
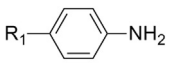
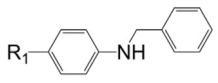
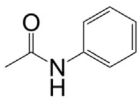
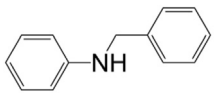
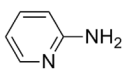
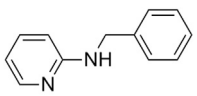
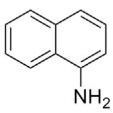
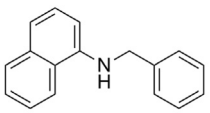
2.3. N-alkylation of anilines with various primary alcohols

Reactions of different primary alcohols with aniline (**1a**) were examined to extend the scope of this catalytic system. Benzyl alcohol bearing electron-donating groups of $-CH_3$, $-OMe$, and naphthalene methanol were successfully alkylated with aniline in moderate to good yield (Table 3, entries 1–3). The electron-withdrawing group of $-Cl$ substituted benzyl alcohol were tolerated in the reaction while a small amount of **3aa** as a dehalogenation byproduct was formed (Table 3, entry 4), which could be ascribed to the catalytic reduction of the desired product **3ae** with the intermediate Au–H species. However, no desired product was obtained in the reaction using benzyl alcohol bearing the strong

Table 2
N-alkylation of primary amines with benzyl alcohol (**2a**) affording secondary amines[a]

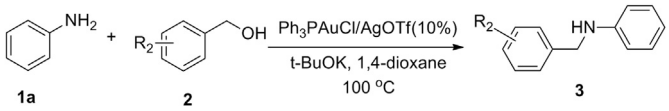


1 2a 3

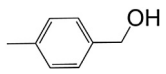
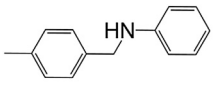
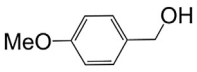
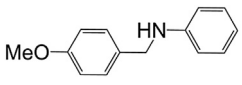
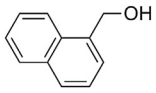
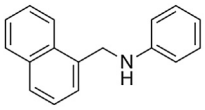
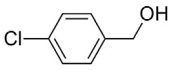
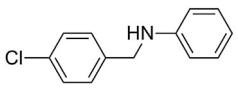
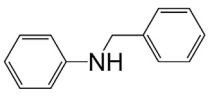
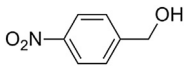
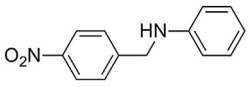
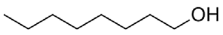
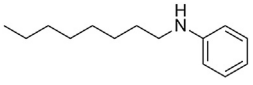
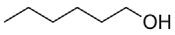
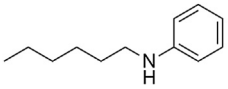
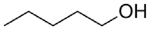
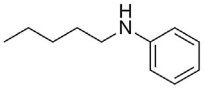
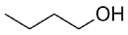
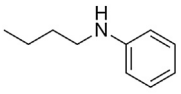
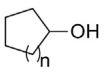
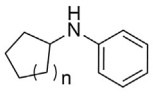
Entry	Amine	Product	Yield/%[b]
1		 (**3ba**)	90
2		 (**3ca**)	87
3		 (**3da**)	92
4		 (**3ea**)	72
5		 (**3fa**)  (**3aa**)	76 12
6		 (**3ga**)  (**3aa**)	78 14
7		 (**3ha**)  (**3aa**)	73 15
8	 R_1 = NO_2, CH_3CO, F_3C	 (**3ia**)	0
9		 (**3aa**)	63
10		 (**3ka**)	87
11		 (**3la**)	81

[a] Reaction conditions: **1** (1.0 mmol), **2a** (1.2 mmol), Ph_3PAuCl (0.1 mmol), AgOTf (0.1 mmol) in 1,4-dioxane (2 mL), *t*-BuOK (1.0 equiv), 100 °C.
[b] Isolated yield.

Table 3
N-alkylation of anilines (**1a**) with various primary alcohols affording secondary amines[a]



1a 2 3

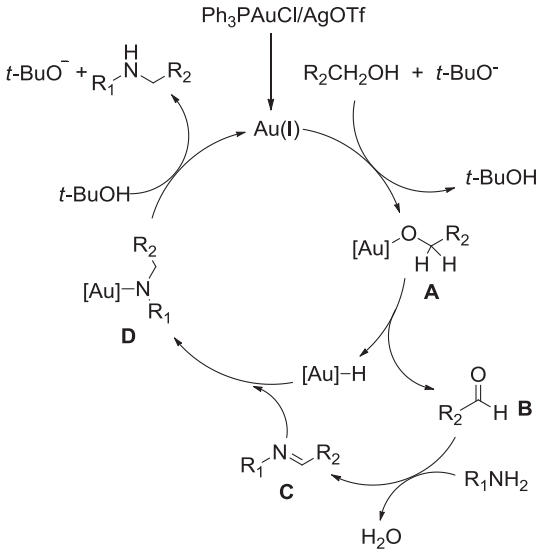
Entry	Alcohol	Product	Yield/%[b]
1		 (**3ab**)	80
2		 (**3ac**)	78
3		 (**3ad**)	75
4		 (**3ae**)  (**3aa**)	64 13
5		 (**3af**)	0
6[c]		 (**3ag**)	63
7[c]		 (**3ah**)	60
8[c]		 (**3ai**)	64
9[c]		 (**3aj**)	58
10[d]	 n=1,2	 (**3ak**)	0

[a] Reaction conditions: **1a** (1.0 mmol), **2** (1.2 mmol), Ph_3PAuCl (0.1 mmol), AgOTf (0.1 mmol) in 1,4-dioxane (2 mL), *t*-BuOK (1.0 equiv), 100 °C.
[b] Isolated yield.
[c] The reaction times were 3 d.
[d] The reaction time was 4 d.

electron-withdrawing group of $-NO_2$ at the *para*-position (Table 3, entry 5). Non-activated aliphatic alcohols proceeded smoothly to produce the corresponding secondary amines in moderate yields (Table 3, entries 6–9). Cyclic secondary alcohols were not applicable in this catalytic system, which attribute to the difficulty of being oxidized to ketone by this Au(I) catalyst system due to their steric effect (Table 3, entry 10).

2.4. Mechanistic consideration of the N-alkylation of amines with alcohols catalyzed by gold(I) complex

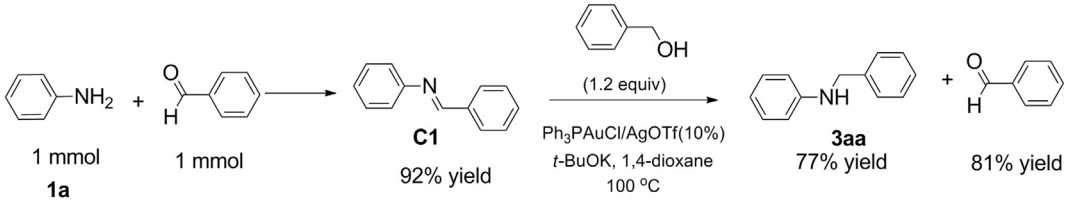
Although the exact mechanism for the present reaction is not clear yet, a possible mechanism is shown in Scheme 2. The reaction mechanism involves three elementary steps (Scheme 2). At the first step, a hydrido-gold species would be formed from the



Scheme 2. The plausible mechanism for N-alkylation of primary amines with alcohols catalyzed by Au(I).

alcohol to [Au]. Initially, $Ph_3PAuOTf$, which generated from Ph_3PAuCl and AgOTf, provides the cationic Au(I), then reacts with alcohol to afford alkoxo-gold species **A** in the presence of *t*-BuOK. [Au]–H would be generated by β-hydrogen elimination of alkoxo moiety with the formation of the corresponding aldehyde **B**. The second step involves the formation of imine **C** intermediates by the dehydration condensation reaction between aldehyde and primary amine. At the last step, [Au] catalyst would be regenerated from [Au]–H to imine **C** intermediates. The amido gold species **D** would be formed by the addition of the [Au]–H to the C=N of imine **C**. Then the secondary amine **3** was released from imine **D** and *t*-BuOH accompanying with regeneration of the catalytically active Au(I).

In order to support the above mechanism of the hydrogen autotransfer reaction, we carried out the following reactions. Aniline and benzaldehyde were stirred to generate *N*-benzylideneaniline (C1) in 92% yield for 4 h without catalyst at room temperature. Then benzyl alcohol as the hydrogen donor and the $Ph_3PAuCl/AgOTf$ as catalyst were added to the solution of C1 under the optimized condition. The expected product (**3aa**) and benzaldehyde were obtained in 77% and 81% yields, respectively (Scheme 3). It shows that the key imine intermediate in the third reduction mechanism step could afford the product **3aa** with the gold hydride species.



Scheme 3. Reaction of the key imine intermediate with benzyl alcohol to support the proposed mechanism.

3. Conclusions

We have developed a new and highly efficient homogeneous gold(I) catalytic system for N-alkylation of primary amines with alcohols through a hydrogen autotransfer process. It should be noted that the reaction has excellent selectivity for the formation of secondary amines with this catalyst system (only secondary amines as product). Besides, compared with the known catalytic system of ruthenium or rhodium, the present catalytic system can be carried out under moderate temperature of 100 °C.

4. Experimental section

4.1. General consideration

Most of the chemical reagents were purchased from Aldrich and used without further purification in most cases. Solvents are commercially available and used without further purification. ^1H NMR and ^{13}C spectra were recorded on 500 MHz Brucker instrument. Chemical shifts are in parts per million from tetramethylsilane (TMS). Melting points were determined on an electrothermal apparatus and uncorrected. All the major products were isolated by flash column chromatography on silica gel, with eluents of mixed solvents (ethyl acetate and petroleum ether). TLC was performed on a Merck Kieselgel F_{254}, 0.2 mm thick.

4.2. General procedure for the N-mono-alkylation of amines with alcohols catalyzed by gold(I) complex

After a mixture of Ph_3PAuCl (13 mg, 0.02 mmol) and AgOTf (7 mg, 0.02 mmol) was stirred in 1,4-dioxane (2 mL) for 10 min in a Schlenk tube, amine derivatives (**1**, 1.0 mmol), alcohol derivatives (**2**, 1.2 mmol), and *t*-BuOK (112 mg, 1.0 equiv) were added to the mixture. The reaction mixture was heated to 100 °C. After 48 h, the reaction mixture was filtered out and the filtrate was evaporated under reduced pressure. Then the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the corresponding product **3**.

4.3. Selected physical and spectroscopic data

*4.3.1. N-Benzylaniline (**3aa**).*[16] The crude product was purified by column chromatography on silica gel (40:1; petroleum ether/EtOAc). Yellow oil was obtained (142.7 mg, 78%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–7.34 (m, 4H), 7.31 (t, J=7.0 Hz, 1H), 7.24–7.16 (m, 2H), 6.75 (t, J=7.3 Hz, 1H), 6.71–6.63 (m, 2H), 4.36 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.23, 138.53, 128.36, 127.72, 126.59, 126.31, 119.98, 116.64, 111.93, 47.37.

*4.3.2. N-Benzyl-4-methylbenzenamine (**3ba**).*[17] The crude product was purified by column chromatography on silica gel (50:1; petroleum ether/EtOAc). Yellow oil was obtained (177.3 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.56–7.46 (m, 4H), 7.43 (t, J=6.8 Hz, 1H), 7.16 (d, J=8.2 Hz, 2H), 6.71 (d, J=8.2 Hz, 2H), 4.44 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.12, 138.89, 128.95, 127.78, 126.68, 126.32, 125.82, 112.20, 47.75, 19.63.

*4.3.3. N-Benzyl-2-methylbenzenamine (**3ca**).*[17] The crude product was purified by column chromatography on silica gel (50:1; petroleum ether/EtOAc). Yellow oil was obtained (171.0 mg, 87%). ^1H

NMR (500 MHz, acetone-d_6) δ 7.42 (d, J=7.6 Hz, 2H), 7.33 (t, J=7.6 Hz, 2H), 7.24 (t, J=7.3 Hz, 1H), 7.10–6.92 (m, 2H), 6.63–6.48 (m, 2H), 4.44 (d, J=5.4 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, acetone-d_6) δ 145.43, 139.51, 128.86, 127.38, 126.13, 125.80, 125.72, 120.90, 115.43, 108.96, 46.31, 16.08.

*4.3.4. N-Benzyl-4-methoxybenzenamine (**3da**).*[18] The crude product was purified by column chromatography on silica gel (45:1; petroleum ether/EtOAc). Yellow oil was obtained (196.1 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dt, J=7.7, 6.6 Hz, 4H), 7.33 (t, J=7.0 Hz, 1H), 6.87–6.80 (m, 2H), 6.70–6.63 (m, 2H), 4.33 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.25, 141.54, 138.78, 127.65, 126.60, 126.22, 113.98, 113.18, 54.85, 48.28.

*4.3.5. N-Benzyl-4-(trifluoromethoxy)benzenamine (**3ea**).*[19] The crude product was purified by column chromatography on silica gel (40:1; petroleum ether/EtOAc). Dark yellow oil was obtained (192.1 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.37 (m, 4H), 7.37–7.31 (m, 1H), 7.10 (d, J=8.4 Hz, 2H), 6.73 (d, J=8.8 Hz, 2H), 4.36 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.18, 140.71, 136.74, 127.81, 126.94–126.76 (d, J=22.68 Hz), 122.80–116.70 (q, J=768.6 Hz), 121.43, 113.71, 48.45.

*4.3.6. N-Benzyl-3-chlorobenzenamine (**3fa**).*[20] The crude product was purified by column chromatography on silica gel (45:1; petroleum ether/EtOAc). Dark yellow oil was obtained (165.0 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 4H), 7.35–7.30 (m, 1H), 7.09 (t, J=8.0 Hz, 1H), 6.73–6.68 (m, 1H), 6.64 (t, J=2.1 Hz, 1H), 6.54–6.49 (m, 1H), 4.33 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.28, 137.80, 134.06, 129.26, 127.78, 126.50, 116.44, 111.54, 110.17, 47.12.

*4.3.7. N-Benzyl-4-chlorobenzenamine (**3ga**).*[18] The crude product was purified by column chromatography on silica gel (50:1; petroleum ether/EtOAc). Dark yellow oil was obtained (169.4 mg, 78%). ^{1}H NMR (500 MHz, acetone-d_6) δ 7.42 (d, J=7.6 Hz, 2H), 7.33 (t, J=7.6 Hz, 2H), 7.24 (t, J=7.3 Hz, 1H), 7.10–6.85 (m, 2H), 6.65–6.43 (m, 2H), 4.92 (s, 1H), 4.44 (d, J=5.4 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 146.72, 138.85, 127.69, 127.42, 126.26, 125.87, 119.40, 112.88, 46.31.

*4.3.8. N-Benzyl-4-bromobenzenamine (**3ha**).*[1b] The crude product was purified by column chromatography on silica gel (40:1; petroleum ether/EtOAc). Dark yellow oil was obtained (191.1 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.34 (m, 4H), 7.31 (dd, J=8.7, 4.4 Hz, 1H), 7.28–7.24 (m, 2H), 6.52 (d, J=8.7 Hz, 2H), 4.32 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.06, 137.87, 130.96, 127.74, 126.42, 113.45, 108.15, 47.26.

*4.3.9. N-Benzylpyridin-2-amine (**3ka**).*[17] The crude product was purified by column chromatography on silica gel (25:1; petroleum ether/EtOAc). Pale yellow solid was obtained (159.8 mg, 87%). Mp 97–99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J=4.8 Hz, 1H), 7.24–7.15 (m, 5H), 7.10 (3, J=6.8 Hz, 1H), 6.43–6.40 (m, 2H), 6.19 (d, J=8.4 Hz, 2H), 4.94 (s, 1H), 4.33 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.71, 147.17, 138.21, 136.57, 127.67, 126.43, 126.26, 112.14, 105.80, 45.35.

*4.3.10. N-(4-Chlorobenzyl)benzenamine (**3ae**).*[21] The crude product was purified by column chromatography on silica gel (35:1; petroleum ether/EtOAc). Dark yellow oil was obtained (139.2 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.29 (m, 4H), 7.24 (dd, J=8.4, 7.4 Hz, 2H), 6.80 (t, J=7.3 Hz, 1H), 6.67 (d, J=7.7 Hz, 2H), 4.35 (s, 2H), 4.09 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.92, 137.12, 131.90, 130.00, 128.39, 127.79, 116.86, 111.97, 46.64.

*4.3.11. N-Benzylnaphthalen-1-amine (**3la**).*[22] The crude product was purified by column chromatography on silica gel (35:1; petroleum ether/EtOAc). Brown solid was obtained (188.5 mg, 81%). Mp 71–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J=11.5, 4.6 Hz, 2H), 7.46–6.96 (m, 9H), 6.50 (d, J=7.2 Hz, 1H), 4.34 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.23, 138.15, 133.40, 127.82, 126.85, 126.51, 125.72, 124.86, 123.87, 122.73, 122.50, 119.04, 116.81, 103.98, 47.72.

*4.3.12. N-(4-Methylbenzyl)benzenamine (**3ab**).*[1a] The crude product was purified by column chromatography on silica gel (30:1; petroleum ether/EtOAc). Yellow oil was obtained (157.3 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J=8.0 Hz, 2H), 7.31–7.24 (m, 4H), 6.86–6.80 (m, 1H), 6.75–6.70 (m, 2H), 4.37 (s, 2H), 4.05 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.36, 135.96, 135.52, 128.43, 128.38, 126.64, 116.60, 111.97, 47.17, 20.24.

*4.3.13. N-(4-Methoxybenzyl)benzenamine (**3ac**).*[4d] The crude product was purified by column chromatography on silica gel (50:1; petroleum ether/EtOAc). Pale yellow solid was obtained (166.1 mg, 78%). Mp 59–61 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J=8.4 Hz, 2H), 7.28 (t, J=7.7 Hz, 2H), 6.98 (d, J=8.4 Hz, 2H), 6.83 (t, J=7.3 Hz, 1H), 6.73 (d, J=8.0 Hz, 2H), 4.33 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.95, 147.32, 130.53, 128.35, 127.90, 116.58, 113.12, 111.95, 54.37, 46.85.

*4.3.14. N-(Naphthalen-1-ylmethyl)benzenamine (**3ad**).*[23] The crude product was purified by column chromatography on silica gel (40:1; petroleum ether/EtOAc). Dark yellow solid was obtained (174.5 mg, 75%). Mp 67–69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–7.96 (m, 1H), 7.93–7.83 (m, 1H), 7.79 (d, J=8.2 Hz, 1H), 7.55–7.45 (m, 3H), 7.45–7.36 (m, 1H), 7.27–7.16 (m, 2H), 6.76 (t, J=7.3 Hz, 1H), 6.68–6.60 (m, 2H), 4.66 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.40, 133.52, 133.04, 130.71, 128.50, 127.95, 127.31, 125.49, 125.15, 125.01, 124.73, 122.76, 116.72, 111.91, 45.50.

*4.3.15. N-Octylbenzenamine (**3ag**).*[24] The crude product was purified by column chromatography on silica gel (60:1; petroleum ether/EtOAc). Yellow oil was obtained (129.1 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, J=7.9 Hz, 2H), 6.62 (t, J=7.3 Hz, 1H), 6.54 (d, J=7.8 Hz, 2H), 3.04 (t, J=7.1 Hz, 2H), 1.67–1.48 (m, 2H), 1.30–1.07 (m, 12H), 0.83 (t, J=6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.55, 128.23, 116.10, 111.72, 43.04, 30.85, 28.60, 28.44, 28.29, 26.21, 21.68, 13.11.

*4.3.16. N-Hexylbenzenamine (**3ah**).*[25] The crude product was purified by column chromatography on silica gel (60:1; petroleum ether/EtOAc). Pale yellow oil was obtained (106.1 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, J=8.5, 7.4 Hz, 2H), 6.70 (t, J=7.3 Hz, 1H), 6.65–6.56 (m, 2H), 3.12 (t, J=7.1 Hz, 2H), 1.63 (dt, J=14.8, 7.2 Hz, 2H), 1.34 (ddd, J=10.9, 7.5, 3.8 Hz, 7H), 0.91 (dd, J=11.5, 4.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.57, 128.23, 116.08, 111.71, 43.03, 30.68, 28.73, 28.58, 25.88, 21.65, 13.06.

*4.3.17. N-Pentylbenzenamine (**3ai**).*[26] The crude product was purified by column chromatography on silica gel (55:1; petroleum ether/EtOAc). Yellow oil was obtained (104.1 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, J=7.9 Hz, 2H), 6.72 (t, J=7.3 Hz, 1H), 6.65 (d, J=7.8 Hz, 2H), 3.13 (t, J=7.2 Hz, 2H), 1.70–1.58 (m, 2H), 1.44–1.35 (m, 5H), 0.93 (dd, J=12.0, 4.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.26, 128.25, 116.38, 111.96, 43.22, 28.35, 28.21, 21.52, 13.05.

*4.3.18. N-Butylbenzenamine (**3aj**).*[27] The crude product was purified by column chromatography on silica gel (55:1; petroleum ether/EtOAc). Yellow oil was obtained (86.2 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, J=8.4, 7.4 Hz, 2H), 6.70 (t, J=7.3 Hz, 1H), 6.62 (d, J=7.7 Hz, 2H), 3.13 (t, J=7.1 Hz, 2H), 1.63 (dt, J=14.7, 7.3 Hz, 2H), 1.45 (dd, J=15.0, 7.5 Hz, 2H), 1.01–0.94 (m, 3H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 147.57, 128.23, 116.09, 111.70, 42.70, 30.71, 19.32, 12.92.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.10.007.

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