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Efficient and chemoselective direct reductive amination of aromatic aldehydes catalyzed by oxo–rhenium complexes containing heterocyclic ligands

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A B S T R A C T

This work describes the catalytic activity of 17 oxo–rhenium complexes containing heterocyclic ligands in the direct reductive amination of 4-nitrobenzaldehyde with 4-chloroaniline, using phenylsilane as reducing agent. In general, all of the catalysts tested gave excellent yields of the secondary amine, although, the best result was obtained with the catalytic system $PhSiH_3/ReOBr_2(Hhmpbta)(PPh_3)$ (2.5 mol %). This system was also applied to the synthesis of a large variety of secondary amines in good to excellent yields and tertiary amines in moderate yields, with tolerance of different functional groups.

1. Introduction

Reductive amination of carbonyl compounds with amines remains one of the most versatile and useful synthetic route for the preparation of amines and their derivatives, which are synthetically useful organic intermediates in pharmaceuticals and agrochemicals.[1] This reaction involves the formation of an imine or iminium as intermediate, followed by *in situ* reduction. The importance of reductive amination procedures is exemplified by the enormous number of its synthetic uses.

There are two types of reducing agents employed for direct reductive amination of aldehydes with amines. These two strategies are mainly based on metal catalyzed hydrogenation,[1] and hydride reducing agents, such as $NaBH_4$,[2] $NaBH_3CN$,[3] $NaBH(OAc)_3$,[4] and pyridine–BH_3.[5] However, in terms of functional group tolerance and side reactions, most of these reagents may have one or more drawbacks. For example, catalytic hydrogenation is incompatible with compounds containing other reducible functional groups, such as double and triple bonds, nitro, and cyano groups. $NaBH_4$ sometimes requires harsh reaction conditions, cyanoborohydride is highly toxic and generate toxic by-products, such as HCN or NaCN, and pyridine–BH_3 is unstable to heat and must be handled with extreme care.

With increasing environmental concerns and constraints, there exists a tremendous potential for development of new reductive amination methodologies. Organosilanes are mild and environmentally benign reducing agents, and in recent years, several reagent systems containing silanes, such as $Et_3SiH/InCl_3$,[6] $Et_3SiH/[IrCl(cod)]_2$,[7] $PhSiH_3/Bu_2SnCl_2$,[8] $PhSiH_3/MoO_2Cl_2$,[9] polymethylhydrosiloxane (PMHS)/$Ti(O^iPr)_4$,[10] $FeCl_3$/PMHS[11] have also been employed in reductive amination.

Previously, our group have demonstrated that several oxo–rhenium complexes were good catalysts for the direct reductive amination of aldehydes using silanes as reducing agents.[12] The results obtained demonstrate that the catalytic system $PhSiH_3/ReIO_2(PPh_3)_2$ (2.5 mol %) was very efficient for the synthesis of secondary amines in high yields and good chemoselectivity, and also for the synthesis of tertiary amines in moderate yields. Later, Ghorai and Das[13] developed an efficient method for direct reductive amination of aldehydes with electron-deficient protected amines, such as Cbz–, Boc–, EtOCO–, Fmoc–, Bz–, $ArSO_2$–, Ar_2PO–, etc., using Re_2O_7 as catalyst and silanes as reducing agent.

Due to the biological and chemical importance of amines, the search for novel catalyst systems, leading to efficient and highly chemoselective methods for their preparation, remains an important target in organic synthesis. The rhenium complexes containing heterocyclic moieties constantly attract the interest of chemists and pharmacists on account of their versatile biological activity and

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industrial applications. Surprisingly, catalytic studies using rhenium complexes incorporating such ligands have been relatively rare. In continuation of our work about the use of oxo-complexes as efficient catalysis in organic chemistry,[14] herein we report the catalytic activity of 17 oxo–rhenium complexes containing heterocyclic ligands in direct reductive amination of aldehydes.

2. Results and discussion

Initially, we studied the catalytic activity of the 17 oxo–rhenium complexes containing the heterocyclic ligands namely 2-(2′-hydroxy-5′-methylphenyl)benzotriazole (Hhmpbta),[15] 2-(2-hydroxyphenyl)-2-benzothiazole (Hhpbt),[16] 2-(2-hydroxyphenyl)-2-benzoxazole (Hhpbo),[17] 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi)[18] (Fig. 1) in the direct reductive amination of 4-nitrobenzaldehyde with 4-chloroaniline, using $PhSiH_3$ as reducing agent (Table 1). In general, all the oxo–rhenium complexes were very efficient, affording high yields of the secondary amine. The reaction catalyzed by 2.5 mol % of $ReOBr_2(Hhmpbta)(PPh_3)$ at refluxing THF gave the best result, producing the amine in 98% yield after only 13 min (Table 1, entry 1). The results obtained also demonstrate that in general the catalysts with Br ligands (Table 1, entries 1, 2, 6, 7, 10, 11, and 14) are more reactive than the complexes containing Cl ligands. Comparison between the oxo–rhenium complexes containing the heterocyclic ligands with the similar complexes without the heterocyclic ligands shows that the catalysts $ReOBr_2(L)(PPh_3)$ (Table 1, entries 1, 7, 10, and 14) are more efficient than $ReOBr_3(PPh_3)_2$ (Table 1, entry 18), in contrast, the reactions with the catalysts $ReOCl_2(L)(PPh_3)$ (Table 1, entries 3, 9, 13, and 16) or $ReOCl_2(L)(AsPh_3)$ (Table 1, entries 4, 8, 12, and 15) required more time than the reactions with the complexes $ReOCl_3(PPh_3)_2$ or $ReOCl_3(AsPh_3)_2$ (Table 1, entries 19 and 20). Finally, no reductive amination was observed with phenylsilane in the absence of catalyst (Table 1, entry 21), demonstrating the catalytic role of the oxo–rhenium complex.

the faster (13 min) (Table 2, entry 1) in contrast to the reduction with PMHS that required 24 h (Table 2, entry 4). No reaction was observed using Ph_3SiH (Table 2, entry 5) or without silane (Table 2, entry 6).

In Table 3 are summarized the results of the search for the appropriate solvent. We found that THF was the best solvent for this reaction at reflux temperature, affording the amine in 98% conversion after only 13 min (Table 3, entry 1). At room temperature, this reaction required 24 h and only moderate conversion of the amine was obtained (Table 3, entry 2). Chloroform, toluene, and benzene also gave good to excellent conversions of the product, but these reductions required 24 h (Table 3, entries 3–5). Finally, the reductions performed in acetonitrile and dichloromethane produced the amine in moderate conversions after 24 h (Table 3, entries 6 and 7).

In order to study the scope and the limitations of the catalytic system $PhSiH_3/ReOBr_2(Hhmpbta)(PPh_3)$ (2.5 mol %), the direct reductive amination was explored with a variety of aldehydes and aniline (Table 4). In general, all the secondary amines were obtained in good to excellent yields within short reaction times, including the amines prepared from aldehydes bearing electron-withdrawing or electron-donating groups. This reaction showed broad substrate scope, tolerating several functional groups, such as $-NO_2$, $-CF_3$, $-SO_2R$, $-Br$, $-CO_2R$, $-OCH_3$, $-SCH_3$, $-NCOR$, and furfuryl ring.

Another interesting result was the chemoselective reductive amination of cinnamaldehyde with aniline in 81% yield without affecting the double bond (Table 4, entry 11). Heteroaromatic aldehyde 2-furaldehyde also reacted with aniline affording the corresponding secondary amine in excellent yield (Table 4, entry 2).

In this work, we have also studied the reductive amination of 4-methoxybenzaldehyde with different anilines (Table 5). All the reactions afforded the corresponding secondary amines in good to excellent yields. The reactions carried out with anilines containing electron-withdrawing groups were much faster (Table 5, entries 1–3) than the reactions with anilines containing electron-donating groups (Table 5, entries 4 and 5).

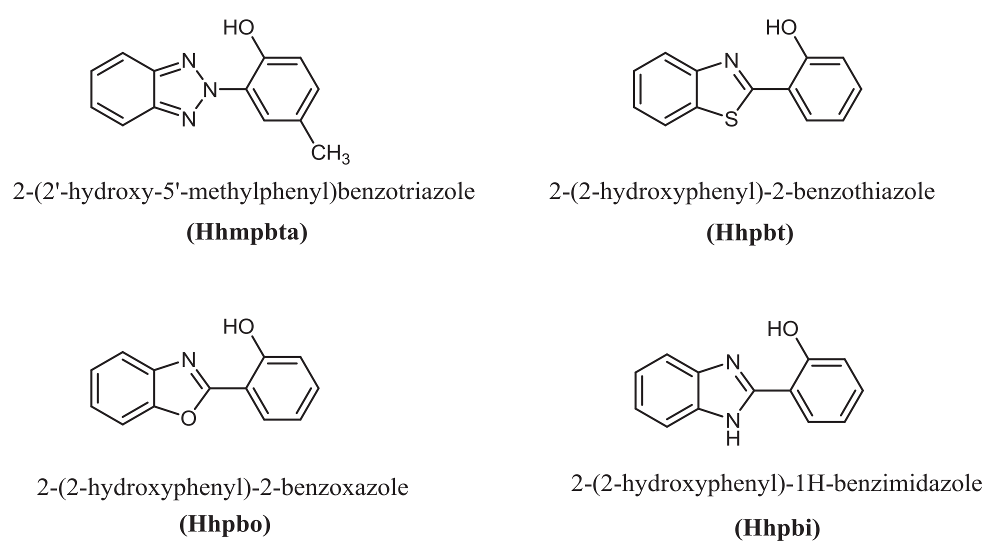
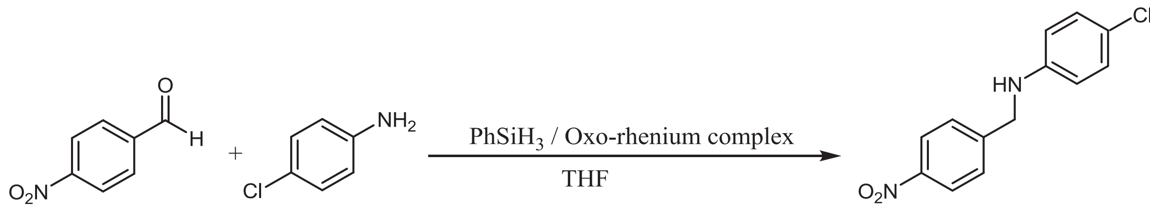


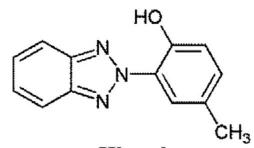
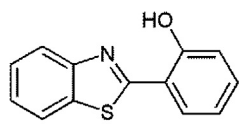
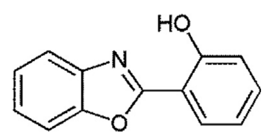
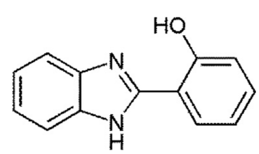
Fig. 1. Structure of heterocyclic ligands.

Direct reductive amination of 4-nitrobenzaldehyde with aniline was studied using several silanes namely phenylsilane, dimethylphenylsilane (DMPSH), triethylsilane, triphenylsilane, and polymethylhydrosiloxane (PMHS). The reductions carried out with $PhSiH_3$, DMPSH, Et_3SiH, and PMHS produced the amine in excellent yields (Table 2, entries 1–4), although, the reaction with $PhSiH_3$ is

The catalytic activity of the system $PhSiH_3/ReOBr_2(Hhmpbta)(PPh_3)$ (2.5 mol %) was also explored for the synthesis of tertiary amines in the reactions between *N*-methylaniline and several aldehydes (Table 6). These reductions were carried out with heteroaromatic aldehydes

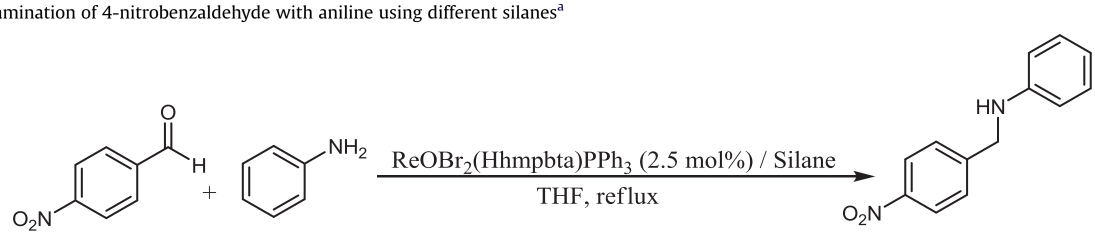
Table 1
Direct reductive amination of 4-nitrobenzaldehyde with 4-chloroaniline catalyzed by oxo–rhenium complexes[a]



Entry	Catalyst	Ligand	Time	Yield[b] (%)
1	$[ReOBr_2(L)(PPh_3)]$	 **Hhmpbta**	13 min	98
2	$[ReOBr_2(L)(AsPh_3)]$		22 min	99
3	$[ReOCl_2(L)(PPh_3)]$		30 min	95
4	$[ReOCl_2(L)(AsPh_3)]$		60 min	92
5	$[ReOBr(L)_2]$		6 h	87
6	$[ReOBr_2(L)(AsPh_3)]$	 **Hhpbt**	14 min	94
7	$[ReOBr_2(L)(PPh_3)]$		20 min	94
8	$[ReOCl_2(L)(AsPh_3)]$		1 h	89
9	$[ReOCl_2(L)(PPh_3)]$		1 h 30 min	86
10	$[ReOBr_2(L)(PPh_3)]$	 **Hhpbo**	15 min	93
11	$[ReOBr_2(L)(AsPh_3)]$		22 min	94
12	$[ReOCl_2(L)(AsPh_3)]$		1 h 16 min	90
13	$[ReOCl_2(L)(PPh_3)]$		1 h 20 min	91
14	$[ReOBr_2(L)(PPh_3)]$	 **Hhpbi**	23 min	99
15	$[ReOCl_2(L)(AsPh_3)]$		2 h 40 min	98
16	$[ReOCl_2(L)(PPh_3)]$		3 h	98
17	$[ReOBr_2(L)(AsPh_3)]$		6 h	96
18	$ReOBr_3(PPh_3)_2$	—	25 min	92
19	$ReOCl_3(PPh_3)_2$	—	20 min	94
20	$ReOCl_3(AsPh_3)_2$	—	40 min	91
21	Without catalyst	—	24 h	No reaction

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of 4-chloroaniline, and 120 mol % of $PhSiH_3$ and 2.5 mol % of catalyst.
[b] Isolated yields.

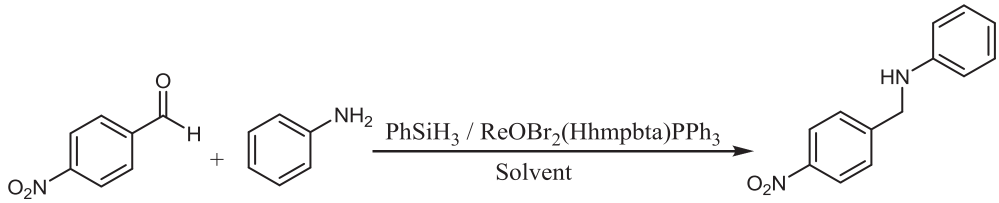
Table 2
Direct reductive amination of 4-nitrobenzaldehyde with aniline using different silanes[a]



Entry	Silane	Silane (mol %)	Time	Conversion[b] (%)
1	$PhSiH_3$	120	13 min	98
2	DMPSH	250	30 min	97
3	Et_3SiH	300	1 h 30 min	97
4	PMHS	200	24 h	96
5	Ph_3SiH	250	24 h	No reaction
6	Without silane	—	24 h	No reaction

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, and 2.5 mol % of $ReOBr_2(Hhmpbta)(PPh_3)$.
[b] Conversion was determined by ^1H NMR.

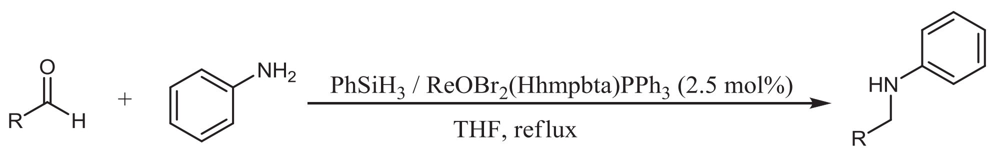
Table 3
Direct reductive amination of 4-nitrobenzaldehyde with aniline in different solvents[a]



Entry	Solvent	Temp	Time	Conversion[b] (%)
1	THF	Reflux	13 min	98
2	THF	rt	24 h	64
3	$CHCl_3$	Reflux	24 h	98
4	Toluene	Reflux	24 h	87
5	Benzene	Reflux	24 h	85
6	CH_3CN	Reflux	24 h	75
7	CH_2Cl_2	Reflux	24 h	69

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol % of $PhSiH_3$, and 2.5 mol % of $ReOBr_2(Hhmpbta)(PPh_3)$.
[b] Conversion was determined by ^1H NMR.

Table 4
Direct reductive amination of aldehydes with the catalytic system $PhSiH_3/ReOBr_2(Hhmpbta)PPh_3$[a]



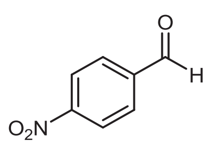
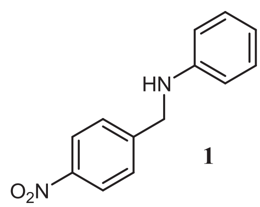
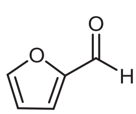
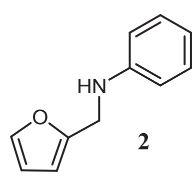
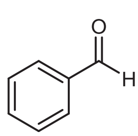
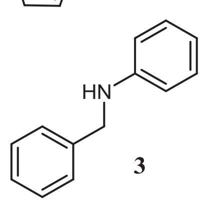
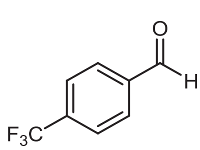
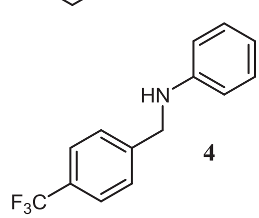
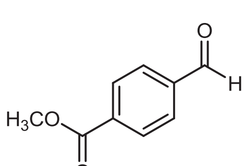
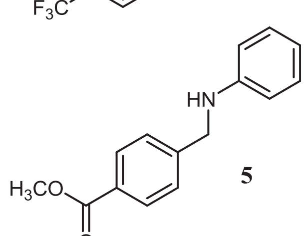
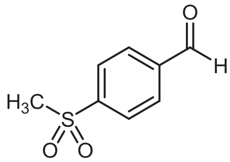
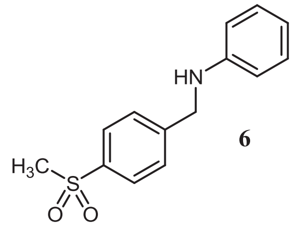
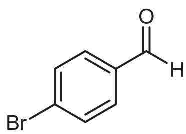
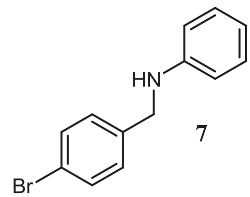
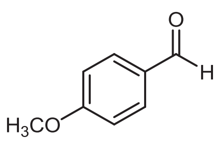
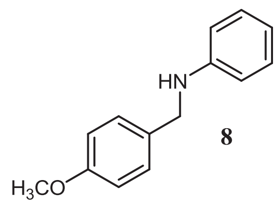
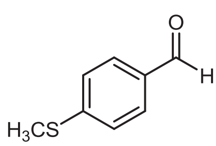
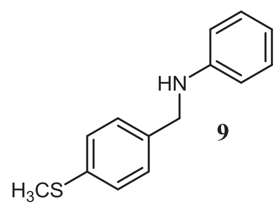
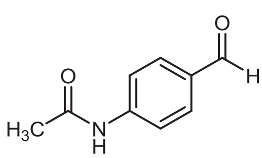
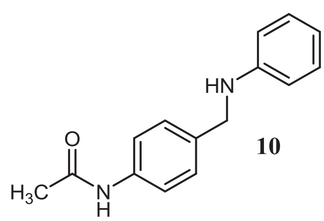
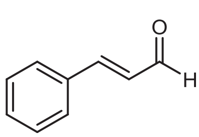
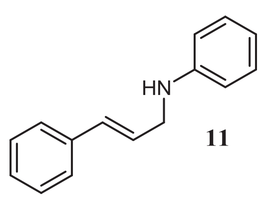
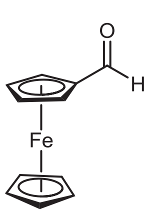
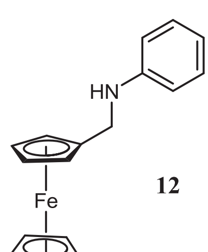
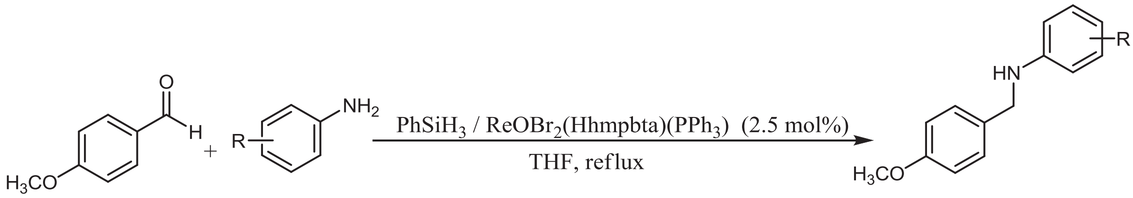
Entry	Aldehyde	Product	Time	Yield[b] (%)
1		 1	13 min	98
2		 2	30 min	96
3		 3	15 min	94
4		 4	22 min	90
5		 5	10 min	87

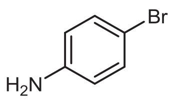
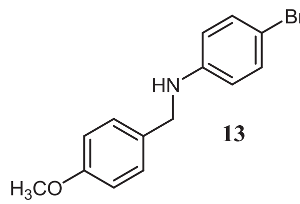
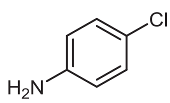
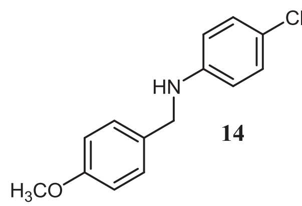
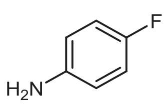
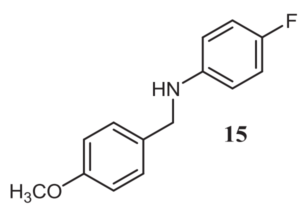
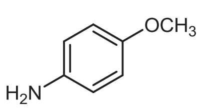
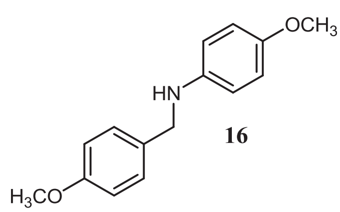
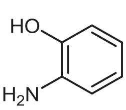
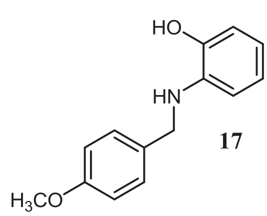
Table 4 (*continued*)

Entry	Aldehyde	Product	Time	Yield[b] (%)
6		 **6**	10 min	85
7		 **7**	10 min	85
8		 **8**	7 min	82
9		 **9**	5 min	80
10		 **10**	15 min	76
11		 **11**	1 h	81
12		 **12**	23 min	71

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol % of $PhSiH_3$, and 2.5 mol % of $ReOBr_2(Hhmpbta)(PPh_3)$.
[b] Isolated yield.

Table 5
Direct reductive amination of 4-methoxybenzaldehyde with different anilines using the catalytic system $PhSiH_3$/$ReOBr_2$(Hhmpbta)(PPh_3)[a]



Entry	Aniline	Product	Time	Yield[b] (%)
1		 **13**	5 min	93
2		 **14**	10 min	94
3		 **15**	45 min	95
4		 **16**	1 h 30 min	77
5		 **17**	4 h 30 min	72

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of aniline, 120 mol % of $PhSiH_3$, and 2.5 mol % of $ReOBr_2$(Hhmpbta)(PPh_3).
[b] Isolated yield.

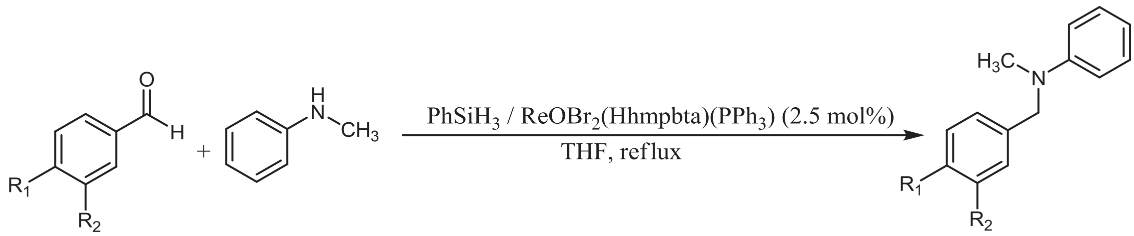
and different aromatic aldehydes bearing electron-withdrawing or electron-donating groups, affording the corresponding tertiary amines in moderate yields.

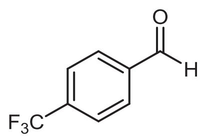
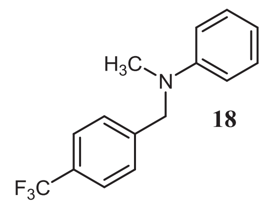
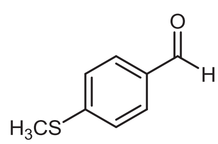
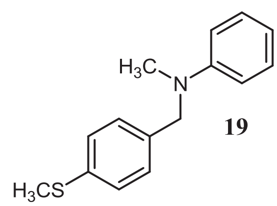
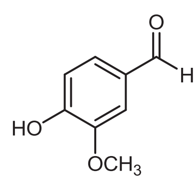
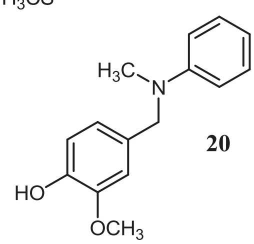
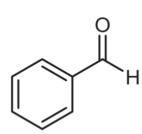
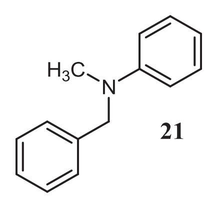
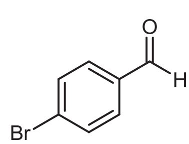
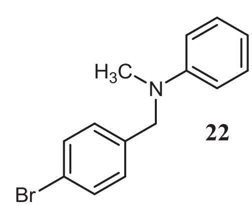
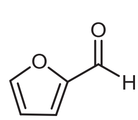
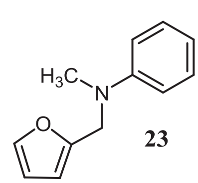
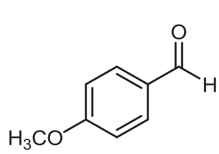
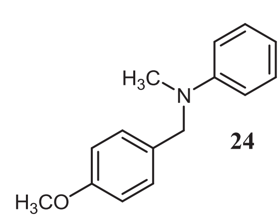
We propose a mechanism for the direct reductive amination of aldehydes with the catalytic system $PhSiH_3$/$ReOBr_2$(Hhmpbta)(PPh_3) that should start by the formation of the imine, and coordination of this molecule to the catalyst by substitution of the phosphine, affording the complex $ReOBr_2$(Hhmpbta)(imine). In the second step, a hydride species is formed as result of the addition of the Si–H bond of the silane to the oxo–rhenium bond. Then, the hydrosilylation of the imine occurs, followed by hydrolysis to the corresponding amine.

3. Conclusions

In conclusion, we have studied the catalytic activity of 17 oxo–rhenium complexes containing the heterocyclic ligands Hhmpbta, Hhpbt, Hhpbo, and Hhpbi as catalysts in the direct reductive amination of 4-nitrobenzaldehyde with 4-chloroaniline, using phenylsilane as reducing agent. All the catalysts tested show good to excellent catalytic activities. The best results was obtained with the catalytic system $PhSiH_3$/$ReOBr_2$(Hhmpbta)(PPh_3) (2.5 mol %), which proved to be also very efficient for the synthesis of several secondary amines in excellent yields and for the

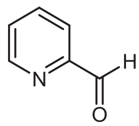
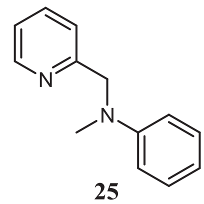
Table 6
Direct reductive amination of aldehydes with *N*-methylaniline using the catalytic system $PhSiH_3/ReOBr_2(Hhmpbta)(PPh_3)$[a]



Entry	Aldehyde	Product	Time	Yield[b] (%)
1		 **18**	15 min	68
2		 **19**	15 min	66
3		 **20**	15 min	61
4		 **21**	20 min	62
5		 **22**	30 min	57
6		 **23**	1 h 30 min	69
7		 **24**	2 h	65

(*continued on next page*)

Table 6 (*continued*)

Entry	Aldehyde	Product	Time	Yield[b] (%)
8		 **25**	3 h 30 min	66

[a] All reactions were carried out with 1.0 mmol of aldehyde, 1.0 mmol of *N*-methylaniline, 120 mol % of $PhSiH_3$, and 2.5 mol % of $ReOBr_2(Hhmpbta)(PPh_3)$.
[b] Isolated yield.

preparation of tertiary amines in moderate yields. This method is also highly chemoselective, tolerating a large range of functional groups, such as $-NO_2$, $-CF_3$, $-SO_2R$, $-CO_2R$, −F, −Cl, −Br, −OH, $-OCH_3$, $-SCH_3$, −NCOR, double bond and furfuryl ring.

In comparison to other procedures reported in the literature, this method is more chemoselective than some hydrogenation systems in the reductive amination of substrates containing double bonds, nitro, and halo groups. Furthermore, this methodology has other advantages including high isolated yields, low catalyst loading (2.5 mol %), fast reactions, simple experimental operation, stability of the catalysts toward air and moisture, allowing the reaction to be carried out under air atmosphere. We believe that this new procedure can be an attractive and useful alternative to the methods described in the literature and can also bring great benefits to both academia and industry for the production of fine chemicals, such as bioactive and pharmaceutical compounds.

The results obtained confirm the use of oxo−rhenium complexes as effective catalysts for C−N bond formation. Further applications of the catalytic system silane/oxo−rhenium complexes to other organic reductions and C−X bond forming reactions are now in progress in our group.

4. Experimental section

4.1. General information

All the reactions were carried out in air atmosphere and without any dry solvent. Aldehydes and anilines were obtained from commercial suppliers and were used without further purification. The catalysts were prepared according to the literature procedures.[15–18] Flash chromatography was performed on MN Kieselgel 60M 230−400 mesh. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance II 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard.

4.2. General procedure for direct reductive amination of aldehydes with the system $PhSiH_3/ReOBr_2(Hhmpbta)(PPh_3)$

To a mixture of aldehyde (1.0 mmol), aniline (1.0 mmol), and $ReOBr_2(Hhmpbta)(PPh_3)$ (2.5 mol %) in THF (3 mL) at reflux temperature was added $PhSiH_3$ (120 mol %). The reaction mixture was stirred under air atmosphere (the reaction times are indicated in Tables 4−6) and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with the appropriate mixture of *n*-hexane and ethyl acetate to afford the amines.

*4.2.1. N-(4-Nitrobenzyl)benzenamine (**1**).*[19] Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, 2H, *J*=8.4 Hz), 7.56 (d, 2H, *J*=8.4 Hz), 7.21 (t, 2H, *J*=8.0, 7.6 Hz), 6.78 (t, 1H, *J*=7.6 Hz), 6.61 (d, 2H, *J*=8.0 Hz), 4.51 (s, 2H), 4.29 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.4, 147.3, 129.5, 127.8, 124.0, 118.3, 113.0, 47.7. IR (neat, cm^{-1}): 3419, 3052, 2849, 1602, 1517, 1345, 1267, 1109, 752, 693; Anal. Calcd (%) for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.29; H, 5.17; N, 12.01.

*4.2.2. N-((Furan-2-yl)methyl)benzenamine (**2**).*[20] Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.13 (t, 2H, *J*=8.3, 7.5 Hz), 6.67 (t, 1H, *J*=7.6, 7.6 Hz), 6.54 (d, 2H, *J*=8.3 Hz), 6.20 (t, 1H, *J*=3.3, 1.9 Hz), 6.11 (d, 1H, *J*=3.1 Hz), 4.14 (s, 2H), 3.87 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 147.8, 141.9, 129.3, 118.0, 113.2, 110.5, 107.0, 41.4. IR (neat, cm^{-1}): 3419, 3052, 3026, 2921, 2853, 1602, 1505, 1453, 1325, 1267, 1252, 1180, 1028, 990, 869, 750, 732, 693; Anal. Calcd (%) for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 75.99; H, 6.27; N, 7.88.

*4.2.3. N-Benzylbenzenamine (**3**).*[21] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.29 (m, 5H), 7.21 (t, 2H, *J*=8.0 Hz), 6.76 (t, 1H, *J*=7.2 Hz), 6.67 (d, 2H, *J*=8.0 Hz), 4.36 (s, 2H), 4.05 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.5, 129.4, 128.7, 127.6, 127.3, 117.7, 113.0, 48.4. IR (neat, cm^{-1}): 3418, 3051, 3022, 2925, 1603, 1513, 1329, 1181, 984, 737, 689; Anal. Calcd (%) for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.04; H, 6.99; N, 7.48.

*4.2.4. N-(4-(Trifluoromethyl)benzyl)benzenamine (**4**).*[12] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 2H, *J*=8.4 Hz), 7.33 (d, 2H, *J*=8.4 Hz), 7.05 (t, 2H, *J*=7.6, 7.2 Hz), 6.61 (t, 1H, *J*=7.2 Hz), 6.47 (d, 2H, *J*=7.6 Hz), 4.24 (s, 2H), 3.82 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.9, 129.4, 127.5, 125.7, 125.6, 122.5, 118.0, 113.0, 47.8; IR (neat, cm^{-1}): 3398, 1604, 1506, 1325, 1164, 1120, 1066, 751, 692; Anal. Calcd for $C_{14}H_{12}F_3N$: C, 66.93; H, 4.81; N, 5.57. Found: C, 66.76; H, 4.61; N, 5.34.

*4.2.5. Methyl 4-((phenylamino)methyl)benzoate (**5**).*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 2H, *J*=8.4 Hz), 7.44 (d, 2H, *J*=8.4 Hz), 7.17 (t, 2H, *J*=7.2, 8.0 Hz), 6.73 (t, 1H, *J*=7.2, 7.2 Hz), 6.61 (d, 2H, *J*=8.0 Hz), 4.41 (s, 2H), 4.13 (br s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 147.8, 145.1, 129.9, 129.2, 128.9, 127.1, 117.7, 112.8, 52.0, 47.8; IR (neat, cm^{-1}): 3414, 1720, 1602, 1508, 1278, 1112, 751; Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.50; H, 6.31; N, 5.71.

*4.2.6. N-(4-(Methylsulfonyl)benzyl)benzenamine (**6**).*[12] White solid; mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, *J*=8.0 Hz), 7.48 (d, 2H, *J*=8.0 Hz), 7.09 (t, 2H, *J*=7.6, 8.0 Hz), 6.66 (t, 1H, *J*=7.6 Hz), 6.50 (d, 2H, *J*=8.0 Hz) 4.37 (s, 2H), 4.20 (br s, 1H); 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 146.5, 139.3, 129.4, 128.0, 127.8, 118.2, 113.0, 47.7, 44.6; IR (KBr, cm^{-1}): 3414, 1604, 1508, 1298, 1148, 747, 690; Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 64.09; H, 5.51; N, 4.98; S, 11.97.

*4.2.7. N-(4-Bromobenzyl)benzenamine (**7**).*[12] Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, *J*=8.4 Hz), 7.20 (d, 2H, *J*=8.4 Hz), 7.14

(t, 2H, J=8.4, 7.2 Hz), 6.70 (t, 1H, J=7.2 Hz), 6.57 (d, 2H, J=8.4 Hz), 4.24 (s, 2H), 3.94 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.6, 131.8, 129.4, 129.1, 121.0, 117.9, 113.0, 47.7; IR (neat, cm^{-1}): 3419, 1603, 1506, 1486, 1324, 1070, 1011, 751, 692; Anal. Calcd for $C_{13}H_{12}BrN$: C, 59.56; H, 4.61; N, 5.34. Found: C, 59.39; H, 4.48; N, 5.19.

*4.2.8. N-(4-Methoxybenzyl)benzenamine (**8**).*[12] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 2H, J=8.4 Hz), 7.09 (t, 2H, J=7.6 Hz), 6.79 (d, 2H, J=8.4 Hz), 6.63 (t, 1H, J=7.6 Hz), 6.55 (d, 2H, J=7.6 Hz), 4.47 (s, 1H), 4.16 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.3, 131.5, 129.4, 128.9, 117.6, 114.1, 113.0, 55.4, 47.9. IR (neat, cm^{-1}): 3419, 3003, 2932, 2837, 1934, 1604, 1508, 1303, 1248, 1173, 1033, 815, 753, 694; Anal. Calcd (%) for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.59; H, 6.88; N, 6.33.

*4.2.9. N-((4-Methylthio)benzyl)benzenamine (**9**).*[12] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 2H, J=8.4 Hz), 7.32 (d, 2H, J=8.4 Hz), 7.26 (t, 2H, J=7.6 Hz), 6.81 (t, 1H, J=7.6 Hz), 6.71 (d, 2H, J=7.6 Hz), 4.38 (s, 2H), 4.09 (br s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 137.3, 136.5, 129.4, 128.1, 127.1, 117.8, 113.0, 48.0, 16.1; IR (neat, cm^{-1}): 3350, 2963, 1602, 1505, 1261, 1099, 1015, 806, 750, 694; Anal. Calcd for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11; S, 13.98. Found: C, 73.03; H, 6.32; N, 5.87; S, 13.59.

*4.2.10. N-(4-((Phenylamino)methyl)phenyl)acetamide (**10**).*[12] Yellow solid; mp 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, 2H, J=8.4 Hz), 7.24 (d, 2H, J=8.4 Hz), 7.09 (t, 2H, J=7.6 Hz), 6.64 (t, 1H, J=7.6 Hz), 6.55 (d, 2H, J=7.6 Hz), 4.21 (s, 2H), 3.94 (br s, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 148.2, 137.0, 135.6, 129.4, 128.2, 120.3, 117.7, 113.0, 48.0, 24.7; IR (KBr, cm^{-1}): 3427, 3301, 1663, 1603, 1512, 1316, 746; Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.67; H, 6.62; N, 11.34.

*4.2.11. N-(Cinnamyl)benzenamine (**11**).*[19] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, J=7.2 Hz), 7.36 (t, 2H, J=8.0, 7.2 Hz), 7.30–7.23 (m, 3H), 6.79 (t, 1H, J=7.6, 7.2 Hz), 6.73–6.65 (m, 3H), 6.41–6.34 (m, 1H), 3.98 (dd, 2H, J=1.2, 5.6 Hz), 3.88 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 136.9, 131.6, 129.4, 128.7, 127.6, 127.1, 126.4, 117.7, 113.1, 46.3. IR (neat, cm^{-1}): IR (neat, cm^{-1}): 3415, 3052, 3023, 2918, 2834, 1601, 1504, 1317, 966, 747, 691; Anal. Calcd (%) for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.01; H, 6.52; N, 6.98.

*4.2.12. N-((Ferrocenyl)methyl)benzenamine (**12**).*[12] Red solid; mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, 2H, J=7.6 Hz), 6.74 (t, 1H, J=7.6 Hz), 6.68 (d, 2H, J=7.6 Hz), 4.26 (s, 2H), 4.20 (s, 5H), 4.16 (br s, 2H), 4.10 (br s, 1H), 3.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 129.4, 117.7, 113.0, 86.6, 68.6, 68.2, 68.0, 43.5; IR (KBr, cm^{-1}): 3401, 2923, 2853, 1605, 1505, 1105, 808, 748, 693, 486; Anal. Calcd for $C_{17}H_{17}FeN$: C, 70.12; H, 5.88; N, 4.81. Found: C, 69.87; H, 5.61; N, 4.63.

*4.2.13. 4-Bromo-N-(4-methoxybenzyl)benzenamine (**13**).*[12] White solid; mp 62–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, 4H, J=8.8 Hz), 6.85 (d, 2H, J=8.8 Hz), 6.46 (d, 2H, J=8.8 Hz), 4.18 (s, 2H), 3.95 (br s, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.2, 132.0, 130.9, 128.8, 114.5, 114.2, 109.1, 55.4, 47.8; IR (KBr, cm^{-1}): 3402, 1591, 1514, 1494, 1255, 1244, 1031, 814; Anal. Calcd for $C_{14}H_{14}BrNO$: C, 57.55; H, 4.83; N, 4.79. Found: C, 57.31; H, 4.52; N, 4.47.

*4.2.14. 4-Chloro-N-(4-methoxybenzyl)benzenamine (**14**).*[2d] White solid, mp 78–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, 2H, J=8.8 Hz), 7.12 (d, 2H, J=8.8 Hz), 6.89 (d, 2H, J=8.4 Hz), 6.54 (d, 2H, J=8.4 Hz), 4.22 (s, 2H), 3.98 (br s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 146.8, 131.0, 129.1, 128.8, 122.0, 114.1, 114.0, 55.3, 47.9. IR (KBr, cm^{-1}): 3409, 1596, 1497, 1246, 1174, 1029, 815; Anal. Calcd (%) for $C_{14}H_{14}ClNO$: C, 67.88; H, 5.70; N, 5.65. Found: C, 68.72; H, 5.41; N, 5.53.

*4.2.15. 4-Fluoro-N-(4-methoxybenzyl)benzenamine (**15**).*[12] White solid; mp 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, 2H, J=8.4 Hz), 6.81–6.77 (m, 4H), 6.49–6.45 (m, 2H), 4.12 (s, 2H), 3.78 (br s, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 157.1, 154.8, 144.7, 144.7, 131.3, 128.9, 115.9, 115.6, 114.2, 113.8, 113.7, 55.4, 48.5; IR (KBr, cm^{-1}): 3402, 1610, 1508, 1245, 1204, 1174, 1029, 820, 741; Anal. Calcd for $C_{14}H_{14}FNO$: C, 72.71; H, 6.10; N, 6.06. Found: C, 72.44; H, 6.15; N, 5.89.

*4.2.16. 4-Methoxy-N-(4-methoxybenzyl)benzenamine (**16**).*[8a] White crystalline solid. Mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2H, J=8.8 Hz), 6.84 (d, 2H, J=8.8 Hz), 6.74 (d, 2H, J=8.8 Hz), 6.57 (d, 2H, J=8.8 Hz), 4.58 (s, 1H), 4.17 (s, 2H), 3.76 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.3, 142.6, 131.8, 128.9, 115.0, 114.2, 114.1, 55.9, 55.4, 48.8; IR (KBr, cm^{-1}): 3373, 2925, 1611, 1513, 1248, 1032, 821; Anal. Calcd (%) for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.89; H, 6.90; N, 5.67.

*4.2.17. 2-((4-Methoxybenzyl)amino)phenol (**17**).*[12] Brown solid; mp 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, 2H, J=8.4 Hz), 6.89–6.82 (m, 3H), 6.74–6.63 (m, 3H), 4.81 (br s, 1H), 4.27 (s, 2H), 4.19 (br s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.7, 137.1, 131.6, 129.0, 121.8, 117.9, 114.4, 114.1, 112.7, 55.4, 48.2; IR (KBr, cm^{-1}): 3396, 3335, 1610, 1512, 1248, 1174, 1111, 1029, 824, 748. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.02; H, 6.28; N, 6.07.

*4.2.18. N-Methyl-N-(4-(trifluoromethyl)benzyl)benzenamine (**18**).*[12] Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H, J=10.8 Hz), 7.35 (d, 2H, J=10.8 Hz), 7.22 (d, 2H, J=9.6 Hz), 6.74 (t, 3H, J=9.6 Hz), 4.58 (s, 2H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.5, 129.4, 127.1, 127.0, 125.7, 125.6, 117.2, 112.6, 56.6, 38.8; IR (neat, cm^{-1}): 1600, 1507, 1326, 1163, 1122, 1066, 1017, 935, 822, 750, 692; Anal. Calcd for $C_{15}H_{14}F_3N$: C, 67.91; H, 5.32; N, 5.28. Found: C, 67.56; H, 5.39; N, 4.98.

*4.2.19. N-Methyl-N-(4-(methylthio)benzyl)benzenamine (**19**).*[12] Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 6H), 6.75–6.68 (m, 3H), 4.47 (s, 2H), 2.98 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 136.8, 136.2, 129.3, 127.5, 127.2, 116.7, 112.5, 56.3, 38.6, 16.2; IR (neat, cm^{-1}): 1599, 1507, 1372, 1213, 1116, 800, 749, 692; Anal. Calcd for $C_{15}H_{17}NS$: C, 74.03; H, 7.04; N, 5.76; S, 13.18. Found: C, 73.70; H, 6.77; N, 5.62; S, 12.81.

*4.2.20. 2-Methoxy-4-((methyl(phenyl)amino)methyl)phenol (**20**).*[12] Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, 2H, J=8.0, 8.4 Hz), 6.89 (d, 1H, J=8.4 Hz), 6.82–6.74 (m, 5H), 5.56 (br s, 1H), 4.47 (s, 2H), 3.85 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 146.8, 144.6, 131.0, 129.3, 119.8, 116.9, 114.4, 112.8, 109.4, 56.8, 56.0, 38.4; IR (neat, cm^{-1}): 3507, 1599, 1506, 1373, 1270, 1120, 1034, 750, 693; Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.82; H, 6.78; N, 5.41.

*4.2.21. N-Benzyl-N-methylbenzenamine (**21**).*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.16 (m, 7H), 6.72–6.66 (m, 3H), 4.47 (s, 2H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 139.1, 129.3, 128.6, 126.9, 126.8, 116.6, 112.4, 56.7, 38.5; IR (neat, cm^{-1}): 1599, 1506, 1452, 1355, 1214, 1118, 749, 729, 692; Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.98; H, 7.38; N, 6.88.

*4.2.22. N-(4-Bromobenzyl)-N-methylbenzenamine (**22**).*[12] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 2H, J=8.4 Hz), 7.19 (t, 2H,

J=8.0 Hz), 7.08 (d, 2H, J=8.4 Hz), 6.72–6.69 (m, 3H), 4.44 (s, 2H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 138.2, 131.8, 129.4, 128.6, 120.7, 117.0, 112.6, 56.4, 38.7; IR (neat, cm^{-1}): 1599, 1507, 748, 692; Anal. Calcd for $C_{14}H_{14}BrN$: C, 60.89; H, 5.11; N, 5.07. Found: C, 60.54; H, 4.89; N, 4.77.

*4.2.23. N-((Furan-2-yl)methyl)-N-methylbenzenamine (**23**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.16 (t, J=7.5, 7.8 Hz, 2H), 6.75 (d, 2H, J=8.3 Hz), 6.67 (t, 1H, J=7.3, J=7.2 Hz), 6.21 (br s, 1H), 6.05 (d, 1H, J=1.7 Hz), 4.37 (s, 2H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.9, 142.3, 129.6, 117.6, 113.6, 110.7, 107.7, 50.3, 38.8. IR (neat, cm^{-1}): 2926, 1600, 1506, 1367, 1346, 1195, 1147, 1013, 994, 930, 748, 691, 599. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.73; H, 6.79; N, 7.33.

*4.2.24. N-(4-Methoxybenzyl)-N-methylbenzenamine (**24**).*[6a] Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.17 (m, 2H), 7.12 (d, 2H, J=8.8 Hz), 6.82 (d, 2H, J=8.8 Hz), 6.74–6.66 (m, 3H), 4.43 (s, 2H), 3.75 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 149.9, 131.0, 129.3, 128.1, 116.6, 114.1, 112.6, 56.2, 55.4, 38.4; IR (neat, cm^{-1}): 3419, 2932, 2834, 1600, 1510, 1246, 1035, 748, 692; Anal. Calcd (%) for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.08; H, 7.42; N, 6.07.

*4.2.25. N-Methyl-N-(pyridin-2-ylmethyl)benzenamine (**25**).* Orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, 1H, J=4.7 Hz), m (1H, 7.64–7.59), 7.28–7.16 (m, 4H), 6.76–6.73 (m, 3H), 4.68 (s, 2H), 3.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 149.8, 149.6, 137.2, 129.6, 122.3, 121.1, 117.0, 112.6, 59.1, 39.4; IR (neat, cm^{-1}): 2924, 1604, 1587, 1569, 1508, 1470, 1436, 1345, 1241, 1191, 765, 757, 695; Anal. Calcd (%) for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.51; H, 6.98; N, 13.99.

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