Smiles rearrangement for the synthesis of diarylamines

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Abstract
A protocol for the one-pot synthesis of diarylamines via Smiles rearrangement under microwave irradiation has been developed. Various diarylamines were effectively synthesized starting from readily available substituted phenols, arylamines and chloroacetyl chloride in moderate to good yields (58–92%).

Keywords: Smiles rearrangement, diarylamines, phenol, amine, synthesis

Introduction

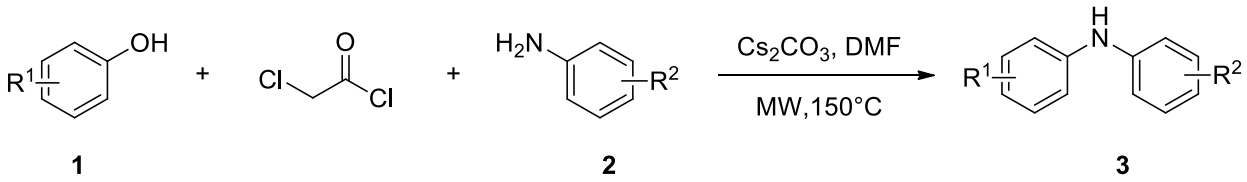
Diarylamines represent an important class of compounds due to their wide applications and special pharmacological activities.[1,2] Therefore, a facile and reliable access to diarylamine derivatives is of great importance. Among numerous methods to prepare diarylamines, the use of metallic catalysts, especially $Pd_2(dba)_3$ and $Pd(OAc)_2$, is one of the most attractive routes.[3–10] These metals catalyze the reaction only in the form of metal-organic complexes, which constitute the active catalysts in many C–N bond formation cross-coupling methodologies for the synthesis of diarylamines, while such complexes are quite difficult to prepare and extremely air sensitive.[11] Although the reactions can sometimes be catalyzed by diverse ligands, the different kind and concentration of ligands may lead to various products. Accordingly, the amount of ligands must be selected carefully.[12]

On the other hand, Wolfe *et al.*[13] developed a general procedure for the Pd-catalyzed inter-molecular amination which proceeds at ambient temperatures, but only aryl iodides can react with a few substituted arylamines in the presence of a strong base like NaO*t*-Bu. An alternative method of C–N bond formation for the preparation of *N*-arylamines is the Smiles rearrangement.

Solid-liquid phase-transfer catalyst tris(3,6-dioxaheptylamine) (TDA-1) activates *N*-alkylation of chlorinated phenoxyacetamides in the presence of KOH via Smiles rearrangement; however, the substrates are limited to trichlorophenol.[14] Substituted aryloxyacetamides with oxygen and nitrogen separated by the CH_2CO group undergo Smiles rearrangement to give *N*-alkyl- and *N*-arylamines under EtONa/EtOH or NaH/DMF conditions, while only aryloxy rings containing only a weak or no electron-withdrawing group proceed in such a rearrangement.[15] Acemoglu found that the major side reactions to form *N*-arylamines can be avoided by using K_2CO_3/*i*-PrOH system followed by MeONa/MeOH.[16] It was also found that a Smiles rearrangement is involved in the preparation of nitro group containing alkylarylamines,[17] and *N*-arylamines.[18]

Results and Discussion

Our interest in reactions via Smiles rearrangement with two or more reagents being used simultaneously led us to use substituted 2-chlorophenols and arylamines, activated by chloroacetyl chloride for C–N bond formation to obtain diarylamines and arylalkylamines.[19] The limitation of our methodology is that all phenols contain a chlorine atom in *ortho* position of the phenolic hydroxyl group. This work, combined with our Smiles rearrangement reaction system has recently led us to design the reaction of diverse phenols, amines and chloroacetyl chloride to prepare diarylamines, with chloroacetyl chloride activating these reactions (Scheme 1).



Scheme 1. One-pot synthesis of diarylamines **3**.

According to our previous study, the use of Cs_2CO_3 in DMF was found to be the most effective catalyst. The reaction was explored as follows: 4-Methoxyaniline (1.0 equiv.) was dissolved in anhydrous DMF with Cs_2CO_3 (3.2 equiv.) as base. Addition of chloroacetyl chloride (1.2 equiv.) was followed by *m*-cresol. The reaction went smoothly under microwave irradiation for 60 min to give *N*-(4-methoxyphenyl)-3-methylaniline **3a** (77% yield; Table 1, entry 1). Physical and spectral data (mp, ^{1}H and ^{13}C NMR) of **3a** were in agreement with the structure.[20]

The scope and electronic effect of the present method were examined using a variety of substituted phenols and anilines. As shown in Table 1, *m*- and *p*-cresol, *p*-nitrophenol, and *p*-hydroxybenzaldehyde, and aniline, *p*-methoxyaniline, *o*-, *m*-, *p*-toluidine, *p*-nitroaniline were well tolerated in this reaction. The reaction of electron-deficient phenols and electron-rich anilines is more favorable for the rearrangement. Thus, the reactions of electron-deficient 4-nitrophenol **1c** and 4-hydroxybenzaldehyde **1d** with electron-rich substituted anilines **2a**–**d, 2f**

were completed within a short time (30–40 min), and the yields of diarylamines **3l**–**s** were satisfactory (75–92%). For the reaction of 4-hydroxybenzaldehyde **1d** with electron-deficient 3-nitroaniline **2g**, the yield was lower (65%). In other cases, *m*-cresol **1a** and *p*-cresol **1b** reacted with anilines **2a**–**f** to give the corresponding diarylamines **3a**–**k** after a longer reaction time (60–80 min). Considering a stronger base may shorten the reaction time of the Smiles rearrangement,[21] NaOH was employed, but no products were found under this condition.

Table 1. One-pot synthesis of diarylamine **3**

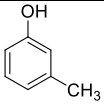
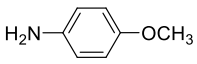
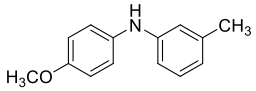
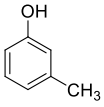
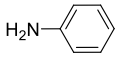
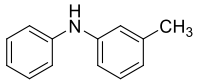
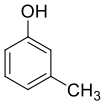
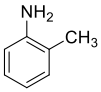
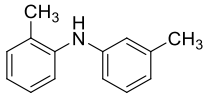
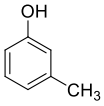
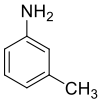
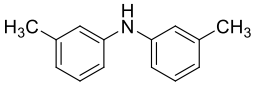
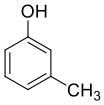
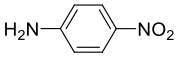
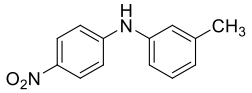
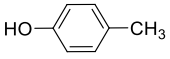
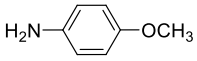
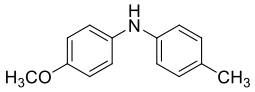
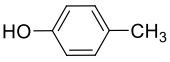
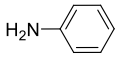
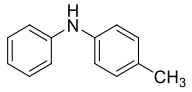
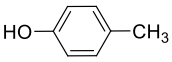
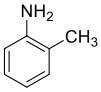
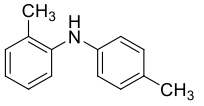
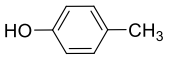
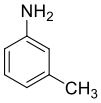
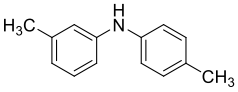
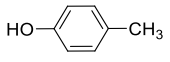
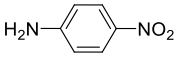
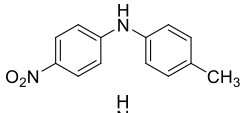
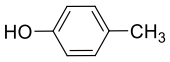
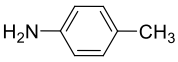
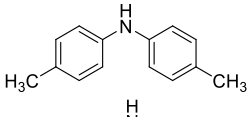
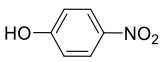
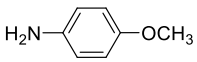
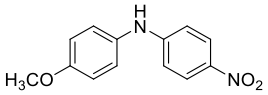
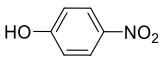
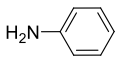
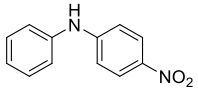
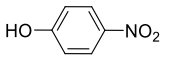
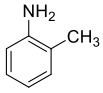
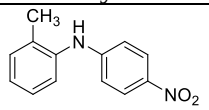
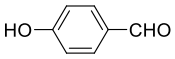
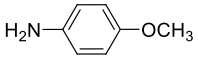
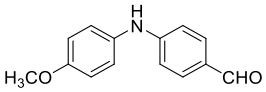
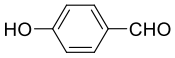
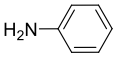
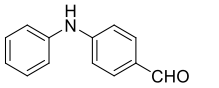
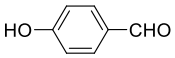
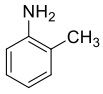
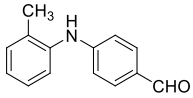
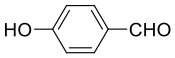
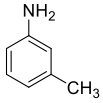
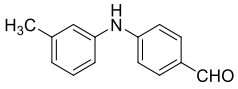
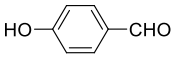
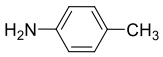
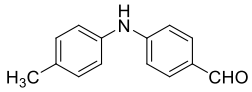
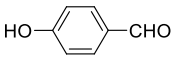
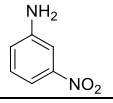
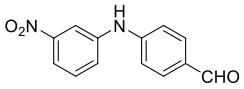
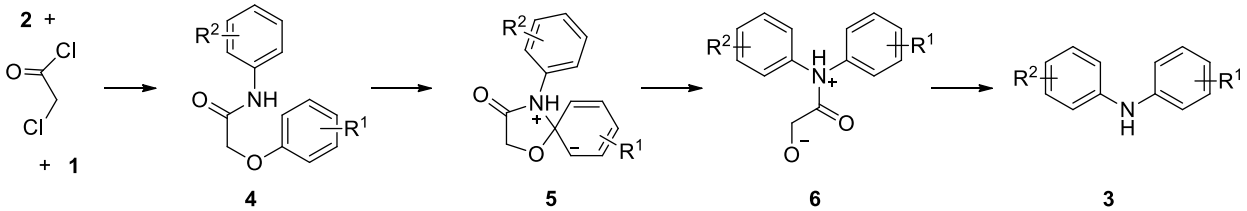
Entry	Phenol		Amine		Diarylamine		Yield %[a]
1		**1a**		**2a**		**3a**	77
2		**1a**		**2b**		**3b**	90
3		**1a**		**2c**		**3c**	67
4		**1a**		**2d**		**3d**	81
5		**1a**		**2e**		**3e**	65
6		**1b**		**2a**		**3f**	80
7		**1b**		**2b**		**3g**	90
8		**1b**		**2c**		**3h**	63
9		**1b**		**2d**		**3i**	68
10		**1b**		**2e**		**3j**	58
11		**1b**		**2f**		**3k**	74
12		**1c**		**2a**		**3l**	75
13		**1c**		**2b**		**3m**	88

Table 1. Continued

Entry	Phenol		Amine		Diarylamine		Yield %[a]
14		**1c**		**2c**		**3n**	80
15		**1d**		**2a**		**3o**	92
16		**1d**		**2b**		**3p**	89
17		**1d**		**2c**		**3q**	82
18		**1d**		**2d**		**3r**	89
19		**1d**		**2f**		**3s**	89
20		**1d**		**2g**		**3t**	65

[a]Yield of isolated product. Reaction conditions: phenols (1.0 mmol), amines (1.0 mmol), chloroacetyl chloride (1.2 mmol), Cs_2CO_3 (3.2 mmol), DMF (25 mL), 150 °C, MW irradiation.

A hypothesized explanation for the results is given in Scheme 2. The O-alkylated phenol **4** undergoes Smiles rearrangement by nucleophilic attack of the nitrogen at the benzene ring carbon atom attached to oxygen forming a new C–N bond to give spiro-intermediate **5**. Rearomatization and opening of the oxazolidinone ring in **5** followed by alkaline hydrolysis of the resulting intermediate **6** in the presence of Cs_2CO_3 affords the diarylamine derivative **3**. As shown by the reactivity of examples mentioned above, the intramolecular nucleophilic aromatic substitution of **4** forming intermediate **5** is favored by electron-donating groups R^2 in the aniline ring and by electron-withdrawing groups R^1 in the phenol ring.



Scheme 2. Proposed mechanism for the formation of diarylamines **3** via Smiles rearrangement.

Conclusions

In summary, various diarylamines **3** were effectively synthesized starting from readily available substituted phenols, anilines, and chloroacetyl chloride (1.0:1.0:1.2 equiv.) via Smiles rearrangement. Mechanistic studies of this method, as well as further applications in the preparation of biologically interesting compounds are under active investigation in our laboratory.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra (at 300 MHz and 75 MHz, respectively) were recorded in $CDCl_3$ with tetramethylsilane as internal reference on a Bruker Advance 300 FT spectrometer. Chemical shifts were reported in parts per million. Mass spectra (MS) were measured by ESI. $CDCl_3$ was used as delivered from Sigma-Aldrich. Silica gel (70–230 mesh) was used for flash column chromatography. All reactions were monitored by TLC using 0.25 mm silica gel plates with UV indicator (Merck 60F254). The microwave-assisted reaction time is the hold time at the final temperature. Unless otherwise noted, other reagents were obtained from commercial suppliers and used without further purification. Microwave XH-100B (made in Beijing XiangHu Science and Technology Development Co., LTD, P.R. China) was used to carry out the reactions.

Smiles rearrangement for the synthesis of diarylamines (3). General procedure
To a magnetically stirred solution of arylamine **2** (1.0 mmol) and Cs_2CO_3 (1042.6 mg, 3.2 mmol) in dry DMF, cooled in an ice bath, were added chloroacetyl chloride (135.5 mg, 1.2 mmol) and substituted phenol **1** (1.0 mmol). The reaction mixture was stirred for 30 min at room temperature, then placed in a microwave oven (600 W, 150 °C) and irradiated for 30–80 min. The solvent was removed under vacuum, and water (20 mL) was added into the residue. The mixture was then extracted with ethyl acetate (4 x 30 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, and evaporated under vacuum to give the crude product **3**. The pure product **3** was obtained by column chromatography on silica gel.
***N*-(4-Methoxyphenyl)-3-methylaniline (3a).**[22] Gray solid; mp 72–75 °C (lit.[22] 75–76 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H; CH_3), 3.80 (s, 3H; OCH_3), 5.45 (s, br, 1H; NH), 6.64–7.24 (m, 8H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5 (CH_3), 55.6 (OCH_3), 112.8 (CH), 114.6 (CH), 116.3 (CH), 120.5 (CH), 122.2 (CH), 129.1 (CH), 135.9 (C), 139.1 (C), 145.1 (C), 155.2 (C).
3-Methyl-*N*-phenylaniline (3b).[23] Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H; CH_3), 5.58 (s, 1H; NH), 6.85–7.28 (m, 9H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7 (CH_3), 116.8 (CH), 117.8 (CH), 118.9 (CH), 120.2 (CH), 120.9 (CH), 129.3 (CH), 129.8 (CH), 130.9 (CH), 140.2 (C), 143.9 (C).

2-Methyl-*N*-(*m*-tolyl)aniline (3c).[24] Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H; CH_3), 2.28 (s, 3H; CH_3), 5.29 (s, br, 1H; NH), 6.69–7.23 (m, 8H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8 (CH_3), 21.45 (CH_3), 114.5 (CH), 118.1 (CH), 118.8 (CH), 121.3 (CH), 121.8 (CH), 126.7 (CH), 128.1 (C), 129.1 (CH), 130.8 (CH), 139.1 (C), 141.2 (C), 143.8 (C).

Di-(*m*-tolyl)amine (3d).[25] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 6H; CH_3), 5.46 (s, br, 1H; NH), 6.69 (d, J = 7.2 Hz, 2H; H_{Ar}), 6.79–6.83 (m, 4H; H_{Ar}), 7.07–7.12 (m, 2H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4 (CH_3), 114.8 (CH), 118.5 (CH), 121.6 (CH), 129.0 (CH), 139.0 (C), 143.1 (C).

3-Methyl-*N*-(4-nitrophenyl)aniline (3e). Brown solid; mp 130–133 °C. R_f = 0.45 (petroleum ether/AcOEt, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H; CH_3), 6.29 (s, br, 1H; NH), 6.94, 6.91 (AA'; 2H; H_{Ar}), 6.97–7.02 (m, 3H; H_{Ar}), 7.25–7.27 (m, 1H, H_{Ar}), 8.13, 8.10 (XX'; 2H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4 (CH_3), 113.6 (CH), 119.0 (CH), 122.6 (CH), 125.5 (CH), 126.2 (CH), 129.5 (C), 139.4 (C), 139.6 (C), 139.7 (C), 150.3 (C). MS (ESI): *m/z* (%) 229 (8) [M+1], 212 (57), 182 (74), 167 (100). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.40; H, 5.30; N, 12.27. Found: C, 68.64; H, 5.66; N, 11.98.

4-Methoxy-*N*-(*p*-tolyl)aniline (3f).[20] Gray solid; mp 80–82 °C (lit.[20] 82 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H; CH_3), 3.78 (s, 3H; OCH_3), 5.38 (s, br, 1H; NH), 6.83–6.85 (m, 4H; H_{Ar}), 7.00–7.04 (m, 4H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (CH_3), 55.6 (OCH_3), 114.6 (CH), 116.5 (CH), 121.1 (CH), 129.3 (C), 129.8 (CH), 136.6 (C), 142.4 (C), 154.7 (C).

4-Methyl-*N*-phenylaniline (3g).[26] White solid; mp 85–87 °C (lit.[26] 87 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H; CH_3), 5.49 (s, br, 1H; NH), 6.54–7.22 (m, 9H; H_{Ar}).

2-Methyl-*N*-(*p*-tolyl)aniline (3h).[27] Yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H; CH_3), 2.30 (s, 3H; CH_3), 5.29 (s, br, 1H; NH), 6.85–6.95 (m, 3H; H_{Ar}), 7.06–7.24 (m, 5H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8 (CH_3), 20.6 (CH_3), 117.2 (CH), 118.6 (CH), 121.0 (CH), 126.7 (CH), 126.9 (C), 129.8 (CH), 130.4 (C), 130.8 (CH), 141.0 (C), 142.0 (C).

3-Methyl-*N*-(*p*-tolyl)aniline (3i).[28] Yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H; CH_3), 2.28 (s, 3H; CH_3), 5.49 (s, br, 1H; NH), 6.68 (d, J = 7.2 Hz, 1H; H_{Ar}), 6.80–7.21 (m, 7H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 (CH_3), 21.5 (CH_3), 113.9 (CH), 117.5 (CH), 118.8 (CH), 121.1 (CH), 129.1 (CH), 129.8 (CH), 130.7 (C), 139.1 (C), 140.3 (C), 143.8 (C).

4-Methyl-*N*-(4-nitrophenyl)aniline (3j).[29] Brown solid; mp 132–135 °C (lit.[29] 137 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H; CH_3), 6.29 (s, br, 1H; NH), 6.88, 6.85 (AA'; 2H; H_{Ar}), 7.12, 7.09 (AA'; 2H; H_{Ar}), 7.21, 7.18 (BB'; 2H; H_{Ar}), 8.10, 8.07 (XX'; 2H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 (CH_3), 113.1 (CH), 122.6 (CH), 126.2 (CH), 130.2 (CH), 134.8 (C), 136.6 (C), 139.2 (C), 150.8 (C).

Di-(*p*-tolyl)amine (3k).[30] Light yellow solid; mp 74–77 °C (lit.[30] 73–75 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 6H; CH_3), 5.49 (s, br, 1H; NH), 6.95, 6.92 (AA'; 4H; H_{Ar}), 7.07, 7.04 (BB'; 4H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 (CH_3), 117.9 (CH), 129.8 (CH), 130.1 (C), 141.1 (C).

4-Methoxy-*N*-(4-nitrophenyl)aniline (3l).[31] Brown solid; mp 149–152 °C (lit.[31] 152–153 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H; OCH_3), 6.16 (s, 1H; NH), 6.78, 6.75 (AA'; 2H; H_{Ar}),

6.95, 6.92 (AA'; 2H; H_{Ar}), 7.17, 7.14 (BB'; 2H; H_{Ar}), 8.10, 8.07 (XX'; 2H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5 (OCH_3), 112.6 (CH), 114.9 (CH), 125.5 (CH), 126.3 (CH), 131.9 (C), 139.0 (C), 151.7 (C), 157.4 (C).

4-Nitro-*N*-phenylaniline (3m).[32] Brown solid; mp 131–133 °C (lit.[32] 131 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.40 (s, 1H; NH), 6.96, 6.93 (AA'; 2H; H_{Ar}), 7.14-7.42 (m, 5H; H_{Ar}), 8.13, 8.10 (XX'; 2H; H_{Ar}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.6 (CH), 121.9 (CH), 124.6 (C), 126.2 (CH), 129.7(CH), 139.4 (C), 139.6 (C), 150.2 (C).

2-Methyl-*N*-(4-nitrophenyl)aniline (3n). Brown solid; mp 130–133 °C. R_f = 0.48 (petroleum ether/AcOEt, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H; CH_3), 6.10 (s, 1H; NH), 6.73, 6.70 (AA'; 2H; H_{Ar}), 7.18–7.31 (m, 4H; H_{Ar}), 8.10, 8.07 (XX'; 2H; H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8 (CH_3), 113.0 (CH), 124.7 (CH), 126.1 (CH), 126.2 (CH), 127.1 (CH), 131.4 (CH), 133.2 (C), 137.5 (C), 139.1 (C), 151.3 (C). MS (ESI): *m/z* (%) 229 (9) [M+1], 212 (100), 182 (77), 168 (94). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.40; H, 5.30; N, 12.27. Found: C, 68.40; H, 5.43; N, 12.36.

4-(4-Methoxyphenylamino)benzaldehyde (3o).[33] Brown solid; mp 108–111 °C (lit.[33] 113 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H; OCH_3), 6.08 (s, 1H; NH), 6.87, 6.84 (AA'; 2H; H_{Ar}), 6.94, 6.91 (AA'; 2H; H_{Ar}), 7.17, 7,14 (BB'; 2H; H_{Ar}), 7.72, 7.69 (XX'; 2H; H_{Ar}), 9.75 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5 (OCH_3), 113.4 (CH), 114.8 (CH), 125.1 (CH), 127.8 (C), 132.2 (CH), 132.6 (C), 151.4 (C), 157.0 (C), 190.2 (CHO).

4-(Phenylamino)benzaldehyde (3p).[34] Brown solid; mp 94–97 °C (lit.[34] 95–97 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.38 (s, 1H; NH), 7.04, 7.01 (AA'; 2H; H_{Ar}), 7.09–7.39 (m, 5H; H_{Ar}), 7.75, 7.72 (XX'; 2H; H_{Ar}), 9.78 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.4 (CH), 121.3 (CH), 123.8 (CH), 128.4 (C), 129.5 (CH), 132.1 (CH), 140.0 (C), 149.8 (C), 190.4 (CHO).

4-(*o*-Tolylamino)benzaldehyde (3q). Brown solid; mp 85–87 °C. R_f = 0.26 (petroleum ether /AcOEt, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H; CH_3), 6.00 (s, 1H; NH), 6.83, 6.80 (AA'; 2H; H_{Ar}), 7.13–7.27 (m, 4H; H_{Ar}), 7.73, 7.70 (XX'; 2H; H_{Ar}), 9.76 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.9 (CH_3), 113.8 (CH), 124.1 (CH), 125.4 (CH), 127.0 (CH), 127.9 (C), 131.3 (CH), 132.1 (CH), 132.6 (C), 138.0 (C), 151.0 (C), 190.3 (CHO). MS (ESI): *m/z* (%) 212 (28) [M+1], 184 (12), 183 (9), 182 (14), 169 (52), 168 (24), 103 (48), 88 (100), 75 (11), 60 (10). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.42; H, 6.32; N, 6.66.

4-(4-(*m*-Tolylamino)benzaldehyde (3r). Brown solid; mp 117–119 °C. R_f = 0.23 (petroleum ether/AcOEt, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H; CH_3), 6.37 (s, 1H; NH), 6.92–7.24 (m, 6H; H_{Ar}), 7.74, 7.71 (AA', 2H; H_{Ar}), 9.77 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4 (CH_3), 114.4 (CH), 118.3 (CH), 121.9 (CH), 124.7 (CH), 128.2 (C), 129.3 (CH), 132.1 (CH), 139.5 (C), 139.9 (C), 150.0 (C), 190.4 (CHO). MS (ESI): *m/z* (%) 212 (33) [M+1], 183 (21), 169 (69), 103 (81), 88 (100), 75 (34), 73 (6), 60 (21). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.20; H, 6.35; N, 6.61.

4-(*p*-Tolylamino)benzaldehyde (3s). Brown solid; mp 85–88 °C. R_f = 0.20 (petroleum ether/ AcOEt, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H; CH_3), 6.20 (s, 1H; NH), 6.97, 6.94 (AA'; 2H; H_{Ar}), 7.12, 7.09 (AA'; 2H; H_{Ar}), 7.19, 7.16 (BB'; 2H; H_{Ar}), 7.73, 7.70 (XX'; 2H; H_{Ar}),

9.77 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8 (CH_3), 113.9 (CH), 122.1 (CH), 128.1 (C), 130.1 (CH), 132.1 (CH), 134.0 (C), 137.2 (C), 150.5 (C), 190.3 (CHO). MS (ESI): *m/z* (%) 243 (16) [M+1], 197 (42), 168 (80), 167 (100). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.42; H, 6.36; N, 6.55.

4-(3-Nitrophenylamino)benzaldehyde (3t). Yellow solid; mp 152–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.35 (s, 1H; NH), 7.16, 7.13 (AA'; 2H; H_{Ar}), 7.49-7.52 (m, 2H; H_{Ar}), 7.85, 7.82 (XX'; 2H; H_{Ar}), 7.87–8.04 (m, 2H; H_{Ar}), 9.87 (s, 1H; CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1 (CH), 116.1 (CH), 117.6 (CH), 122.3 (C), 125.2 (C), 130.4 (C), 132.1 (CH), 142.1 (C), 147.6 (C), 148.5 (C), 190.3 (CHO).

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