

SUPPORTING DATA

Experimental

Melting points were determined in an open capillary and uncorrected. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{\max} in cm^{-1}) on KBr disks. ^1H NMR (300 MHz, 400 MHz, 500 MHz) spectra were recorded on a Bruker DPX-300, Varian-400 FT-NMR, Bruker DPX-500 and spectrometer in CDCl_3 (chemical shift in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a Leco 932 CHNS analyzer and on a TOF MASS ES+ instrument respectively. Silica gel [(60-120 mesh), spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60 $^\circ\text{C}$ -80 $^\circ\text{C}$.

General Procedure for the Preparation of 1,3-Dimethyl-5-mercapto Uracil: (2)

Compound **2** was prepared according to our earlier published procedure from 5-bromo-1,3-dimethyl uracil [8].

General Procedure for the Preparation of 1,3-Dimethyl-5-(4-aryloxy-2-but-ynylthio) Pyrimidine-2,4-Dione

To a mixture of 1,3-dimethyl-5-mercapto uracil (**2**, 0.2 g, 1 mmol), 1-chloro-4-aryloxybut-2-yne (**3a-g**, 0.24 g, 1 mmol) in CH_2Cl_2 (50 ml) is added to a solution of Tetrabutyl ammonium bromide (TBAB) in 5 % aqueous NaOH (50 ml) and the mixture was stirred at room temperature 2-2.5 h. The reaction mixture was then diluted with water and extracted with CH_2Cl_2 (3x25 ml). The combined extract was washed successively with 2N HCl (3x25 ml), brine, and dried (Na_2SO_4). The solvent was removed in *vacuo* and the residual crude mass was purified by column chromatography over silica gel.

5-(4-(4-bromophenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4a)

Yield: 83 %; mp 110 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2953 (C-H stretching), 2224 (C=C), 1707 (C=O), 1656, 1439 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 3.29 (s, 3H, -NCH₃), 3.35 (s, 3H, -NCH₃), 3.55 (t, $J = 2.1$ Hz, 2H, -SCH₂), 4.65 (t, $J = 2.1$ Hz, 2H, -OCH₂), 6.83-7.40 (m, 4H, ArH), 7.44 (s, 1H, C₆-H); MS: $m/z = 394, 396$ (M^+); Anal calcd for $\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{O}_3\text{S}$ require C, 48.60; H, 3.80; N, 7.09 % found C, 48.39; H, 3.83; N, 7.16 %.

5-(4-(3,5-dimethylphenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4b)

Yield: 80 %; mp 95 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2960 (C-H stretching), 2226 (C=C), 1697 (C=O), 1641, 1440 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 2.27 (s, 6H, ArCH₃), 3.21 (s, 3H, -NCH₃), 3.33 (s, 3H, -NCH₃), 3.51 (t, $J = 1.8$ Hz, 2H, -SCH₂), 4.62 (t, $J = 1.8$ Hz, 2H, -OCH₂), 6.55-6.67 (m, 3H, ArH), 7.40 (s, 1H, C₆-H); MS: $m/z = 344$ (M^+); Anal calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ require C, 62.79; H, 5.81; N, 8.13 % found C, 62.53; H, 5.79; N, 8.14 %.

5-(4-(4-chloro-3,5-dimethylphenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4c)

Yield: 85 %; mp 95 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2956 (C-H stretching), 2224 (C=C), 1708 (C=O), 1645, 1442 cm^{-1} ; ^1H

NMR (CDCl_3 , 400 MHz): δ 2.34 (s, 6H, ArCH₃), 3.26 (s, 3H, -NCH₃), 3.33 (s, 3H, -NCH₃), 3.53 (t, $J = 1.8$ Hz, 2H, -SCH₂), 4.62 (t, $J = 1.8$ Hz, 2H, -OCH₂), 6.66 (m, 2H, ArH), 7.43 (s, 1H, C₆-H); MS: $m/z = 378, 380$ (M^+); Anal calcd for $\text{C}_{18}\text{H}_{19}\text{ClN}_2\text{O}_3\text{S}$ require C, 56.99; H, 5.01; N, 7.38 % found C, 57.02; H, 4.99; N, 7.59 %.

5-(4-(2,4-dichlorophenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4d)

Yield: 81 %; mp 125 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2956 (C-H stretching), 2225 (C=C), 1697 (C=O), 1639, 1439 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 3.33 (s, 3H, -NCH₃), 3.35 (s, 3H, -NCH₃), 3.55 (t, $J = 1.8$ Hz, 2H, -SCH₂), 4.74 (t, $J = 1.8$ Hz, 2H, -OCH₂), 6.97-7.38 (m, 3H, ArH), 7.47 (s, 1H, C₆-H); MS: $m/z = 384, 388$ (M^+); Anal calcd for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_3\text{S}$ require C, 49.74; H, 3.62; N, 7.25 % found C, 49.98; H, 3.59; N, 7.28 %.

5-(4-(4-chloro-3-methylphenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4e)

Yield: 76 %; mp 80 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2953 (C-H stretching), 2225 (C=C), 1708 (C=O), 1658, 1439 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 2.34 (s, 3H, ArCH₃), 3.28 (s, 3H, -NCH₃), 3.34 (s, 3H, -NCH₃), 3.54 (t, $J = 1.8$ Hz, 2H, -SCH₂), 4.63 (t, $J = 1.8$ Hz, 2H, -OCH₂), 6.70-7.23 (m, 3H, ArH), 7.46 (s, 1H, C₆-H); MS: $m/z = 364, 366$ (M^+); Anal calcd for $\text{C}_{17}\text{H}_{17}\text{ClN}_2\text{O}_3\text{S}$ require C, 55.91; H, 4.65; N, 7.67 % found C, 55.86; H, 4.42; N, 7.85 %.

5-(4-(2-bromo-4,6-dimethylphenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4f)

Yield: 75 %; mp 85 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2923 (C-H stretching), 2226 (C=C), 1708 (C=O), 1657, 1439 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 2.25 (s, 3H, ArCH₃), 2.28 (s, 3H, ArCH₃), 3.36 (s, 3H, -NCH₃), 3.38 (s, 3H, -NCH₃), 3.52 (t, $J = 2$ Hz, 2H, -SCH₂), 4.57 (t, $J = 2$ Hz, 2H, -OCH₂), 6.91 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.62 (s, 1H, C₆-H); MS: $m/z = 422, 424$ (M^+); Anal calcd for $\text{C}_{18}\text{H}_{19}\text{BrN}_2\text{O}_3\text{S}$ require C, 51.06; H, 4.49; N, 6.61 % found C, 51.27; H, 4.50; N, 6.65 %.

5-(4-(4-methoxyphenoxy)but-2-ynylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4g)

Yield: 78 %; mp 84 $^\circ\text{C}$; IR (KBr) ν_{\max} : 2960 (C-H stretching), 2225 (C=C), 1710 (C=O), 1650, 1440 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 3.26 (s, 3H, -NCH₃), 3.35 (s, 3H, -NCH₃), 3.53 (t, $J = 1.8$ Hz, 2H, -SCH₂), 3.77 (s, 3H, -OCH₃), 4.61 (t, $J = 1.8$ Hz, 2H, -OCH₂), 6.80-6.89 (m, 4H, ArH), 7.46 (s, 1H, C₆-H); MS: $m/z = 346$ (M^+); Anal calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ require C, 58.96; H, 5.20; N, 8.09 % found C, 59.09; H, 5.25; N, 8.28 %.

General Procedure for the Oxidation and Rearrangement of (4a-g)

m-CPBA (0.1 g, 50 %, 0.3 mmol) in CH_2Cl_2 (50 ml) was slowly added to stirred solution of the sulfides (**4a-g**) (0.1 g, 0.3 mmol) in CH_2Cl_2 (30 ml) at 0-5 $^\circ\text{C}$ over a period of 30 minutes. The mixture was stirred for half an hour more. Some *m*-chloroperbenzoic acid separated as insoluble solid at 0 $^\circ\text{C}$. After completion of the reaction the solution was washed with 5 % Na_2CO_3 solution to remove the organic acid. The sulfoxides were refluxed in CHCl_3 (20

ml) for 5-6 h. The solvent was removed and residual mass was subjected to column chromatography over silica gel to give products (**6a-g**) as crystalline solids.

7-(2-(4-bromophenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6a)

Yield: 71 %; mp 115 °C; IR (KBr) max : 1697 (C=O), 1651, 1471 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): H 3.45 (s, 3H, -NCH₃), 4.46 (s, 3H, -NCH₃), 5.02 (s, 2H, -OCH₂), 6.80-7.41 (m, 4H, ArH), 8.33 (s, 1H, -SCH); MS: m/z = 408, 410 (M^+); Anal calcd for $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_4\text{S}$ require C, 46.94; H, 3.17; N, 6.84 % found C, 46.96; H, 3.08; N, 6.98 %.

7-(2-(3,5-dimethylphenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6b)

Yield: 76 %; mp 108 °C; IR (KBr) max : 1702 (C=O), 1654, 1489 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): H 2.26 (s, 6H, ArCH₃), 3.44 (s, 3H, -NCH₃), 3.46 (s, 3H, -NCH₃), 4.99 (s, 2H, -OCH₂), 6.49-6.64 (m, 3H, ArH), 8.35 (s, 1H, -SCH); MS: m/z = 359 ($\text{M}^+\text{+H}$); Anal calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ require C, 60.33; H, 5.03; N, 7.82 % found C, 60.52; H, 5.04; N, 7.93 %.

7-(2-(4-chloro-3,5-dimethylphenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6c)

Yield: 73 %; mp 80 °C; IR (KBr) max : 1695 (C=O), 1655, 1473 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): H 2.32 (s, 6H, ArCH₃), 3.41 (s, 3H, -NCH₃), 3.46 (s, 3H, -NCH₃), 4.99 (s, 2H, -OCH₂), 6.61 (s, 2H, ArH), 8.33 (s, 1H, -SCH); MS: m/z = 393 ($\text{M}^+\text{+H}$); Anal calcd for $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_4\text{S}$ require C, 54.92; H, 4.34; N, 7.12 % found C, 54.68; H, 4.27; N, 7.23 %.

7-(2-(2,4-dichlorophenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6d)

Yield: 81 %; mp 170 °C; IR (KBr) max : 1703 (C=O), 1655, 1480 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): H 3.45 (s,

3H, -NCH₃), 3.47 (s, 3H, -NCH₃), 5.05 (s, 2H, -OCH₂), 6.84-7.39 (m, 3H, ArH), 8.46 (s, 1H, -SCH); MS: m/z = 399, 403 ($\text{M}^+\text{+H}$); Anal calcd for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_4\text{S}$ require C, 47.95; H, 3.01; N, 6.96 % found C, 48.17; H, 3.07; N, 7.01 %.

7-(2-(4-chloro-3-methylphenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6e)

Yield: 65 %; mp 110 °C; IR (KBr) max : 1703 (C=O), 1652, 1480 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): H 2.32 (s, 3H, ArCH₃), 3.45 (s, 3H, -NCH₃), 3.47 (s, 3H, -NCH₃), 5.01 (s, 2H, -OCH₂), 6.64-6.81 (m, 3H, ArH), 8.34 (s, 1H, -SCH); MS: m/z = 379, 381 ($\text{M}^+\text{+H}$); Anal calcd for $\text{C}_{17}\text{H}_{15}\text{ClN}_2\text{O}_4\text{S}$ require C, 53.82; H, 3.95; N, 7.38 % found C, 53.76; H, 3.81; N, 7.44 %.

7-(2-(2-bromo-4,6-dimethylphenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6f)

Yield: 69 %; mp 115 °C; IR (KBr) max : 1706 (C=O), 1659, 1479 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): H 2.27 (s, 3H, ArCH₃), 2.31 (s, 3H, ArCH₃), 3.47 (s, 3H, -NCH₃), 3.56 (s, 3H, -NCH₃), 4.89 (s, 2H, -OCH₂), 6.91 (s, 1H, ArH), 7.18 (s, 1H, ArH), 8.47 (s, 1H, -SCH); MS: m/z = 461 ($\text{M}^+\text{+Na}$); Anal calcd for $\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{O}_4\text{S}$ require C, 49.42; H, 3.89; N, 6.41 % found C, 49.51; H, 3.85; N, 6.52 %.

7-(2-(4-methoxyphenoxy)acetyl)-1,3-dimethylthioeno[3,2-d]pyrimidine-2,4(1H,3H)-dione (6g)

Yield: 79 %; mp 87 °C; IR (KBr) max : 1708 (C=O), 1660, 1450 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): H = 3.41 (s, 3H, -NCH₃), 3.45 (s, 3H, -NCH₃), 3.75 (s, 3H, -OCH₃), 4.98 (s, 2H, -OCH₂), 6.82 (m, 4H, ArH), 8.33 (s, 1H, -SCH); MS: m/z = 361 ($\text{M}^+\text{+H}$), 383 ($\text{M}^+\text{+Na}$); Anal calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5\text{S}$ require C, 56.66; H, 4.44; N, 7.77 % found C, 56.62; H, 4.31; N, 7.91 %.