One-pot copper nanoparticle-catalyzed synthesis of S-aryl- and S-vinyl dithiocarbamates in water: high diastereoselectivity achieved for vinyl dithiocarbamates†

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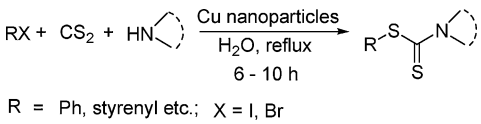
A convenient, green and efficient procedure for the synthesis of aryl and vinyl dithiocarbamates has been developed by a simple one-pot three component condensation of an amine, carbon disulfide, and an aryl iodide or a styrenyl bromide catalyzed by copper nanoparticles in water. Significantly, the (*E*)- and (*Z*)-styrenyl bromides provide the corresponding (*E*)- and (*Z*)-styrenyl dithiocarbamates in high diastereoselectivities. The catalyst is recycled.

1. Introduction

Reactions in water have attracted considerable interest in recent times because of their environmental acceptability, abundance and low cost.[1] In addition, water often exhibits unique reactivity and selectivity that cannot be attained in conventional organic solvents.[2] Thus, development of an efficient procedure for an organic reaction using water as the reaction medium has received high priority in the design of a chemical process.

Organic dithiocarbamates are of much importance as versatile synthetic intermediates,[3] and linkers in solid phase organic synthesis.[4] Moreover, their occurrence in a variety of biologically active compounds,[5] their pivotal roles in agriculture,[6] and their medicinal and biological properties,[7] prompted interest in the development of convenient synthetic procedures for these compounds. Conventional methods involve reactions of amines with thiophosgene and its derivatives, which are not desirable for environmental concerns.[8] Several one-pot procedures by reaction of amines with carbon disulfide and alkyl halides or α,β-unsaturated compounds have also been reported.[9] However, although these methods were satisfactory for the synthesis of alkyl dithiocarbamates, they were not effective for aryl or vinyl derivatives. The procedures for the synthesis of aryl and vinyl dithiocarbamates are rather limited and the available methods involved reaction of the sodium salt of dithiocarbamic acid with hypervalent iodine compounds[10] and the Wittig reaction of aldehydes with phosphonium ylides[11] among others.[12] Recently, a new protocol based on the Ullmann-type coupling of sodium dithiocarbamates with aryl iodides and vinyl bromides catalyzed by CuI in the presence of a ligand, *N*,*N*-dimethylglycine in DMF, has been reported.[13]

In recent times, interest in nanoparticle-catalysis has increased considerably because of its high efficiency under environmentally benign reaction conditions in the context of green chemistry.[14] As a part of our continued activites[15] to explore catalysis by metal nanoparticles in water we report here a one-pot three-component condensation of an amine, carbon disulfide and an aryl iodide or styrenyl bromide catalyzed by copper nanoparticles in water under ligand- and base-free conditions leading to the synthesis of aryl or styrenyl dithiocarbamates (Scheme 1).



Scheme 1

2. Results and discussion

The experimental procedure is very simple. A mixture of aryl iodide or styrenyl bromide, carbon disulfide, amine was heated under reflux in water in the presence of copper nanoparticles for a required period of time (TLC). Standard work-up provided the product. The aqueous part containing Cu nanoparticles, remaining after work up, was recycled upto four times without appreciable loss of efficiency for a representative reaction of 2-(4-methylphenyl)vinyl bromide and pyrrolidine (entry 11, Table 1) (Fig. 1).

The best results in terms of yields were obtained using water as reaction medium compared to conventional organic solvents such as DMF, toluene and THF. The amount of Cu nanoparticles was optimized to 3.0 mol%. Use of base such as K_2CO_3 and K_3PO_4 in water fails to show any effect on reaction. Thus, contrary to several conventional procedures no base is used for this Cu-nanoparticles catalyzed reaction. Copper nanoparticles were prepared from copper sulfate by reduction with hydrazine hydrate in ethylene glycol.[16] The identity and size (2–6 nm) of Cu nanoparticles were established by transmission electron microscope (TEM) (Fig. 2), energy dispersive X-ray spectroscopy (EDS) (Fig. 3), and UV spectroscopy (Fig. 4).

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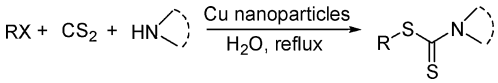
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra of all products in Table 1. CCDC reference number 684382. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b809200a

Table 1 Copper nanoparticles catalyzed coupling of aryl and vinyl halides with dithiocarbamate anion



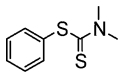
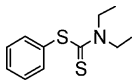
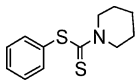
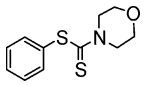
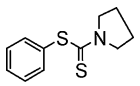
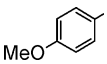
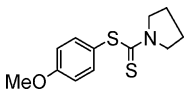
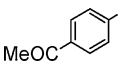
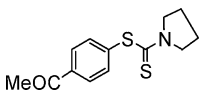
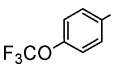
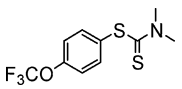
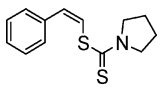
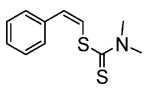
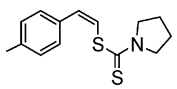
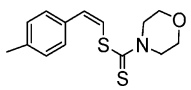
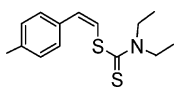
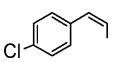
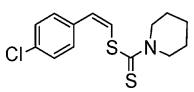
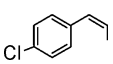
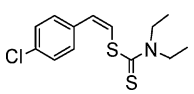
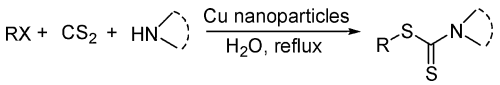
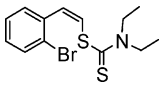
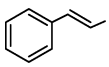
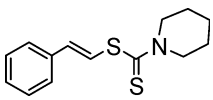
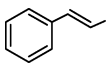
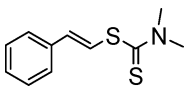
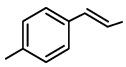
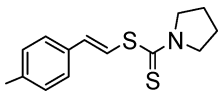
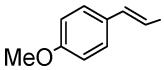
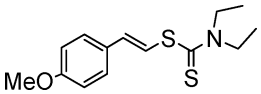
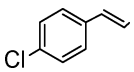
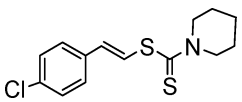
Entry	R	X	Amine	Time/h	Product	Yield (%)[a]	Ref.
1		I	$HNMe_2$	8		94	10
2		I	$HNEt_2$	8		91	10
3		I		8		92	10
4		I		8.2		88	18
5		I		8		87	19
6		I		9		75	
7		I		8.5		80	
8		I	$HNMe_2$	8		85	
9		Br		6		92	
10		Br	$HNMe_2$	6		95	13
11		Br		7		91	
12		Br		9		87	
13		Br	$HNEt_2$	8		88	
14		Br		8.2		89	
15		Br	$HNEt_2$	8		92	

Table 1 (*Contd.*)



Entry	R	X	Amine	Time/h	Product	Yield (%)[a]	Ref.
16		Br	$HNEt_2$	10		76	
17		Br		8.2		86[b]	13
18		Br	$HNMe_2$	8		89[b]	13
19		Br		8.5		84[b]	
20		Br	$HNEt_2$	8.4		92[b]	
21		Br		8		86	

[a] Isolated yields of pure products (^1H and ^{13}C). [b] The substrates in entries 17–20 gave a trace amount (1–3%) of the corresponding Z-isomers as determined by ^1H NMR.

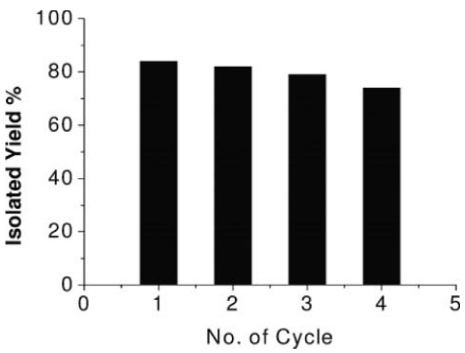


Fig. 1 Recyclability chart.

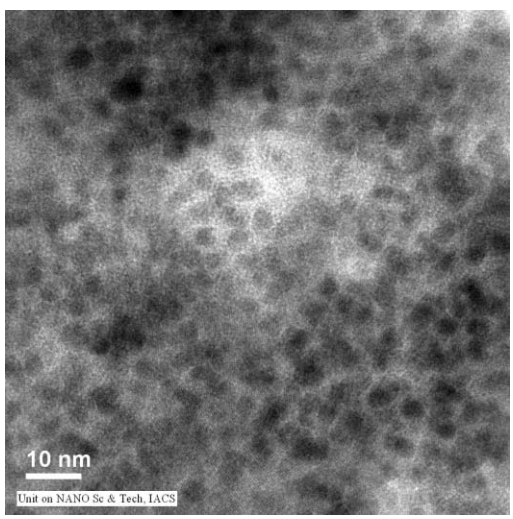


Fig. 2 TEM image of Cu nanoparticles.

Several substituted aryl iodides and styrenyl bromides underwent coupling with the dithiocarbamate anion, generated *in situ* by the reaction of carbon disulfide and amine to provide the corresponding dithiocarbamate derivatives. The results are summarized in Table 1.

A variety of substituents in the aromatic ring, such as Cl, OCH_3, OCF_3, $COCH_3$ are compatible in this reaction. The open-chain as well as cyclic amines participated uniformly. Significantly, the reactions of vinyl bromides are highly stereoselective. The (*Z*)-vinyl bromides (Table 1, entries 9–16) provided the corresponding (*Z*)-vinyl dithiocarbamates (no *E*-isomer was detected/isolated), while the (*E*)-bromides (Table 1, entries 17–21) furnished the (*E*)-dithiocarbamates predominantly with a trace amount (1–3%) of (*Z*)-isomers. The (*E*)- and (*Z*)-isomers were characterized by their ^1H and ^{13}C NMR spectroscopy. Our analysis was also confirmed by the X-ray structure[17] of one of the styrenyl dithiocarbamates (Table 1, entry 21) as shown in Fig. 5.

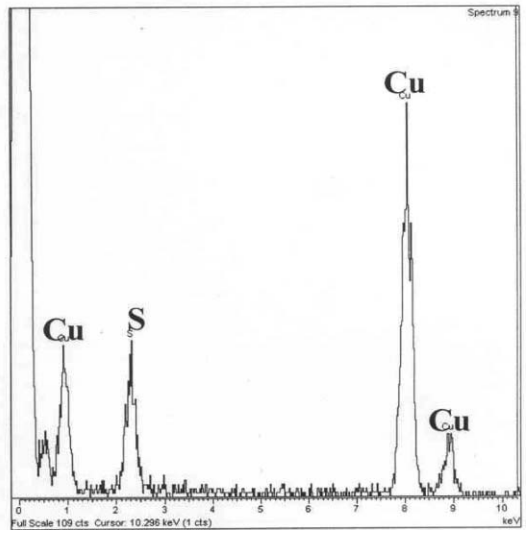


Fig. 3 EDS of Cu nanoparticles on a Cu grid.

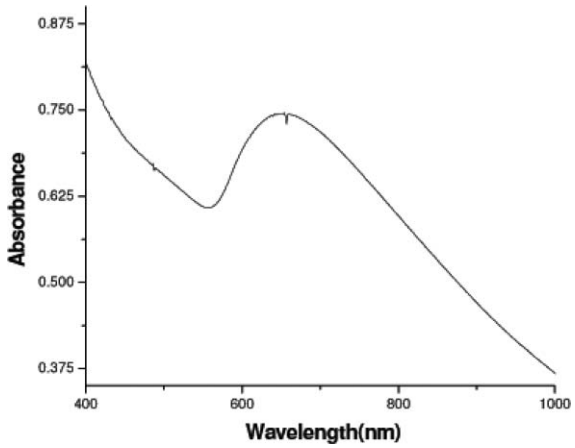


Fig. 4 UV spectrum of Cu nanoparticles.

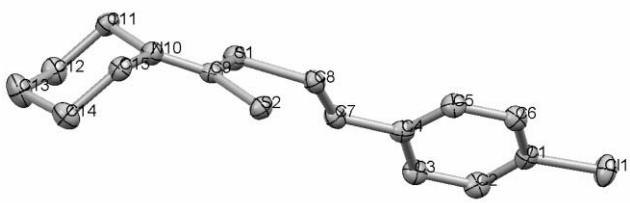
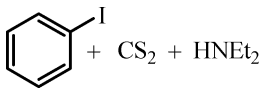
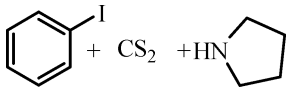
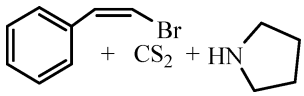
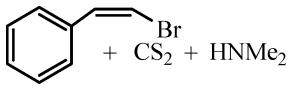
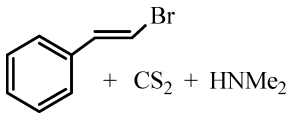
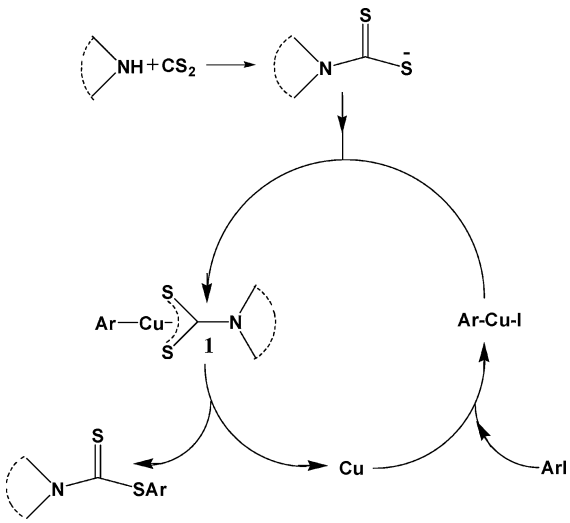


Fig. 5 ORTEP diagram of the dithiocarbamate (Table 1, entry 21).

We believe that the reaction proceeds in a catalytic cycle where the aryl/styrenyl halide undergoes oxidative addition to Cu to form ArCuI which combines with dithiocarbamate anion, generated *in situ* by the reaction of amine and carbon disulfide, to give an intermediate **1**, which leads to the product by subsequent reductive elimination. The liberated Cu(0) initiates a further reaction and propagates the cycle (Scheme 2). We believe that Cu nanoparticles facilitate oxidative coupling with aryl iodide because of their inherent character to transfer electrons[20] more easily than metallic Cu (Table 2). Presumably, use of water also makes this reaction more facile because of its amphoteric nature and thus not requiring any base.[2b]

Table 2 Comparison of results of reactions catalyzed by metallic Cu powder with Cu nanoparticles

Entry	Reaction	Yield (%) metallic Cu	Yield (%) Cu nanoparticles
1		12	91
2		20	87
3		35	92
4		23	95
5		21	89



Scheme 2

The reactions were very clean and high yielding and no side products were isolated. A comparison of results of reactions by Cu nanoparticles with those by metallic Cu (Table 2) distinctly demonstrates the superior efficiency of Cu nanoparticles compared to metallic Cu. Our procedure also offers significant improvements to that catalyzed by CuI[13] with regard to catalyst loading (3.0 *vs.* 15 mol%), reaction medium (H_2O *vs.* DMF) and reaction time (6–10 h *vs.* 22 h). The present procedure provides a one-pot operation and avoids the use of sodio-salt of dithiocarbamic acid used in the CuI one. The preparation and purification of the sodio-salt is very tedious and is also commercially very expensive. In addition, our reaction did not require a ligand or a base, whereas the CuI-catalyzed one[13] did not proceed without ligand. The stereoselectivities achieved for vinyl dithiocarbamates by this Cu nanoparticle

catalyzed reaction are also better than those for the CuI-catalyzed ones. In fact, highly diastereoselective synthesis of vinyl dithiocarbamates was not addressed in earlier reports.[8–12]

3. Experimental section

Preparation of Cu nanoparticles

A solution of $N_2H_4{\cdot}H_2O$ (0.75 mL, 80% aqueous solution, 12 mmol) and NaOH (0.016 g, 0.4 mmol) in ethylene glycol (80 mL) was added to another solution of $CuSO_4{\cdot}5H_2O$ (2.00 g, 8 mmol) in ethylene glycol (80 mL) with stirring at room temperature (30 °C). The mixture was then subjected to irradiation in a conventional microwave oven (BPL, India, 1080 Watt, working cycle of 19 s on and 6 s off) for 3.5 min. The solution turned black and was allowed to come to room temperature. Cu nanoparticles were centrifuged, washed with ethanol five times and dried under vacuum. The particles were characterized by TEM (4–6 nm), EDX and UV spectra (Fig. 2, 3 and 4). Cu nanoparticles can be preserved under an argon atmosphere for 3 weeks.

General experimental procedure for the synthesis of dithiocarbamates. Representative experimental procedure for condensation of amine, CS_2 and aryl/styrenyl halide (entry 9, Table 1). To a well stirred mixture of *cis*-(2-bromovinyl)benzene (185 mg, 1 mmol) and carbon disulfide (190 mg, 2. 5 mmol) in water (2 mL) was added pyrrolidine (84 mg, 1.2 mmol) drop by drop at 0–5 °C. After stirring for 5 min Cu nanoparticles (2 mg, 3.0 mol%) were added and the reaction mixture was heated under reflux for 6 h (TLC). The reaction mixture was extracted with ethyl acetate (3 × 7 mL) and the extract was washed with brine and dried (Na_2SO_4). Evaporation of organic solvent left the crude product which was purified by column chromatography over silica gel (hexane–ether 85 : 15) to provide the corresponding dithiocarbamate, pyrrolidine-1-carbodithionic acid styryl ester as a white solid, mp 120 °C, IR (KBr): 2964, 2925, 2898, 1463, 1440, 1330, 1155, 1004, 958, 840, 783, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85–1.94 (m, 2H), 1.95–2.04 (m, 2H), 3.65 (t, $J = 6.65$, 2H), 3.89 (t, $J = 6.75$, 2H), 6.70 (d, $J = 11.06$, 1H), 7.17 (t, $J = 7.05$, 1H), 7.28 (t, $J = 7.33$, 2H), 7.36 (d, $J = 7.41$, 2H), 7.45 (d, $J = 11.12$, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 26.0, 50.9, 55.4, 123.8, 127.5, 128.1, 128.4 (2C), 128.8 (2C), 136.5, 189.0; HRMS Calcd for $C_{13}H_{15}NS_2$ $[M + H]^+$:250.0646; found: 250.0719. The aqueous part after organic extract containing Cu(0) nanoparticles was reused for subsequent reactions (no loss of efficiency up to four times).

This procedure was followed for all the reactions listed in Table 1. Although this procedure was described with a 1 mmol scale, 10 mmol scale reactions also provided uniform results. Several products are known compounds and were easily identified by comparison of their spectroscopic data and mp's with those reported (see refs in Table 1). The unknown compounds (entries 6–8, 11–17, 19–21, Table 1) were properly characterized by their spectroscopic (IR, ^1H NMR, ^{13}C NMR, HRMS) data which are provided below in order of their entries in Table 1.

Pyrrolidine-1-carbodithioic acid 4-methoxy-phenyl ester (Table 1, entry 6). Brown viscous oil; IR (neat) 2952, 2922, 2852, 1712, 1589, 1492, 1427, 1245, 1157, 1026, 1001, 954, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99 (q, $J = 7.20$ Hz, 2H), 2.11 (q, $J = 6.81$ Hz, 2H), 3.79 (t, $J = 6.97$ Hz, 2H), 3.84 (s, 3H), 3.93 (t, $J = 7.06$ Hz, 2H), 6.96 (d, $J = 8.66$ Hz, 2H), 7.39 (d, $J = 8.65$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 26.4, 51.0, 55.3, 55.4, 114.8 (2C), 122.0, 138.5 (2C), 161.2, 194.3; HRMS Calcd for $C_{12}H_{15}NOS_2$ $[M + Na]^+$: 276.0493; Found: 276.0488.

Pyrrolidine-1-carbodithioic acid 4-acetyl-phenyl ester (Table 1, entry 7). White solid (mp 79 °C; IR (KBr) 2923, 2869, 2862, 1683, 1433, 1259, 1159, 1002, 954 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99–2.03 (m, 2H), 2.12–2.16 (m, 2H), 2.62 (s, 3H), 3.80 (broad, 2H), 3.92 (broad, 2H), 7.59 (d, $J = 8.25$ Hz, 2H), 7.99 (d, $J = 8.26$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 26.4, 26.8, 51.3, 55.4, 128.8 (2C), 136.7, 137.0 (2C), 137.8, 197.5, HRMS Calcd for $C_{13}H_{15}NOS_2$ $[M + Na]^+$: 288.0493; Found: 288.0497.

Dimethyl-dithiocarbamic acid 4-trifluoromethoxy-phenyl ester (Table 1, entry 8). Pale yellow solid (mp 65 °C); IR (KBr) 2927, 2846, 1487, 1373, 1255, 1215, 1170, 981, 920, 842, 513 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 3H), 3.58 (s, 3H), 7.30 (d, $J = 8.29$ Hz, 2H), 7.53 (d, $J = 8.65$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.0, 45.8, 118.7, 121.1 (2C), 130.2, 138.7 (2C), 150.5, 196.6; HRMS Calcd. for $C_{10}H_{10}F_3NOS_2$ $[M + H]^+$: 282.0234; Found: 282.0226.

Pyrrolidine-1-carbodithioic acid 2-*p*-tolyl vinyl ester (Table 1, entry 11). White solid (mp 112 °C); IR (KBr) 2966, 2945, 2916, 2868, 1467, 1440, 1330, 1161, 1006, 958, 854, 821, 790, 520 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89 (q, $J = 6.68$ Hz, 2H), 1.97 (q, $J = 6.66$ Hz, 2H), 2.25 (s, 3H), 3.63 (t, $J = 6.41$ Hz, 2H), 3.87 (t, $J = 6.56$ Hz, 2H), 6.66 (d, $J = 11.04$ Hz, 1H), 7.07 (d, $J = 7.89$ Hz, 2H), 7.25 (d, $J = 7.94$ Hz, 2H), 7.37 (d, $J = 11.08$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 24.1, 25.9, 50.8, 55.3, 122.6, 128.1, 128.7 (2C), 129.1 (2C), 133.6, 137.4, 189.0; HRMS Calcd for $C_{14}H_{17}NS_2$ $[M + H]^+$: 264.0881; Found: 264.0872.

Morpholine-4-carbodithioic acid 2-*p*-tolyl vinyl ester (Table 1, entry 12). Yellow solid; (mp 118 °C); IR (KBr) 2954, 2920, 2850, 1473, 1425, 1261, 1222, 1110, 1028, 985, 852, 823, 524 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.74–3.77 (m, 4H), 4.19 (broad, 4H), 6.83 (d, $J = 10.97$ Hz, 1H), 7.18 (d, $J = 7.86$ Hz, 2H), 7.33 (d, $J = 7.97$ Hz, 2H), 7.41 (d, $J = 10.97$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 51.0 (2C), 66.2 (2C), 122.1, 128.7 (2C), 129.1 (2C), 129.2, 133.3, 137.6, 193.9; HRMS Calcd for $C_{14}H_{17}NOS_2$ $[M + H]^+$: 280.0830; Found: 280.0825.

Diethyl-dithiocarbamic acid 2-*p*-tolyl-vinyl ester (Table 1, entry 13). Colorless viscous oil; IR (neat) 2977, 2931, 1488, 1417, 1353, 1269, 1205, 1143, 1008, 981, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27–1.35 (m, 6H), 2.36 (s, 3H), 3.79 (q, $J = 6.94$ Hz, 2H), 4.04 (q, $J = 6.87$ Hz, 2H), 6.78 (d, $J = 11.07$ Hz, 1H), 7.18 (d, $J = 7.92$ Hz, 2H), 7.36 (d, $J = 7.98$ Hz, 2H), 7.44 (d, $J = 11.08$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 12.7, 21.2, 46.8, 49.9, 123.0, 128.2, 128.7 (2C), 129.0 (2C), 133.5, 137.3, 191.9; HRMS Calcd for $C_{14}H_{19}NS_2$ $[M + H]^+$: 266.1037; Found: 266.1030.

Piperidine-1-carbodithioic acid 2-(4-chloro-phenyl)-vinyl ester (Table 1, entry 14). Colorless viscous liquid; IR (neat) 2937, 2923, 2854, 1488, 1475, 1427, 1242, 1226, 1089, 1010, 974, 850,

829; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (broad, 6H), 3.93 (broad, 2H), 4.29 (broad, 2H), 6.73 (d, $J = 11.10$ Hz, 1H), 7.23–7.35 (m, 4H), 7.50 (d, $J = 11.10$ Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.8, 25.9 (2C), 52.1, 53.9, 125.4, 127.5, 128.9 (2C), 130.4 (2C), 133.5, 135.3, 191.8; HRMS Calcd for $C_{14}H_{16}ClNS_2$ $[M + H]^+$: 298.0491; Found: 298.0483.

Diethyl-dithiocarbamic acid 2-(4-chloro-phenyl)-vinyl ester (Table 1, entry 15). Colorless viscous oil; IR (neat) 2977, 2931, 2869, 1488, 1417, 1203, 1091, 1010, 829 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18–1.33 (m, 6H), 3.73 (q, $J = 6.94$ Hz, 2H), 3.99 (q, $J = 6.94$ Hz, 2H), 6.67 (d, $J = 11.11$ Hz, 1H), 7.18–7.31 (m, 4H), 7.42 (d, $J = 11.10$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.9, 13.2, 47.3, 50.4, 125.4, 127.4, 128.9 (2C), 130.4 (2C), 133.5, 135.3, 191.7; HRMS Calcd for $C_{13}H_{16}ClNS_2$ $[M + H]^+$: 286.0491; Found: 286.0602.

Diethyl-dithiocarbamic acid 2-(bromo-phenyl)vinyl ester (Table 1, entry 16). Viscous yellow liquid; IR (neat) 2976, 2929, 2869, 2852, 1488, 1417, 1354, 1269, 1203, 1143, 1024, 764 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, $J = 7.05$ Hz, 6H), 3.74 (q, $J = 7.05$ Hz, 2H), 4.04 (q, $J = 7.05$ Hz, 2H), 6.93 (d, $J = 10.89$ Hz, 1H), 7.13 (t, $J = 7.58$ Hz, 1H), 7.26–7.34 (m, 1H), 7.53–7.59 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6, 12.9, 47.0, 50.0, 124.1, 126.9, 127.1, 127.8, 129.1, 129.9, 132.8, 136.6, 191.6; HRMS Calcd for $C_{13}H_{16}BrNS_2$ $[M + H]^+$: 329.9986; Found: 329.9813.

Pyrrolidine-1-carbodithioic acid 2-*p*-tolyl-vinyl ester (Table 1, entry 19). White solid (mp 113 °C); IR (KBr) 2968, 2948, 2913, 2860, 1462, 1438, 1335, 1168, 1012, 938, 848 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (t, $J = 6.67$ Hz, 2H), 2.10 (t, $J = 6.75$ Hz, 2H), 2.33 (s, 3H), 3.67 (t, $J = 6.82$ Hz, 2H), 3.95 (t, $J = 6.79$ Hz, 2H), 6.73 (d, $J = 16.05$ Hz, 1H), 7.13 (d, $J = 7.97$ Hz, 2H), 7.34 (d, $J = 7.98$ v, 2H), 7.47 (d, $J = 16.03$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 24.4, 26.2, 50.8, 54.8, 121.4, 126.6 (2C), 129.4 (2C), 132.2, 133.6, 138.1, 190.5; HRMS Calcd for $C_{14}H_{17}NS_2$ $[M + H]^+$: 264.0881; Found: 264.0873.

Diethyl-dithiocarbamic acid 2-(4-methoxyphenyl)-vinyl ester (Table 1, entry 20). Brownish viscous liquid; IR (neat) 2976, 2931, 2833, 1606, 1510, 1488, 1417, 1269, 1251, 1031, 833, 785 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25–1.32 (m, 6H), 3.72 (q, $J = 6.79$ Hz, 2H), 3.78 (s, 3H), 4.01 (q, $J = 6.73$ Hz, 2H), 6.68 (d, $J = 15.95$ Hz, 1H), 6.85 (d, $J = 8.65$ Hz, 2H), 7.25 (d, $J = 15.88$ Hz, 1H), 7.38 (d, $J = 8.62$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 12.5, 46.9, 49.2, 55.2, 114.0 (2C), 119.7, 127.9 (2C), 129.1, 132.3, 159.5, 193.5; HRMS Calcd for $C_{14}H_{19}NOS_2$ $[M + H]^+$: 282.0986; Found: 282.0980.

Piperidine-1-carbodithioic acid 2-(4-chloro-phenyl)-vinyl ester (Table 1, entry 21). White solid (mp 122 °C); IR (KBr) 2941, 2925, 2854, 1471, 1488, 1429, 1242, 1232, 1118, 1010, 979, 835, 781 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (broad, 6H), 3.88 (broad, 2H), 4.29 (broad, 2H), 6.69 (d, $J = 15.99$ Hz, 1H), 7.30 (d, $J = 8.45$ Hz, 2H), 7.38 (d, $J = 8.43$ Hz, 2H), 7.50 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 25.6 (2C), 51.8, 52.8, 123.8, 127.8 (2C), 128.9 (2C), 130.9, 133.8, 134.9, 192.8; HRMS Calcd for $C_{14}H_{16}ClNS_2$ $[M + H]^+$: 298.0491; Found: 298.0488.

4. Conclusion

The present procedure using copper nanoparticles provides a very efficient and convenient methodology for the synthesis of aryl and styrenyl dithiocarbamates by a one-pot three component condensation of aryl/styrenyl halide, carbon disulfide and amine in water. The advantages offered by this procedure are operational simplicity, general applicability to acyclic and cyclic amines, ligand- and base-free reaction, high yields of products, excellent diastereoselectivity for styrenyl dithiocarbamates, and green protocol providing recyclability of catalyst up to four times without loss of efficiency, and use of water as reaction medium. To the best of our knowledge, condensation of amine, carbon disulfide and aryl/styrenyl halide catalyzed by Cu nanoparticles in water for the synthesis of aryl and styrenyl dithiocarbamates is novel and not reported earlier. Moreover, this methodolgy further demonstrates the potential of Cu nanoparticles and water in organic reactions.

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