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C-N cross-coupling reaction catalysed by reusable $CuCr_2O_4$ nanoparticles under ligand-free condition: A highly efficient synthesis of triarylamines

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A convenient, efficient and ligand-free method for the C-N coupling reaction of anilines and aryl iodides was performed using $CuCr_2O_4$ nanoparticles. Copper chromite nanocatalyst improved rate and facility of the synthesis of triarylamines. The heterogeneous catalyst was fully characterized by scanning electron microscopy, IR and X-ray diffraction techniques. Recyclability, excellent yields of products and short reaction times are the important advantages of this ligand-free procedure by using the $CuCr_2O_4$ nanoparticles.

1. Introduction

The formation of C-N bond is widespread in numerous compounds such as triarylamines which is used in synthesis of biological,[1] pharmaceutical,[2] natural products,[3] dyes[4] and polymers.[5-8] The most common synthetic procedures for the preparation of triarylamines is the palladium[9,10]-or copper[11-13]-assisted classic Ullman coupling reaction. This reaction often needs harsh conditions such as high temperature (>200 °C) and stoichiometric or greater amount of copper reagent.[14-16] Low yield of triarylamines and sensitivity to catalyst type are other limitation of the Ullman reaction. Recently, many resarchs has been focused to develop catalytic systems to decrease the environmental impact of the methods.[17-20] Palladium and complexes with chelating ligands[21-25] have been investigated significantly for the cross-coupling of anilines with aryl halides. In these systems, the electron-rich ligand chelated with the metal displays a critical role in the C-N cross coupling. Different chelating ligands were examined for the single step synthesis of triarylamines. Use of chelating ligands leads to the formation of triarylamine derivatives selectively with high catalytic activity. Bidentate ligands shown higher activity.[26] Diazabutadienes (DABs) were demonstrated as efficient ligands in the Cu-catalyzed C–N coupling reaction for the synthesis of triarylamines.[27] The recent work reported preparation of various triphenylamines in good yields using CuCl with 8-hydroxyquinoline as the chelating ligand.[28].

Gujadhur *et al* reported a synthetic protocol for the synthesis of functionalized diaryl- and triarylamines under mild conditions, using $Cu(PPh_3)_3Br$ as the catalyst and cesium carbonate as the base. With PPh_3 as a ligand the reaction did not proceed efficiently.[29] Furthermore, triarylamines was synthesized by ligand-free copper iodide using Cs_2CO_3 as the base.[30] The ligand-free copper-catalysed Ullman reaction was carried out in tetraethyl orthosilicate (TEOS) as the solvent and this method needs high temperature (145°C) and long reaction time to terminate the reaction.

Also we reported an efficient method for the synthesis of triarylamine derivatives mediated by copper iodide nanoparticles and 1,10-phenanthroline ligand. This system enhanced the rate and ease of reaction and exhibited a high influence in the synthesis of various amine derivatives. But CuI nanoparticle requires a ligand to have effective performance and it is not recyclable.[31]

Nanoparticles containing high surface-to-volume ratio and reactive morphologies have been used as suitable catalysts for organic reactions. [32-34] Moreover the nanomaterial catalyzed synthesis provide the advantages of high atom efficiency, simple separation of product and easy recovery and recyclability of the nanocatalysts. In the recent years, copper chromite ($CuCr_2O_4$) has been applied extensively as a heterogeneous catalyst in many reactions. These

catalyst are inexpensive, very stable with strong resistance to acids and alkalis, and they have high melting points. These properties make it appropriate for use as solid heterogeneous catalysts in organic reactions.[35-37] Copper chromite nanoparticles indicated an important level of performance as catalysts in terms of reactivity and selectivity in improvement of organic synthesis yields.[38-41]

In this research we reported an efficient catalysis of $CuCr_2O_4$ nanoparticles for the C-N cross-coupling reactions of anilines with iodobenzenes. Our procedure is simple, convenient and ligand-free, and the $CuCr_2O_4$ nanoparticles can be recycled.

2. Results and discussion

2.1. Characterization of $CuCr_2O_4$ nanoparticles

Nano crystalline of Copper chromite was characterized by IR, SEM and XRD analysis. Fig.1. represents XRD pattern of $CuCr_2O_4$ nanoparticles. All of the detected diffraction peaks are indexed by the spinel-phase structure of $CuCr_2O_4$ (JCPDS No. 88-0110) demonstrating a high phase purity of the product. The average crystalline size was estimated using the Scherrer formula on the highest intensity peak for each sample. An average size was obtained around 20–30 nm for $CuCr_2O_4$ nanoparticles.

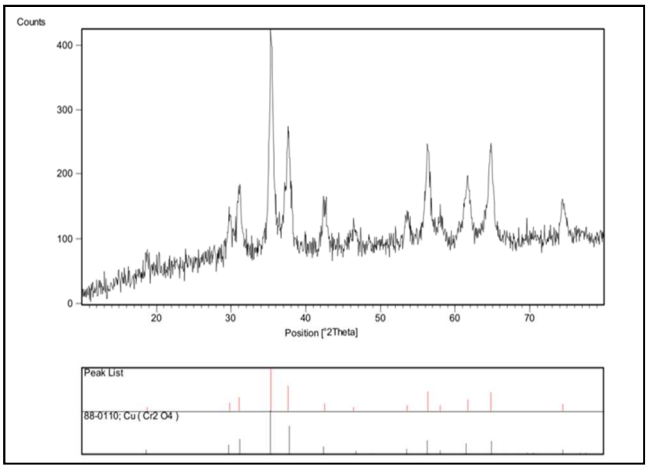


Fig.1. The XRD pattern of $CuCr_2O_4$ nanoparticles

The SEM image of nano $CuCr_2O_4$ proves that the nanoparticles have a uniform size and spherical shape as shown in Fig. 2.

The FT-IR spectra of $CuCr_2O_4$ nanoparticles was illustrated in Fig.3. As shown in this figure, the absorption bands at 615 cm^{-1} and 514 cm^{-1} refers to $Cr_2O_4^{2-}$ group. Also, the bands at 911 cm^{-1} and 999 cm^{-1} were assigned to Cr-O chromate group.

2.2. Synthesis of triaryl amines by $CuCr_2O_4$ nanoparticle

The C-N cross coupling reaction was performed by the Ullman condensation of aryl amine with aryl iodide (molar ratio 1:2) in the presence of potassium hydroxide as the base and $CuCr_2O_4$ nano catalyst in toluene at reflux condition under nitrogen atmosphere (Scheme 1).

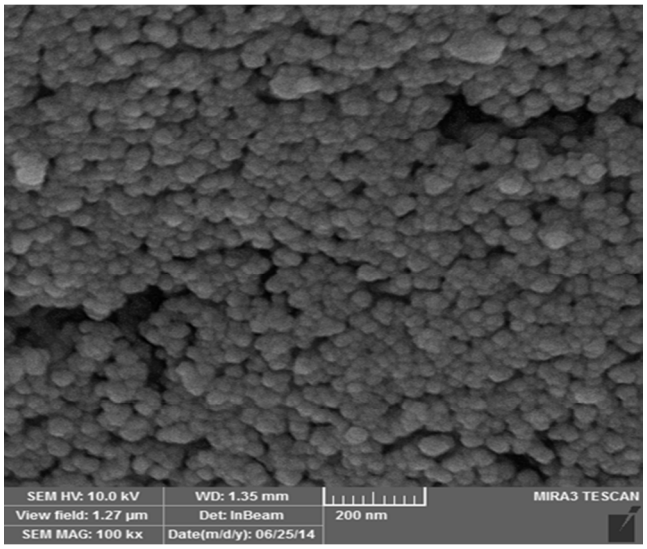


Fig.2. SEM image of $CuCr_2O_4$ nanoparticles

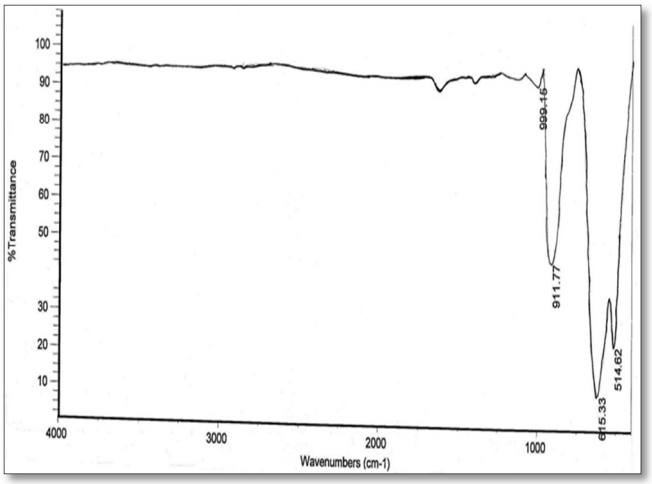
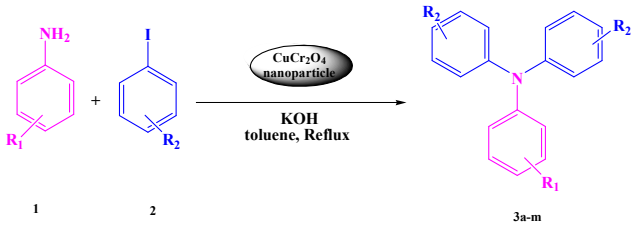


Fig.3. FT-IR spectrum of $CuCr_2O_4$ nanoparticles



Scheme 1. Synthesis of triarylamine derivatives.

Catalytic effects of five types of catalysts including CuBr, CuCl, CuI, CuO, $CuCr_2O_4$ were investigated in the reaction of aniline and iodo-benzene as listed in Table 1. The results of this table shows that the reaction was carried out efficiently in the presence of nano $CuCr_2O_4$. The highest yield was obtained by 4% mol of copper chromite nanoparticle (Table 1, entry 7). Notably, increasing of this amount did not show any change in yield and time of reaction. Also the reaction was performed by nano $CuCr_2O_4$ (4%) and 1,10-phenantroline (4%) as a ligand and it was not obtained better yield

(Table1, entry 8). Entry 9 in Table 1 represent performance of CuI nanoparticles in the synthesis of triphenylamine.[28] This system requires 1,10-phenantroline to achieve good yield of product. While $CuCr_2O_4$ nano catalyst without 1,10-phenantroline shows high influence in the synthesis of triarylamines with better yields. This behaviour can be described that chromite plays role of ligand in the $CuCr_2O_4$. It should be noted that the reaction did not progress in the absence of catalyst (Table 1, entry 10).

Table1. Optimization of model reaction using various catalysts

Entry	Catalytic system (mol%)	Time(h)	Yield [a](%)
1	CuCl (20%)	48	29
2	CuBr (20%)	48	33
3	CuI (20%)	35	48
4	CuO (20%)	35	59
5	$CuCr_2O_4$ (20%)	30	66
6	Nano $CuCr_2O_4$ (3%)	6	92
7	**Nano $CuCr_2O_4$ (4%)**	**6**	**95**
8	Nano $CuCr_2O_4$ (4%), 1,10-phen (4%)	6	93
9	Nano CuI (3%), 1,10-phen (3%)	8	92
10	Without catalyst	48	trace

[a]Isolated yield.

Furthermore we have examined various solvents with varying polarity for this reaction. It was demonstrated that toluene was the best choice over any organic solvents such as 1,4-dioxane, THF, acetonitrile and xylene (Table 2).

We then examined the effect of leaving group in aryl halides applied in the C-N cross-coupling reactions using $CuCr_2O_4$ nanoparticles. Aryl chloride, aryl bromide and aryl iodide were investigated for this protocol. Aryl iodide is more effective for the synthesis of triarylamines as resulted in Table 3. The reaction of aniline with 2.5 equiv of bromobenzene or chlorobenzene afforded triphenylamines in lower yield than iodobenzene (Table 3).

We also applied $CuCr_2O_4$ nano catalyst in synthesis of triarylamine derivatives from various aryl amines and aryl iodides under similar condition as represented in Table 4. The results of this table indicates that the excellent yields were achieved in the C-N cross coupling reaction at the presence of nano $CuCr_2O_4$ (4% mol) under reflux. Electron-withdrawing and electron-donating substituents for aryl halide and aniline were given good to excellent yields of triarylamines under above-mentioned conditions. The highest yields of triarylamine were obtained by the electron donating para-methoxy group as substituent for aryl halide and aniline (Table 4, entries 6 and 12). Although ortho-substituted aniline and aryl halide were resulted in good yield (entries 4 and 10 in Table 4) but, due to steric effects, yields are lower than para-substituted aniline. Aryl iodides represent higher reactivity than aryl bromides in the Ullman reaction. The coupling reaction of 1-bromo-4-iodobenzene and aniline derivatives formed the products containing bromide on the aromatic ring (Table 4, entries 2-7).

Table 2. Optimization of reaction solvent for the synthesis of triphenylamine

Entry	Solvent/condition	Time(h)	Yield[a](%)
1	CH_3CN/ reflux	8	71
2	THF/ reflux	10	62
3	1,4-Dioxane/ reflux	10	65
4	Xylene/ reflux	6	92
5	Toluene/ reflux	6	95
6	Toluene/ 80°C	8	76

[a]Isolated yield.

Table 3. Investigation of leaving group effect in Ar-X for the synthesis of triphenylamine using $CuCr_2O_4$ nanoparticles[a]

Entry	X	Time(h)	Yield[a](%)
1	Cl	18	43
2	Br	15	64
3	I	6	95

[a]Isolated yield.

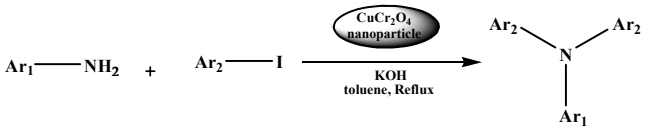
2.3. Proposed mechanism

A probable mechanism for the C-N cross coupling reaction using $CuCr_2O_4$ nanoparticle has been illustrated in Scheme 2. The synthesis of triaryl amines occurs by oxidative addition followed by the reductive elimination. These processes performed on the nano Cu Cr_2O_4 which have highly effective catalytic behaviour in terms of its high surface area.

2.4. Reusability experiments

The $CuCr_2O_4$ nano catalyst is recyclable without loss of activity (Fig.4.). After completion of the Ullman reaction, the mixture was treated with water and CH_2Cl_2. The $CuCr_2O_4$ nanoparticles were recovered from the aqueous phase by centrifugation. It was reused for the new C-N cross-coupling reaction of aniline with iodobenzene for five runs, and minimal loss of activity was detected providing the products in high yield.

Table 4. Synthesis of triaryl amines using $CuCr_2O_4$ nanoparticles[a]



Entry	Product [b]	Ar_1	Ar_2	Time (h)	Yield (%)[c]	Mp(°C)[d]
1	3a	Phenyl	Phenyl	6	95	126-127[42]
2	3b	Phenyl	4-Bromo Phenyl	7	86	-[e]
3	3c	4-Methyl Phenyl	4-Bromo Phenyl	8	91	83-85[43]
4	3d	2-Methoxy Phenyl	4-Bromo Phenyl	9	85	91-92
5	3e	3- Methoxy Phenyl	4-Bromo Phenyl	10	82	110-112
6	3f	4- Methoxy Phenyl	4-Bromo Phenyl	6	93	74-76[44]
7	3g	4-Bromo Phenyl	4-Bromo Phenyl	10	81	140-142[45]
8	3h	4-Bromo Phenyl	Phenyl	10	84	110-112[46]
9	3i	4-Bromo Phenyl	4- Methyl Phenyl	7	88	104-105[47]
10	3j	4-Bromo Phenyl	2- Methoxy Phenyl	10	80	120-121
11	3k	4-Bromo Phenyl	3- Methoxy Phenyl	9	83	89-91[48]
12	3l	4-Bromo Phenyl	4- Methoxy Phenyl	6	87	95-96[49]
13	3m	4-Methyl Phenyl	4-Nitro Phenyl	12	77	190-192[50]
14	3n	4-Methyl Phenyl	4-Carbomethoxy Phenyl	12	68	111-113
15	3o	4,6-Dimethyl-pyrimidin	Phenyl	12	79	115-116[50]

[a] Reactions conditions: aniline and aryl iodides= 1:2.5, $CuCr_2O_4$nanoparticles (4% mol) and potassium hydroxide, toluene, reflux.
[b] All products were characterized from their spectroscopic (IR, ^{1}H NMR and ^{13}C NMR), Mass and CHN analysis
[c] Isolated yield.
[d] Literature references
[e] Viscose liquid

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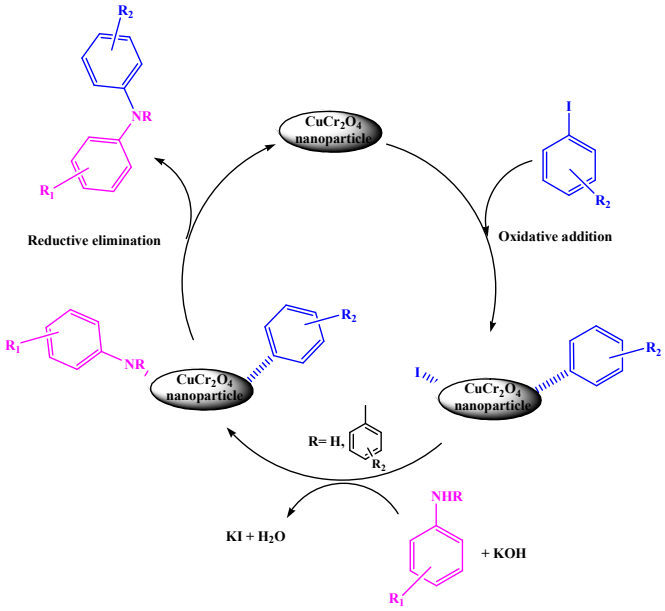

Scheme 2. Proposed reaction mechanism for the praparation of triarylamine by $CuCr_2O_4$ nanoparticles

Fig. 4. Reusability of nano $CuCr_2O_4$ for model reaction

3. Conclusions

In this research a simple and efficient procedure is developed for the C-N cross coupling reaction of anilines and aryl halides using $CuCr_2O_4$ nanoparticles as a highly efficient heterogeneous catalyst under ligand-free conditions. The catalyst is recyclable and provide excellent yields of triarylamines and short reaction times. The conditions was very mild, neutral and environmentally benign.

4. Experimental

4.1. Chemicals and apparatus

All reagents and solvents were purchased from Merck (Germany) and Sigma-Aldrich and used without more purification. Melting points were determined by Electro thermal 9200.^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance-400 MHz. The NMR spectra were achieved in $CDCl_3$ and DMSO-d_6 solution and are reported as parts per million (ppm) downfield from tetramethylsilane as internal standard. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. EIMS (70 eV) was performed by Finnigan-MAT-8430 mass spectrometer in m/z. The elemental analyses (C. H. N) of the samples were carried out using a LECO CHNS 923 analyser.

Powder X-ray diffraction (XRD) of $CuCr_2O_4$ nanoparticles was performed on a Philips diffractometer of X'pert Company with monochromatized Cu Kα radiation (λ = 1.5406 Å).

Microscopic morphology was visualized by SEM (MIRA 3 TESCAN).

4.2. Preparation of $CuCr_2O_4$ nanoparticles

Copper chromite nanoparticle has been prepared by coprecipitation method. Stoichiometric amount of Cu^{+2} (0.005 mol, 1.4 g Cu $(NO_3)_2.6H_2O$) and Cr^{3+} (0.01 mol, 4 g $Cr(NO_3)_3.9H_2O$) were poured in 50 ml distilled water. Afterward the mixture was added into 100 ml distilled water containing capping agent (glycerol, 5% in distilled water) under stirring. Subsequently, 1.5 M aqueous solution of precipitating agent (NaOAc) was added drop-wise until the pH value of the solution adjusted to 10. During the procedure, the temperature of the mixture was maintained about 60°C. Then, the temperature was increased to 80 °C at which the precipitation took place. The precipitates were centrifuged and then washed with distilled water and ethanol several times and then dried at 60°C in an oven for 2 h. Finally, calcination was carried out at 600°C for 5 h. $CuCr_2O_4$ nanoparticles were produced in 86% yield.

4.3. General procedure for the amination reaction

The preparation of triaryl amines derivatives was performed in a two-necked round bottomed flask under nitrogen atmosphere. A 10 mL toluene solution of anilines (1 mmol), aryl iodides (2.5 mmol), $CuCr_2O_4$ nanoparticles (4% mol), potassium hydroxide (0.43 g, 8 mmol) was stirred under nitrogen atmosphere at reflux for a desired time. At the completion of reaction (followed by TLC) the mixture was cooled to room temperature and poured into distilled water. The extraction of products were carried out by CH_2Cl_2 and the organic

layer was dried over anhydrous sodium sulphate (Na_2SO_4). Then the solvent was evaporated *in vacuo*, the products were purified using silica column chromatography by normal hexane to afford triarylamines.

4.4. Spectral data for Triarylamine derivatives

Triphenylamine (3a). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.08 (m, 9H), 7.26 (d, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 124.82, 125.46, 135.62, 147.65. FT-IR (KBr): 3031, 3016, 1590, 1454, 1276 cm^{-1}. MS (EI, 70 eV): m/z 244 (M^+), Anal. Calcd for $C_{18}H_{15}N$: C, 88.16; H, 6.12; N, 5.72%. Found: C, 87.95; H, 6.01; N, 5.62%.

N,N-bis (4-bromophenyl)aniline (3b). Colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.95 (d, 4H), 7.06 (m, 3H), 7.27 (d, 2H), 7.35 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 115.53, 123.82, 124.66, 125.46, 129.62, 132.22, 146.57, 146.96. FT-IR (KBr): 3071, 3056, 1579, 1484, 1274, 1070 cm^{-1}. MS (EI, 70 eV): m/z 400 (M^+), Anal. Calcd for $C_{18}H_{13}NBr_2$: C, 53.87; H, 3.24; N, 3.50%. Found: C, 53.61; H, 3.03; N, 3.35%.

4-Methyl- N,N-bis (4-bromophenyl)aniline (3c). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.32 (s, 3H), 6.91 (d, 4H), 6.96 (d, 2H), 7.09 (d, 2H), 7.31 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.89, 114.94, 124.92, 125.20, 130.25, 132.23, 133.86, 144.29, 146.69. FT-IR (KBr): 3033, 2922, 1578, 1483, 1276, 1070 cm^{-1}. MS (EI, 70 eV): m/z 415 (M^+), Anal. Calcd for $C_{19}H_{15}NBr_2$: C, 54.70; H, 3.60; N, 3.36%. Found: C, 54.63; H, 3.49; N, 3.28%.

2-Methoxy- N,N-bis (4-bromophenyl)aniline (3d). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69 (s, 3H), 6.93 (d, 4H), 7.01 (d, 1H), 7.12 (m, 3H), 7.32 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 56.48, 115.45, 122.32, 124.92, 125.65, 129.25, 132.03, 132.86, 145.12, 145.97. FT-IR (KBr): 3031, 2935, 1585, 1472, 1272, 1072 cm^{-1}. MS (EI, 70 eV): m/z 430 (M^+), Anal. Calcd for $C_{19}H_{15}NOBr_2$: C, 52.68; H, 3.47; N, 3.23%. Found: C, 52.51; H, 3.38; N, 3.21%.

3-Methoxy- N,N-bis (4-bromophenyl)aniline (3e). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.72 (s, 3H), 6.90 (s, 1H), 6.94 (d, 4H), 7.05 (m, 3H), 7.22 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 57.84, 116.14, 120.21, 121.85, 124.36, 131.51, 133.97, 142.65, 144.84, 152.23. FT-IR (KBr): 3033, 2950, 1523, 1454, 1256, 1064 cm^{-1}. MS (EI, 70 eV): m/z 431 (M^+), Anal. Calcd for $C_{19}H_{15}NOBr_2$: C, 52.68; H, 3.47; N, 3.23%. Found: C, 52.57; H, 3.32; N, 3.24%.

4-Methoxy- N,N-bis (4-bromophenyl)aniline (3f). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.75 (s, 3H), 6.90 (d, 2H), 6.96 (d, 4H), 7.08 (d, 2H), 7.39 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 57.98, 115.34, 126.34, 131.50, 133.73, 135.65, 145.67, 146.32, 150.07. FT-IR (KBr): 3056, 2948, 1584, 1457, 1273, 1075 cm^{-1}. MS (EI, 70 eV): m/z 431 (M^+), Anal. Calcd for $C_{19}H_{15}NOBr_2$: C, 52.68; H, 3.47; N, 3.23%. Found: C, 52.54; H, 3.35; N, 3.19%.

4-Bromo- N,N-bis 4-bromophenyl)aniline (3g). Pale green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.97 (d, 6H), 7.08 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 115.23, 125.92, 132.43, 146.59. FT-IR (KBr): 3056, 1585, 1483, 1272, 1071 cm^{-1}. MS (EI, 70 eV): m/z 481 (M^+), Anal. Calcd for $C_{18}H_{12}NBr_3$: C, 44.84; H, 2.49; N, 2.91%. Found: C, 44.32; H, 2.31; N, 2.89%.

4-Bromo- N,N-bis (phenyl)aniline (3h). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.01 (d, 2H), 7.16 (m, 6H), 7.22 (d, 4H), 7.42 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 115.35, 120.64, 124.97, 127.79, 128.44, 136.21, 146.69, 147.74. FT-IR (KBr): 3085, 1590, 1483, 1273, 1075 cm^{-1}.

4-Bromo- N,N-bis (4-methylphenyl)aniline (3i). Yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.35 (s, 6H), 6.92 (d, 2H), 7.01 (d, 4H), 7.09 (d, 4H), 7.31 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.96, 113.07, 124.88, 126.34, 129.52, 132.65, 135.06, 145.84, 146.37. FT-IR (KBr): 3110, 2989, 1568, 1495, 1275, 1069 cm^{-1}.MS (EI, 70 eV): m/z 350 (M^+), Anal. Calcd for $C_{20}H_{18}NBr$: C, 68.20; H, 5.11; N, 3.98%. Found: C, 68.08; H, 4.96; N, 3.73%.

4-Bromo- N,N-bis (2-methoxyphenyl)aniline (3j). Yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.64 (s, 6H), 7.01 (d, 2H), 7.12 (m, 4H), 7.21 (m, 4H), 7.31 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.54, 120.32, 122.64, 125.49, 129.18, 132.78, 135.63, 136.13, 145.22, 146.39, 150.79. FT-IR (KBr): 3051, 2964, 1598, 1422, 1265, 1049 cm^{-1}.MS (EI, 70 eV): m/z 383 (M^+), Anal. Calcd for $C_{20}H_{18}NO_2Br$: C, 62.52; H, 4.69; N, 3.65%. Found: C, 62.43; H, 4.49; N, 3.51%.

4-Bromo- N,N-bis (3-methoxyphenyl)aniline (3k). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.75 (s, 6H), 6.98 (m, 4H), 7.02 (m, 3H), 7.09 (m, 3H), 7.24 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.89, 112.21, 119.82, 124.46, 125.97, 130.52, 132.79, 134.23, 135.17, 145.91, 148.64, 155.01. FT-IR (KBr): 3064, 2922, 1581, 1462, 1272, 1081 cm^{-1}. MS (EI, 70 eV): m/z 382 (M^+), Anal. Calcd for $C_{20}H_{18}NO_2Br$: C, 62.52; H, 4.69; N, 3.65%. Found: C, 62.41; H, 4.56; N, 3.48%.

4-Bromo- N,N-bis (4-methoxyphenyl)aniline (3l). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.81 (s, 6H), 6.98 (d, 2H), 7.21 (d, 4H), 7.28 (d, 2H), 7.43 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 59.36, 115.07, 124.48, 133.97, 134.58, 138.27, 146.19, 147.41, 152.63. FT-IR (KBr): 3088, 2921, 1579, 1475, 1277, 1073 cm^{-1}. MS (EI, 70 eV): m/z 383 (M^+), Anal. Calcd for $C_{20}H_{18}NO_2Br$: C, 62.52; H, 4.69; N, 3.65%. Found: C, 62.35; H, 4.51; N, 3.49%.

4-Methyl- N,N-bis (4-nitrophenyl)aniline (3m). Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.31 (s, 3H), 7.16 (d, 2H), 7.18 (d, 4H), 7.33 (d, 2H), 8.05 (d, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 21.36, 122.34, 125.36, 126.27, 130.58, 132.60, 139.04, 147.23, 147.69. FT-IR (KBr): 3063, 3043, 1548, 1508, 1452, 1335, 1273 cm^{-1}. MS (EI, 70 eV): m/z 348 (M^+), Anal. Calcd for $C_{19}H_{15}N_3O_4$: C, 65.32; H, 4.33; N, 12.03%. Found: C, 65.06; H, 4.12; N, 12.15%.

4-Methyl- N,N-bis (4-carbomethoxy)aniline (3n). Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.35 (s, 3H), 3.61 (s, 6H), 7.06 (d, 2H), 7.21 (d, 4H), 7.32 (d, 2H), 7.94 (d, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 20.05, 60.21, 121.43, 126.54, 127.78, 130.08, 132.52, 138.41, 147.35, 147.74, 167.49. FT-IR (KBr): 3061, 3045, 1735, 1542, 1503, 1459, 1332, 1271 cm^{-1}. MS (EI, 70 eV):

m/z 375 (M^+), Anal. Calcd for $C_{23}H_{21}NO_4$: C, 73.60; H, 5.60; N, 3.73%. Found: C, 73.35; H, 5.46; N, 3.75%.

(4,6-Dimethyl-pyrimidin-2-yl)-diphenyl-amine (3o). White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.15 (s, 6H), 6.39 (s, 1H), 7.05 (m, 2H), 7.14 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 24.84, 115.03, 125.45, 128.71, 129.59, 145.89, 163.01, 167.75. FT-IR (KBr): 3063, 3042, 1545, 1451, 1332, 1275 cm^{-1}. MS (EI, 70 eV): m/z 275 (M^+), Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.55; H, 6.18; N, 15.27%. Found: C, 78.36; H, 6.09; N, 15.25%.

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