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A convenient and efficient synthesis of triarylamine derivatives using CuI nanoparticles

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We report a simple and efficient method for the synthesis of triarylamine derivatives using copper iodide nanoparticles, 1,10-phenanthroline and potassium hydroxide. Copper iodide nanoparticles enhanced the rate and ease of reaction and exhibited a high influence in the efficient synthesis of various amine derivatives. The nanoparticles also increased the yields of products and decreased the reaction times in all cases. The heterogeneous mediator was fully characterized by scanning electron microscopy and X-ray diffraction techniques.

1. Introduction

Triarylamines are an important class of chemical compounds due to their prominent physical, photochemical, electrochemical and special pharmacological properties.[1] Triarylamine has been widely used in many fields of chemistry including the synthesis of natural products,[2] dyes[3] and polymers.[4–7] It also has good electron donating and hole transporting abilities, therefore these compounds have broad applications in organic electroluminescence (EL).[8–11] In recent years, organic photovoltaic functional materials with triarylamine acting as an electron donor have been developed in the field of solar cells.[12–15] Furthermore triarylamines have found applications as photoconductors in xerographic photoreceptors.[16–19] The synthesis of these compounds have been carried out *via* *N*-arylation of aniline by aryl iodides under Ullman coupling using different approaches.[20] These reactions have been developed using palladium[21,22] or copper[23–25] as catalysts. The main limitations of bis-arylation reaction of substituted anilines with two equivalents of aromatic halides are the high temperature of reaction, low yield of triarylamines and sensitivity to catalyst type. These limitations have been widely observed in the synthesis of bromo-substituted triphenylamines[7] which have applications in the synthesis of polymers[7] and dyes.[26,27] Conventionally, the synthesis of these compounds has been reported *via* two steps by arylation followed by bromination with *N*-bromosuccinimide, NBS.[28,29]

In the *N*-arylation reaction, activation of aniline is facile using a copper catalyst with chelating bidentate ligands such as 2,2′-bipyridine and 1,10-phenanthroline. Ligands increase the catalytic activity of the Cu complex by activation of the amine and elimination of iodide.[25] Different ligands have been used in the C–N coupling reaction in various systems. For example, the synthesis of a variety of triphenylamines in good yields using CuCl mediated, 8-hydroxyquinoline as the chelating ligand and K_3PO_4 as the base in DMF at 120 °C has recently been reported.[47]

The copper iodide-mediated synthesis of triarylamines has also been performed using Cs_2CO_3 as the base in the absence of an additive ligand.[46] The ligand-free copper-catalysed Ullman reaction was carried out using tetraethyl orthosilicate (TEOS) as the solvent and this method requires a high temperature (145 °C) and long reaction time to achieve completion.

We attempted to alter the reaction of aryl iodides and aryl amines to obtain triarylamine more conveniently and efficiently by the use of nanoparticles. Nanoparticles can be used as suitable catalysts in organic reactions due to their high surface-to-volume ratio, which provides a larger number of active sites per unit area in comparison to their bulk counterparts.[30] Copper iodide nanoparticles (CuI NPs) have performed significantly as catalysts in terms of reactivity, selectivity, and improvement in the yields of organic reactions.[31–35] We applied a simple and efficient method for the synthesis of various derivatives of triarylamine, including electron withdrawing and bromo-substituted triphenylamine, using CuI NPs and 1,10-phenanthroline as a convenient catalytic system.

2. Results and discussion

2.1. Synthesis

The synthesis of triarylamine *via* Ullman condensation started from the reaction of aryl amine with aryl iodide (molar ratio 1 : 2) in the presence of potassium hydroxide as the base mediated by CuI nanoparticles and 1,10-phenanthroline as a catalytic system,[25] in toluene as a solvent. The reaction mixture was heated to reflux under a nitrogen atmosphere (Scheme 1).

The optimized experimental conditions were obtained by performing this reaction in different solvents and varying the

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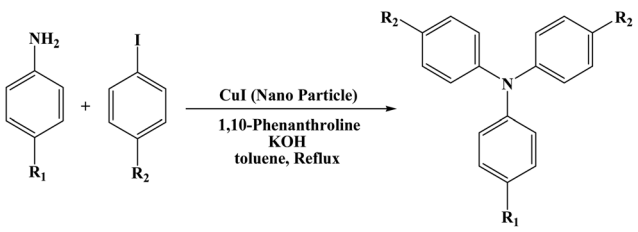


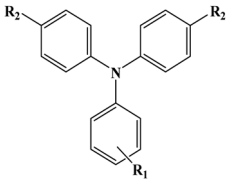
Scheme 1 Synthesis of triarylamine derivatives.

temperature and catalytic system. Reactions were carried out using polar (Table 1, entries 1–3) and non-polar (Table 1, entries 4 and 5) solvents. Obviously, the non-polar solvents were more suitable than polar solvents. The best results were obtained using toluene. The different temperatures (with toluene as solvent) were then investigated for this reaction in which the maximum yields were obtained under reflux conditions (Table 1, entries 5 and 6). In order to find the best catalyst, a variety of copper catalysts were investigated (Table 1, entries 8–10). As a result of these experiments, we observed that the CuI nanoparticle-containing catalyst was the most effective for the aforementioned reaction (Table 1, entry 10). A higher yield was observed using 3 mol% CuI NPs and 3 mol% 1,10-phenanthroline (Table 1, entry 11). It should be noted that the reaction did not proceed in the absence of catalyst (Table 1, entry 7). Furthermore this reaction produced triarylamines in low yields in the absence of 1,10-phenanthroline (Table 1, entry 13).

The increased catalytic activity of CuI nanoparticles over the commercially available bulk CuI can be attributed to their higher surface area.

We also utilized CuI NPs in the synthesis of triarylamine derivatives with various aryl amines and aryl iodides under similar conditions and the results are shown in Table 2. As seen from Table 2, excellent yields were obtained from this reaction under reflux and in the presence of nano copper iodide (3 mol%). Electron-withdrawing and electron-donating substituents for aryl halides and aniline such as CH_3, OCH_3, Br and NO_2 resulted in good to excellent yields of triarylamines under the aforementioned conditions. The highest yields of triarylamine were afforded by the electron donating *para*-methoxy group as the substituent for aryl halides and aniline (Table 2, entries 6 and 12). Although *ortho*-substituted aniline and aryl halides resulted in good yields (Table 2, entries 4 and 10), the yields obtained were lower than *para*-substituted aniline because of steric effects. Aryl iodides showed higher reactivity than aryl bromides in this reaction. The coupling of 1-bromo-4-iodobenzene with aniline derivatives yielded products containing bromide on the aromatic ring (entries 2–7 in Table 2).

Table 2 Synthesis of triarylamines using CuI nanoparticles[a]



Entry	Product[b]	R_1	R_2	Time (h)	Yield[c] (%)	Mp[d] (°C)
1	1a	H	H	8	92	126–127[37]
2	1b	H	4-Br	10	83	—[e]
3	1c	4-Me	4-Br	10	86	83–85[43]
4	1d	2-OMe	4-Br	12	81	91–92
5	1e	3-OMe	4-Br	12	78	110–112
6	1f	4-OMe	4-Br	8	90	74–76[38]
7	1g	4-Br	4-Br	12	75	140–142[39]
8	1h	4-Br	4-H	12	77	110–112[40]
9	1I	4-Br	4-Me	10	80	104–105[41]
10	1J	4-Br	2-OMe	12	76	120–121
11	1k	4-Br	3-OMe	12	78	89–91[44]
12	1L	4-Br	4-OMe	8	83	95–96[42]
13	1m	4-Me	4-NO_2	15	71	190–192[45]

[a] Reactions conditions: aniline and iodobenzene (2 : 5), CuI nanoparticles (3 mol%), 1,10-phenanthroline (3 mol%), potassium hydroxide, toluene, reflux. [b] All products were characterized by spectroscopic (IR, ^{1}H NMR and ^{13}C NMR), mass and CHN analysis. [c] Isolated yield. [d] Literature reference. [e] Viscous liquid.

Table 1 Optimization of reaction conditions for the synthesis of triphenylamine

Entry	Solvent/condition	Catalytic system (mol%)	Time (h)	Yield[a] (%)
1	Acetonitrile/reflux	CuI (15%), 1,10-phen[b] (15%)	48	38
2	THF/reflux	CuI (15%), 1,10-phen (15%)	48	35
3	1,4-Dioxane/reflux	CuI (15%), 1,10-phen (15%)	48	36
4	Xylene/reflux	CuI (15%), 1,10-phen (15%)	32	65
5	Toluene/reflux	CuI (15%), 1,10-phen (15%)	32	69
6	Toluene/80 °C	CuI (15%), 1,10-phen (15%)	48	49
7	Toluene/reflux	None	48	Trace
8	Toluene/reflux	CuCl (15%), 1,10-phen (15%)	32	43
9	Toluene/reflux	CuBr (15%), 1,10-phen (15%)	32	51
10	Toluene/reflux	CuI NPs (5%), 1,10-phen (5%)	8	89
11	**Toluene/reflux**	**CuI NPs (3%), 1,10-phen (3%)**	**8**	**92**
12	Toluene/reflux	CuI NPs (2%), 1,10-phen (2%)	8	85
13	Toluene/reflux	CuI NPs (3%)	12	71

[a] Isolated yield. [b] 1,10-Phenanthroline as chelating ligand.

2.2. Structural analysis of CuI nanoparticles

Fig. 1 shows the XRD pattern of copper iodide nanoparticles. As seen from this figure, all reflection peaks could be indexed to the pure cubic crystal phase of nano crystalline CuI. No specific peaks due to any impurities were observed. This pattern is in good agreement with the reported pattern for copper iodide (JCPDS no. 75–0832). The crystalline size diameter (D) of the synthesized CuI nanoparticles was calculated by the Debye–Scherrer equation ($D = K\lambda/\beta \cos \theta$),[36] where the FWHM (full-width at half-maximum or half-width) is in radians and θ is the position of the maximum of diffraction peak ($\beta = 0.4723[^\circ 2\theta]$), K is the shape factor which usually is a value about 0.9, and λ is the X-ray wavelength. The average diameter of CuI NPs was found to be 20 nm.

In order to confirm the particle size of the CuI nanoparticles, the scanning electron microscopy (SEM) image is shown in Fig. 2. This figure illustrates that CuI NPs were obtained with diameters in the range of nanometers (20 nm) under ultrasonic irradiation. According to the TEM image of CuI NPs, the particle size of the nano CuI was found to be less than or equal to 20 nm (Fig. 3).

2.3. Proposed mechanism

The proposed mechanism for the synthesis of triarylamine using CuI NPs chelated by 1,10-phenanthroline is shown in Scheme 2. In the first step, C–N coupling occurs by oxidative addition followed by a reductive elimination reaction. These processes are carried out on the nano copper surface. Nanoparticles of CuI have high catalytic activity owing to their high surface area.

3. Experimental

3.1. Chemicals and apparatus

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

Powder X-ray diffraction (XRD) of CuI nanoparticles was carried out on a Philips diffractometer (X'pert Company) with monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). Microscopic morphology was visualized using a SEM (LEO 1455VP). The transmission electron microscopy (TEM) image of nano copper iodide was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV.

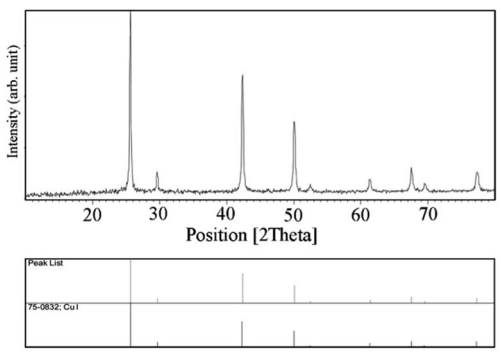


Fig. 1 XRD pattern of the CuI nanoparticles.

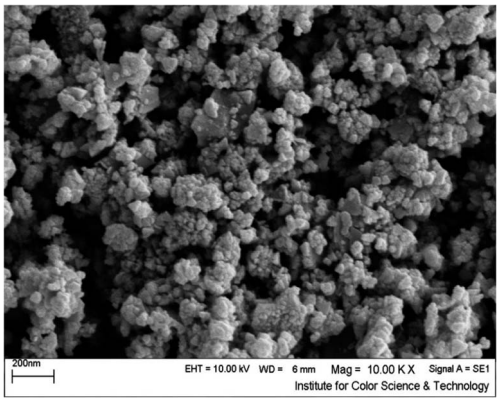


Fig. 2 SEM image of the CuI nanoparticles.

3.2. Preparation of copper iodide nanoparticle

The nanocatalyst was produced by ultrasonic irradiation with copper sulphate ($CuSO_4$) as the Cu source. First, $CuSO_4$ (1 mmol) was cleaned for 20 s in acetone under ultrasonic irradiation followed by repeated rinsing with distilled water. The dried substrate was then dipped slowly into a solution of potassium iodide (1 mmol) in 40 mL of distilled water and the mixture was sonicated for 30 min. When the reaction was completed, the obtained grey precipitate was filtered, washed with distilled water and dried to afford pure CuI NPs. The prepared nanoparticles were fully characterized by SEM, TEM and XRD analyses.

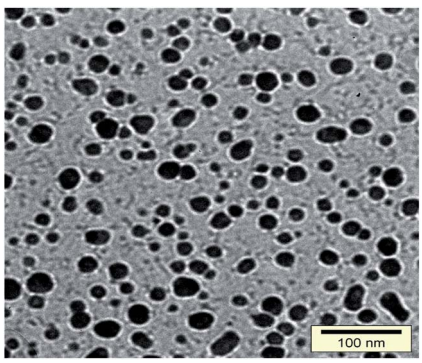
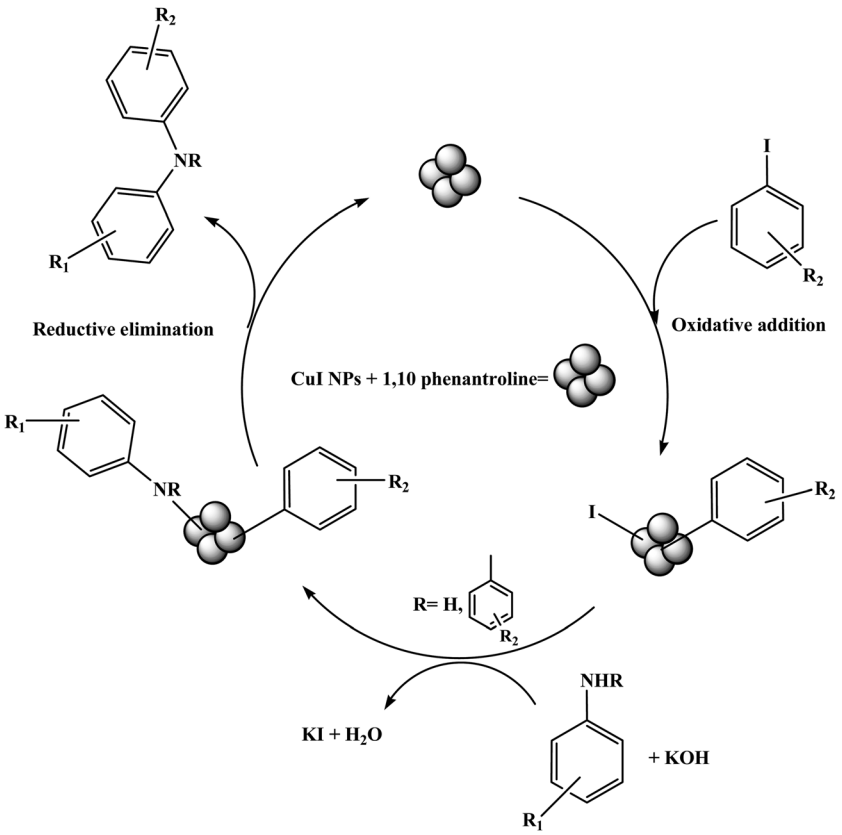


Fig. 3 TEM image of the CuI nanoparticles.



Scheme 2 Proposed reaction pathway for the synthesis of triarylamine mediated by CuI nanoparticles and 1,10-phenanthroline.

3.3. General procedure for the preparation of triarylamines derivatives

The amination reaction was carried out in a two-necked round bottomed flask under a nitrogen atmosphere. In a typical experiment, a mixture of aniline (1 mmol), iodobenzene (2.5 mmol), CuI NPs (3 mol%), 1,10-phenanthroline (3 mol%) and potassium hydroxide (0.43 g, 0.008 mmol) were dissolved in 10 mL of toluene and stirred under a nitrogen atmosphere at reflux for the required time. The reaction was monitored to completion using TLC with hexane as the eluent. At the end of reaction, the mixture was then cooled to room temperature and poured into distilled water. The products were extracted using CH_2Cl_2 and the organic layer was dried over anhydrous sodium sulphate (Na_2SO_4). The solvent was evaporated *in vacuo*, the crude products were purified by silica column chromatography using normal hexane to afford the triarylamines. The products were characterized by IR, NMR analysis, mass spectrum and elemental analysis.

3.4. Spectral data for triarylamine derivatives

Triphenylamine (1a). 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 (1b).** 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 (1c). 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 (1d). 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 (1e). 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 (1f). White solid. ^1H 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 (1g). Pale green solid. ^1H 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 (1h). White solid. ^1H 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 (1I). Yellowish solid. ^1H 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 (1J). Yellowish solid. ^1H 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 (1k). Yellow solid. ^1H 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 (1L). Yellow solid. ^1H 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 (1M). Yellow solid. ^1H 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) 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. Conclusions

In this work a simple and efficient method for the amination of iodobenzene using CuI NPs under reflux was investigated . The mediated system which included nano CuI as the catalyst precursor, 1,10-phenanthroline as the ligand, KOH as the base and toluene as the solvent resulted in good yields of triarylamines. The conditions were very mild, neutral and environmentally benign. Furthermore it was very effective due to the high surface-to-volume ratio of nanoparticles. The products were formed in excellent yields with short reaction times. This method is also suitable for the one-step synthesis of bromo-substituted triphenylamines.

Acknowledgements

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