Supplementary Information

Synthesis of *N*-aminoimidazol-2-thione derivatives using tandem approach

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1. Experimental details

Melting points were taken in open capillaries and are uncorrected. ^{1}H NMR were recorded on a Brucker 300 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 1800 IR spectrophotometer. HTIB, needed for the present study was prepared starting from aniline. Diazotization of aniline followed by reaction with potassium iodide gave iodobenzene which is chlorinated to obtain the I(III) reagent, (dichloroiodo)benzene ($PhICl_2$). It is reacted with Na_2CO_3-NaOH to produce iodosobenzene which is acetoxylated in glacial acetic acid to produce (diacetoxyiodo)benzene (DIB), its treatment with *p*-TsOH in acetonitrile offered HTIB. The various arylhydrazines were prepared from the corresponding anilines by diazotizing them and then reducing the diazonium salts followed by acidification.[1-3]Most of the common chemicals such as propiophenone, potassium thiocyanate, phenyl hydrazine and solvents were obtained from commercial suppliers.

2. Synthesis of *N*-substituted 1-amino-2,3-dihydro-1*H*-imidazole-2-thiones

(a) Method A: Synthesis of 2, 3-dihydro-4-methyl-5-phenyl-1-phenylamino-1*H*-imidazole-2-thione *via* isolation of α-tosyloxypropiophenone and α-thiocyanatopropiophenone

α-Tosyloxypropiophenone (**2**)

To a solution of propiophenone (1.34 g, 10 mmol) in CH_3CN (20 ml) was added HTIB (3.96 g, 10 mmol) and the reaction mixture was refluxed for 2 hrs. The solvent was removed by distillation and the residue was crystallized out by the addition of a little ethanol (2 ml). Filtration and washing with cold ethanol gave the compound **1**. M. p. 64-66 ^oC (Lit. m. p. 68-69 ^oC), yield 2.43 g (79%).[4]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 1.52 (d, J = 6.9 Hz, 3H, C***H***$_3$), 2.33 (s, 3H, $O_3SC_6H_4C$***H***$_3$), 5.69 (q, J = 7.2 Hz, 1H, C***H***CH_3), 7.17-7.84 (m, 9H, C_6***H***$_5$, O_3SC_6***H***$_4$)

α-Thiocyanatopropiophenone (**3**)

To a solution of **1**(1g, 3.3 mmol) in ethanol (20 ml) was added potassium thiocyanate (0.32 g, 3.3 mmol) and the mixture was refluxed for 10 min. The solvent was distilled off and to the resulting residue was added cold water. A gummy product was obtained which was used for further reaction without purification. Formation of **2** was confirmed by IR and ^{1}HNMR. Yield 0.44 g (71%).

IR (υ_{max}): 2156 cm^{-1} (SCN).

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 1.80 (d, J = 7.2 Hz, 3H, C***H***$_3$), 5.01 (q, J = 7.1 Hz, 1H, COC***H***), 7.36-7.49 (m, 2H, 3,5-***H***, aromatic), 7.57-7.62 (m, 1H, 4-***H***, aromatic)7.82-7.89 (m, 2H, 2,6-***H***, aromatic).

2, 3-Dihydro-4-methyl-5-phenyl-1-phenylamino-1H-imidazole-2-thione ***(4a)***

To a solution of **2** (1.91 g, 10 mmol) in glacial acetic acid (20 ml) was added phenylhydrazine (2.81 g, 10 mmol) and the mixture was stirred for 5 hr at room temperature. Most of the solvent was distilled off *in vacuo* and to the residual mixture was added cold water. The resultant residual mass was crystallized from the ethanol to give pure **3a**, m. p. 212 ^oC (lit. m. p. 212-214 ^oC)[5], yield 2.11 g (75%).

(b) Method B: One pot synthesis of *N*-substituted-1-amino-2,3-dihydro-1*H*-imidazole-2-thiones **(4):**

HTIB (3.96 g, 10.1 mmol) was added to a solution of propiophenone (1.34 g, 10 mmol) in acetonitrile (20 ml) and the reaction mixture was stirred for 2 hr. Most of the acetonitrile was removed by distillation and 20 ml glacial acetic acid was added to it. To the resulting solution was added potassium thiocyanate (0.97 g, 10 mmol) and the solution was stirred for 30 min. The subsequent addition of phenylhydrazine was followed by stirring for 5 hr at room temperature. Most of the solvent was distilled off in vacuo and the resulting residue was basified with saturated solution of $NaHCO_3$ and extracted with dichloromethane (3x20 ml). The combined organic phase was dried (anhyd. Na_2CO_3) and concentrated to give crude gummy product which on

recrystallization from EtOH afforded the pure product **4a** in yield 2.00 g (71 %). The same experimental procedure was adopted for the synthesis of other derivatives **4b-i.**

3. Spectral data of title compounds

2,3-Dihydro-4-methyl-5-phenyl-1-phenylamino-1*H*-imidazole-2-thione (4a)

M. p. 212 ^{o}C (Lit.m.p. 212-214^{o}C).[5]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.28 (s, 3H, C***H***$_3$), 6.63-6.66 (m, 2H, 3,5-H, 5-C_6***H***$_5$), 6.89-6.94 (m, 1H, 4-H, C_6***H***$_5$), 7.16-7.21 (m, 2,6-H, 5-C_6***H***$_5$), 7.33-7.38 (m, 5H, NHC_6***H***$_5$)

1-(4-Chlorophenylamino)-2,3-dihydro-4-methyl-5-phenyl-1*H*-imidazole-2-thione (4b)

M. p. 210-212 ^{o}C (Lit. m.p. 212^{o}C).[5]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.28 (s, 3H, C***H***$_3$), 6.59 (d, J = 7 Hz, 2H, 2',6'-H, NHC_6***H***$_4$), 7.14 (d, J = 6.7 Hz, 2H, 3',5'-H, NHC_6***H***$_4$), 7.30-7.47 (m, 5H, 5-C_6***H***$_5$)

1-(2,4-Dichlorophenylamino)-2,3-dihydro-4-methyl-5-phenyl-1*H*-imidazole-2-thione (4c)

M. p. 214-216 ^{o}C.

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.24 (s, 3H, C***H***$_3$), 6.28 (d, 1H, J = 8.7 Hz, 6'-H, NHC_6***H***$_3$) 6.99-7.01 (dd, 1H, J = 8.7 Hz, J = 2.2 Hz, 5'-H, NHC_6***H***$_3$), 7.25 (d, 1H, J = 2.2 Hz, 3'-H, NHC_6***H***$_3$), 7.28-7.39 (m, 5H, 5-C_6***H***$_5$), 7.71 (s, 1H, 1-NN***H***)

HRMS (m/z): Calcd. For C16H13N3SCl2: 349.020725, Found: 349.018960

2,3-Dihydro-4-methyl-1-(4-methylphenylamino)-5-phenyl-1*H*-imidazole-2-thione (4d)

M. p. 192-193 ^{o}C (Lit. M.p. 192-194^{o}C).[5]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.27 (s, 3H, C***H***$_3$), 2.31 (s, 3H, C_6H_4C***H***$_3$), 6.42 (d, J = 7.4 Hz, 2H, 3',5'-H, NHC_6***H***$_4$), 6.94 (d, J = 7.2 Hz, 2H, 2',6'-H, NHC_6***H***$_4$), 7.35-7.42 (m, 5H, 5- C_6***H***$_5$).

2,3-Dihydro-4-methyl-1-(4-methoxyphenylamino)-5-phenyl-1H-imidazole-2-thione (4e)

M. p. 220-221^{o}C (Lit. m.p. 220-222^{o}C).[6]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.26 (s, 3H, C***H***$_3$), 3.74 (s, 3H, OC***H***$_3$), 7.03-7.18 (m, 4H, NHC_6***H***$_4$), 7.25-7.32 (m, 5H, 5-C_6***H***$_5$).

2,3-Dihydro-4-methyl-1-(4-fluorophenylamino)-5-phenyl-1*H*- imidazole-2-thione (4f)

M. p. 227-229 ^oC (Lit. m.p. 228-231^oC).[6]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.28 (s, 3H, C***H***$_3$), 7.10-7.18 (m, 2H, 2',6'-H NHC_6***H***$_4$), 7.20-7.31 (m, 5H, 5-C_6***H***$_5$), 7.42-7.55 (m, 2H, 3',5'-H, NHC_6***H***$_4$).

2,3-Dihydro-4-methyl-1-(4-nitrophenylamino)-5-phenyl-1*H*- imidazole-2-thione (4g)

M. p. 259 ^oC (Lit. m.p. 260-262^oC).[5]

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.29 (s, 3H, C***H***$_3$), 6.59 (d, J = 9.1 Hz,2H, 2',6'-H NHC_6***H***$_4$), 7.27-7.35 (m, 5H, 5-C_6***H***$_5$), 8.02 (d, J = 9.3 Hz, 2H, 3',5'-H, NHC_6***H***$_4$).

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