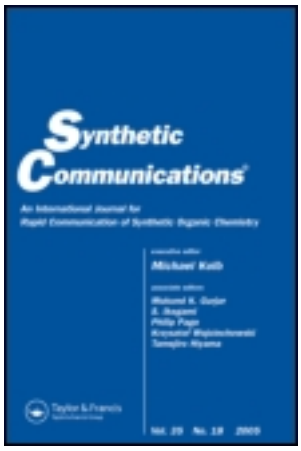

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SYNTHESIS OF N,N-DIARYL-N′,N′-1,4-PHENYLENEDI(OXYACETYL)-DITHIOUREAS AND CORRESPONDING DIUREAS

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SYNTHESIS OF *N*,*N*-DIARYL-*N*′,*N*′-1,4-PHENYLENEDI(OXYACETYL)-DITHIOUREAS AND CORRESPONDING DIUREAS

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ABSTRACT

N,*N*-Diaryl-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithioureas (**3a–l**) are synthesized under solid–liquid phase transfer catalysis. Meanwhile, the corresponding diureas of **3a–l**, *N*,*N*-Diaryl-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diureas (**4a–l**), are further synthesized by the reaction of **3a–l** with potassium iodate in high yield.

Thiourea derivatives have attracted much attention due to their herbicidal,[1] antibacterial,[2] anti-HIV,[3] anti-inflammatory[4] and plant-growth regulating[5] activity. Meanwhile urea derivatives are widely used as medicines and agrochemicals because of their anticonvulsive,[6] herbicidal,[7] antiacetylchlolinesterase,[8] antiulcer,[9] antineoplastic,[10] hypotensive,[11]

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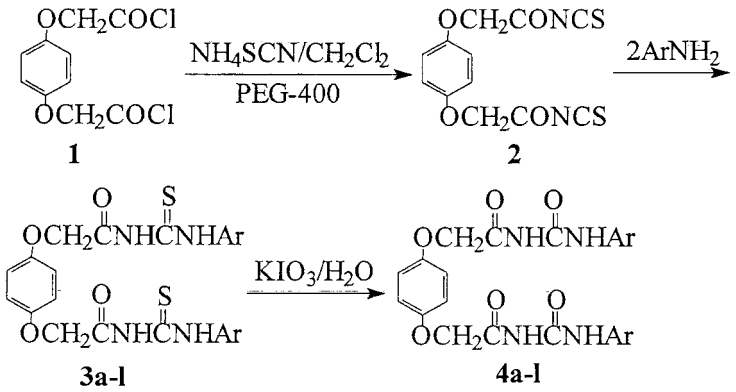
and hypoglycemic[12] activity. In addition, aryloxyacetic acid derivatives have also been used as herbicides and plant-growth regulators.[13–16] These applications prompt us to synthesize some new series of compounds bearing both thiourea and aryloxyacetyl moiety or both urea and aryloxyacetyl moiety, with the objective of further investigating the property and structure–activity relationship of these new compounds and obtaining new biologically active compounds.

In this paper we report a simple, high-rate and high-yield method for preparation of substituted dithioureas under solid–liquid phase transfer catalysts. Meanwhile, an aqueous solution route from substituted dithioureas to corresponding diureas is also introduced.

Reaction of 1,4-phenylenedi(oxyacetyl) dichloride (**1**) with ammonium thiocyanate, using polyethylene glycol-400 (PEG-400) as catalyst, the 1,4-phenylenedi(oxyacetyl) dithioisocyanate (**2**) is given as intermediate, which in situ reacts with arylamines to afford *N*,*N*-diaryl-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithioureas (**3a–l**) in excellent yield. Further, compounds **3a–l** on gentle reflux with potassium iodate in aqueous solution afford corresponding diureas, *N*,*N*-diaryl-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diureas (**4a–l**), in high yield (Sch. 1).



3,4	Ar	3,4	Ar
a	C_6H_5	g	4-BrC_6H_4
b	2-$CH_3C_6H_4$	h	1-Naphthyl
c	4-$CH_3C_6H_4$	i	2-Naphthyl
d	2-$CH_3OC_6H_4$	j	4-$O_2NC_6H_4$
e	2-ClC_6H_4	k	4-$CH_3CONHC_6H_4$
f	4-ClC_6H_4	l	2-Thiazolyl

Scheme 1.

PEG-400 as a phase transfer catalyst is indispensable for these reactions. It can easily react with NH_4SCN to form complex [PEG-400-NH_4^+]SCN^-, which makes the SCN^- possible to readily react with **1** and lead to the formation of intermediate **2**. However, if no PEG-400 is used, there is no intermediate **2** formed, therefore no any target compound **3a–l** are produced at all.

Although the many reagents of transformation of C=S into C=O are introduced in the literatures, such as benzeneselenic anhydride,[17] soft NO^+ species,[18] cuprous chloride-sodium hydroxide,[19] clayfen[20] and trifluoroacetic anhydride,[21] they all give different side reactions. Capps and Dehn[24] used the KIO_3 as desulfuring reagent to transform the thioureas of the type ArNHCSNHAr′ into corresponding ureas efficiently. We extend this method to the preparation of diureas bearing acyl groups successfully. We find that the KIO_3 is quite efficient reagent for the conversion of C=S into C=O. No any by-product is produced in these reactions. Moreover, the color change of the solution from colorless to violet because of the release of I_2 in the reaction can readily indicate the starting of the reaction, and the color change from violet to colorless because of the sublimation of I_2 under the mild reflux condition can readily indicate the termination of the reaction. In addition, it is worthy to mention that KIO_3 used in this paper is an available reagent to identify the presence of C=S group of the organic compounds.

The characterization of compounds **3a–l** and **4a–l** is based on their IR (KBr), ^{1}H NMR and elemental analyses. The IR spectra exhibit a characteristic strong absorption at 1151–1170 cm^{-1} attributable to the C=S of the dithioureas **3a–l**. The carbonyl absorption is observed at 1661–1690 cm^{-1} for **3a–l** and 1671–1698 cm^{-1} for **4a–l**. The ^{1}H NMR spectral data in d_6-dimethylsulfoxide show peaks at 12.08–12.38 (NH) and 11.68–11.82 ppm (NH) for **3a–l**, and 11.77–11.90 (NH) and 10.96–11.10 ppm (NH) for **4a–l**. All elemental analyses of **3a–l** and **4a–l** are good agreement with the structure prepared.

EXPERIMENTAL

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer and ^{1}H NMR spectra on a FT-80A instrument using $(CD_3)_2SO$ as solvent and Me_4Si as internal standard. Elemental analyses were performed on a Vario EI Elemental Analysis instrument. Mass spectra were recorded on a QP-1000A GC-MS using the impact mode (70 eV). Melting points were observed in an open capillary tube and uncorrected. 1,4-Phenylenedi(oxyacetyl) dichloride (**1**) was prepared

according to literature procedure.[23] Arylamines, ammonium thiocyanate, potassium iodate and PEG-400 were commercially available and used as received.

General Procedure for the Preparation of Compounds 3a–l

To a solution of 0.79 g (3.00 mmol) of 1,4-phenylenedi(oxyacetyl) dichloride (**1**) in 15 mL of methylene dichloride, 0.40 g (5.25 mmol) of ammonium thiocyanate and 0.04 g (0.10 mmol) of polyethylene glycol-400 were added. The mixture was stirred for 1 h at room temperature. Then arylamine (2.95 mmol) was added and the reaction mixture was stirred for another 0.5 h at room temperature. To the resulting mixture, 10 mL of water was added so that the inorganic salts were dissolved, then the slurry was filtered, the solid was washed with 3×5 mL water and recrystallized from DMF–EtOH–H_2O (6 : 3 : 1), and the product was given. The physical and spectral data of compounds **3a–l** are reported below.

***N,N*-Diphenyl-*N′,N′*-1,4-phenylenedi(oxyacetyl)-dithiourea (3a):** White solid. Yield: 90%. M.p.: 158–159°C. ^{1}H NMR (DMSO-d_6) δ 12.11 (s, 2H, NH), 11.70 (s, 2H, NH), 7.04–8.20 (m, 14H, Ar-H), 4.70 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}); 3203, 3143, 3061 (N-H), 1684 (C=O), 1156 (C=S). MS: m/z, 495 (M^+). Anal. calcd. for $C_{24}H_{22}N_4O_4S_2$: C, 58.28; H, 4.48; N, 11.33. Found: C, 58.41; H, 4.32; N, 11.39.

***N,N*-Di(2-Methylphenyl)-*N′,N′*-1,4-phenylenedi(oxyacetyl)-dithiourea (3b):** White solid. Yield: 87%. M.p.: 200–201°C. ^{1}H NMR (DMSO-d_6) δ 12.08 (s, 2H, NH), 11.68 (s, 2H, NH), 7.00–8.16 (m, 12H, Ar-H), 4.71 (s, 4H, CH_2), 2.26 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3397 (N-H), 1690 (C=O), 1151 (C=S). MS: m/z, 523 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_4S_2$: C, 59.75; H, 5.01; N, 10.72. Found: C, 59.58; H, 4.94; N, 10.81.

***N,N*-Di(4-Methylphenyl)-*N′,N′*-1,4-phenylenedi(oxyacetyl)-dithiourea (3c):** White solid. Yield: 95%. M.p.: 167–168°C. ^{1}H NMR (DNSO-d_6) δ 12.18 (s, 2H, NH), 11.70 (s, 2H, NH) 7.10–8.03 (m, 12H, Ar-H), 4.68 (s, 4H, CH_2), 2.24 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3305 (N-H), 1674 (C=O), 1160 (C=S). MS: m/z, 523 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_4S_2$: C, 59.75; H, 5.01; N, 10.72. Found: C, 59.66; H, 5.11; N, 10.79.

***N,N*-Di(2-Methoxylphenyl)-*N′,N′*-1,4-phenylenedi(oxyacetyl)-dithiourea (3d):** White solid. Yield: 94%. M.p.: 159–160°C. ^{1}H NMR (DMSO-d_6) δ 12.09 (s, 2H, NH), 11.69 (s, 2H, NH), 6.99–8.21 (m, 12H, Ar-H), 4.71 (s, 4H, CH_2), 3.40 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3267, 3204 (N-H), 1661 (C=O), 1168 (C=S). MS: m/z, 555 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_6S_2$: C, 56.30; H, 4.72; N, 10.10. Found: C, 56.54; H, 4.52; N, 10.22.

***N*,*N*-Di(2-Chlorophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3e):** White solid. Yield: 89%. M.p.: 156–157°C. ^{1}H NMR (DMSO-d_6) δ 12.12 (s, 2H, NH), 11.80 (s, 2H, NH), 7.29–8.16 (m, 12H, Ar-H), 4.73 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3367 (N-H), 1684 (C=O), 1157 (C=S). MS: m/z, 563 (M^+). Anal. calcd. for $C_{24}H_{20}N_4O_4S_2Cl_2$: C, 51.16; H, 3.58; N, 9.94. Found: C, 51.26; H, 3.70; N, 9.87.

***N*,*N*-Di(4-Chlorophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3f):** White solid. Yield: 91%. M.p. 179–180°C. ^{1}H NMR (DMSO-d_6) δ 12.20 (s, 2H, NH), 11.82 (s, 2H, NH), 7.20–8.18 (m, 12H, Ar-H), 4.72 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3370 (N-H), 1681 (C=O), 1156 (C=S). MS: m/z, 563 (M^+). Anal. calcd. for $C_{24}H_{20}N_4O_4S_2Cl_2$: C, 51.16; H, 3.58; N, 9.94. Found: C, 51.35; H, 3.42; N, 9.80.

***N*,*N*-Di(4-Bromophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3g):** White solid. Yield: 92%. M.p.: 224–225°C. ^{1}H NMR (DMSO-d_6) δ 12.30 (s, 2H, NH), 11.70 (s, 2H, NH), 7.10–8.20 (m, 12H, Ar-H), 4.68 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3271 (N-H), 1684 (C=O), 1160 (C=S). MS: m/z, 654 ($M^+ + 2$). Anal. calcd. for $C_{24}H_{20}N_4O_4S_2Br_2$: C, 44.19; H, 3.09; N, 8.59. Found: C, 44.28; H, 3.43; N, 8.25.

***N*,*N*-Di(1-Naphthyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3h):** White solid. Yield: 88%. M.p.: 163–164°C.^{1}H NMR (DMSO-d_6) δ 12.12 (s, 2H, NH), 11.68 (s, 2H, NH), 7.30–8.20 (m, 18H, Ar-H), 4.70 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3269, 3157 (N-H), 1688 (C=O), 1164 (C=S). MS: m/z, 595 (M^+). Anal. calcd. for $C_{32}H_{26}N_4O_4S_2$: C, 64.63; H, 4.41; N, 9.42. Found: C, 64.71; H, 4.39; N, 9.34.

***N*,*N*-Di(2-Naphthyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3i):** White solid. Yield: 91%. M.p.: 263–264°C. ^{1}H NMR (DMSO-d_6) δ 12.13 (s, 2H, NH), 11.70 (s, 2H, NH), 7.36–8.19 (m, 18H, Ar-H), 4.71 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3301, 3175 (N-H), 1690 (C=O), 1170 (C=S). MS: m/z, 595 (M^+). Anal. calcd. for $C_{32}H_{26}N_4O_4S_2$: C, 64.63; H, 4.41; N, 9.42. Found: C, 64.58; H, 4.29; N, 9.57.

***N*,*N*-Di(4-Nitrophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3j):** White solid. Yield: 91%. M.p.: 194–195°C. ^{1}H NMR (DMSO-d_6) δ 12.38 (s, 2H, NH), 11.80 (s, 2H, NH), 7.36–8.20 (m, 12H, Ar-H), 4.76 (s, 4H, CH_2). IR(KBr, ν, cm^{-1}): 3369 (N-H), 1701 (C=O), 1170 (C=S). MS: m/z, 585 (M^+). Anal. calcd. for $C_{24}H_{20}N_6O_8S_2$: C, 49.31; H, 3.45; N, 14.38. Found: C, 49.53; H, 3.43; N, 14.46.

***N*,*N*-Di(4-Acetylamidophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-dithiourea (3k):** White solid. Yield: 86%. M.p.: 294–295°C. ^{1}H NMR (DMSO-d_6) δ 12.30 (s, 2H, NH), 11.78 (s, 2H, NH), 9.31 (s, 2H, NH) 7.11–8.23 (m, 12H, Ar-H), 4.69 (s, 4H, CH_2), 2.57 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3294, 3056 (N-H), 1670 (C=O), 1158 (C=S). MS: m/z, 609 (M^+). Anal. calcd. for $C_{28}H_{29}N_6O_6S_2$: C, 55.25; H, 4.64; N, 13.81. Found: C, 55.12; H, 4.78; N, 13.89.

***N*,*N*-Di(2-Thiazolyl)-*N*′,*N*′-1,4 phenylenedi(oxyacetyl)-dithiourea (3l):** White solid. Yield: 86%. M.p.: 233–234°C. ^{1}H NMR (DMSO-d_6) δ 12.20 (s, 2H, NH), 11.68 (s, 2H, NH), 7.01–8.11 (m, 8H, Ar-H& Th-H), 4.71 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3151 (N-H), 1677 (C=O), 1168 (C=S). MS: m/z, 509 (M^+). Anal. calcd. for $C_{18}H_{16}N_4O_4S_4$: C, 42.51; H, 3.17; N, 16.52. Found: C, 42.64; H, 3.33; N, 16.49.

General Procedure for the Preparation of Compounds 4a–l

A suspension of 0.50 mmol of compound **3** and 0.75 mmol (0.16 g) of potassium iodate in 30 mL of water was refluxed for 1 h. The resulting mixture was filtered, the solid was washed with 3×5 mL water and recrystallized from DMF–EtOH–H_2O (6 : 3 : 1), then the product was given. The physical and spectral data of compounds **4a–l** are reported below.

***N*,*N*-Diphenyl-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4a):** White solid. Yield: 97%. M.p.: 200–201°C. ^{1}H NMR (DMSO-d_6) δ 11.82 (s, 2H, NH), 11.03 (s, 2H, NH), 7.02–8.18 (m, 14H, Ar-H), 4.71 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3164 (N-H), 1682 (C=O). MS: m/z, 462 (M^+). Anal. Calcd. for $C_{24}H_{22}N_4O_6$: C, 62.33; H, 4.79; N, 12.12. Found: C, 62.11; H, 4.58; N, 12.36.

***N*,*N*-Di(2-Methylphenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4b):** White solid. Yield: 93%. M.p.: 131–132°C. ^{1}H NMR (DMSO-d_6) δ 11.80 (s, 2H, NH), 11.06 (s, 2H, NH), 6.96–8.10 (m, 12H, Ar-H), 4.72 (s, 4H, CH_2), 2.23 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3317 (N-H), 1688 (C=O). MS: m/z, 491 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_6$: C, 63.66; H, 5.34; N, 11.42. Found: C, 63.75; H, 5.43; N, 11.68.

***N*,*N*-Di(4-Methylphenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4c):** White solid. Yield: 94%. M.p.: 203–204°C. ^{1}H NMR (DMSO-d_6) δ 11.81 (s, 2H, NH), 11.07 (s, 2H, NH), 7.08–8.09 (m, 12H, Ar-H), 4.69 (s, 4H, CH_2), 2.25 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3305 (N-H), 1673 (C=O). MS: m/z, 491 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_6$: C, 63.66; H, 5.34; N, 11.42. Found: C, 63.55; H, 5.21; N, 11.62.

***N*,*N*-Di(2-Methoxylphenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4d):** White solid. Yield: 98%. M.p.: 165–166°C. ^{1}H NMR (DMSO-d_6) δ 11.79 (s, 2H, NH), 11.06 (s, 2H, NH), 7.03–8.16 (m, 12H, Ar-H), 4.73 (s, 4H, CH_2), 3.41 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3302 (N-H), 1686 (C=O). MS: m/z, 523 (M^+). Anal. calcd. for $C_{26}H_{26}N_4O_8$: C, 59.77; H, 5.02; N, 10.72. Found: C, 59.61; H, 5.13; N, 10.86.

***N*,*N*-Di(2-Chlorophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4e):** White solid. Yield: 90%. M.p.: 161–162°C. ^{1}H NMR (DMSO-d_6) δ 11.81 (s, 2H, NH), 11.06 (s, 2H, NH), 7.10–8.06 (m, 12H, Ar-H), 4.74 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3371, 3064 (N-H), 1690 (C=O). MS: m/z, 531

(M^+). Anal. calcd. for $C_{24}H_{20}N_4O_6Cl_2$: C. 54.25; H, 3.79; N, 10.54. Found: C, 54.37; H, 3.70; N, 10.69.

***N*,*N*-Di(4-Chlorophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4f):** White solid. Yield: 91%. M.p.: 196–197°C. ^{1}H NMR (DMSO-d_6) δ 11.79 (s, 2H, NH), 10.99 (s, 2H, NH), 7.26–8.23 (m, 12H, Ar-H), 4.73 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3300 (N-H), 1681 (C=O). MS: m/z, 531 (M^+). Anal. calcd. for $C_{24}H_{20}N_4O_6Cl_2$: C, 54.25; H, 3.79; N, 10.54. Found: C, 54.20; H, 3.62; N, 10.74.

***N*,*N*-Di(2-Bromophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4g):** White solid. Yield: 95%. M.p.: 191–192°C. ^{1}H NMR (DMSO-d_6) δ 11.83 (s, 2H, NH), 11.07 (s, 2H, NH), 7.19–8.18 (m, 12H, Ar-H), 4.69 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3317 (N-H), 1671 (C=O), 1160 (C=S). MS: m/z, 622 ($M^+ + 2$). Anal. calcd. for $C_{24}H_{20}N_4O_6Br_2$: C, 46.47; H, 3.25; N, 9.03. Found: C, 46.61; H, 3.40; N, 9.23.

***N*,*N*-Di(1-Naphthyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4h):** White solid. Yield: 90%. M.p.: 113–114°C. ^{1}H NMR (DMSO-d_6) δ 11.77 (s, 2H, NH), 10.96 (s, 2H, NH), 7.26–8.09 (m, 18H, Ar-H), 4.74 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3320 (N-H), 1683 (C=O). MS: m/z, 563 (M^+). Anal. calcd. for $C_{32}H_{26}N_4O_6$: C, 68.32; H, 4.66; N, 9.96. Found: C, 68.45; H, 4.40; N, 9.99.

***N*,*N*-Di(2-Naphthyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4i):** White solid. Yield: 94%. M.p.: 257–258°C. ^{1}H NMR (DMSO-d_6) δ 11.80 (s, 2H, NH), 11.01 (s, 2H, NH), 7.30–8.13 (m, 18H, Ar-H), 4.74 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3327 (N-H), 1685 (C=O). MS: m/z, 563 (M^+). Anal. calcd. for $C_{32}H_{26}N_4O_6$: C, 68.32; H, 4.66; N, 9.96. Found: C, 68.21; H, 4.72; N, 9.88.

***N*,*N*-Di(4-Nitrophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4j):** White solid. Yield: 92%. M.p.: 187–188°C. ^{1}H NMR (DMSO-d_6) δ 11.90 (s, 2H, NH), 11.10 (s, 2H, NH), 7.23–8.21 (m, 12H, Ar-H), 4.79 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3370, 3080 (N-H), 1698 (C=O). MS: m/z, 552 (M^+). Anal. calcd. for $C_{24}H_{20}N_6O_{10}$: C, 52.18; H, 3.65; N, 15.21. Found: C, 52.04; H, 3.48; N, 15.36.

***N*,*N*-Di(4-Acetylamidophenyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4k):** White solid. Yield: 95%. M.p.: 298–299°C. ^{1}H NMR (DMSO-d_6) δ 11.86 (s, 2H, NH), 10.99 (s, 2H, NH), 9.31 (s, 2H, NH), 7.19–8.16 (m, 12H, Ar-H), 4.73 (s, 4H, CH_2), 2.60 (s, 6H, CH_3). IR (KBr, ν, cm^{-1}): 3317 (N-H), 1671 (C=O). MS: m/z, 577 (M^+). Anal. calcd. for $C_{28}H_{28}N_6O_8$: C, 58.33; H, 4.89; N, 14.58. Found: C, 58.45; H, 4.79; N, 14.62.

***N*,*N*-Di(2-Thiazolyl)-*N*′,*N*′-1,4-phenylenedi(oxyacetyl)-diurea (4l):** White solid. Yield: 91%. M.p.: 251–252°C. ^{1}H NMR (DMSO-d_6) δ 11.80 (s, 2H, NH), 10.98 (s, 2H, NH), 6.89–8.20 (m, 8H, Ar-H and Th-H), 4.70 (s, 4H, CH_2). IR (KBr, ν, cm^{-1}): 3148 (N-H), 1677 (C=O). MS: m/z, 476 (M^+).

Anal. calcd. for $C_{18}H_{16}N_6O_6S_2$: C, 45.37; H, 3.38; N, 17.64. Found: C, 45.28; H, 3.43; N, 17.79.

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