Electronic Supplementary Material (ESI)

Supporting Information

Iodine-catalyzed regioselective direct sulfenylation of uracil with sulfonyl hydrazide as sulfur source under solvent free condition

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1. General information

All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Reactions were carried out in oven-dried round-bottom flask. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker 600MHz spectrometer (600 MHz and 150 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$:δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$:δ 77.16). Due to improper storage of $CDCl_3$ in the laboratory, it contains a certain amount of water. See its ^{1}H NMR for details (δ 1.60±0.10 S). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Waters G2-XSQTof mass spectrometer. Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. General procedure for the preparation of compounds 3

Uracil (0.5 mmol), various sulfonyl hydrazides (0.75 mmol), and I_2 (0.1mmol) were taken in a 10 mL standard test tube. After that, the reaction mixture was heated at 120°C for 0.5 h. Then, the mixture was cooled and diluted with ethyl acetate and the reaction was quenched with 0.5 mL of saturated sodium thiosulfate. It was concentrated under reduced pressure. The crude product was then purified by column chromatography column chromatography (elution: petroleum ether/ethyl acetate = 3/1).

3. Gram-scale synthesis

Uracil (10 mmol, 1.4 g), 4-methanesulfonyl hydrazide (15 mmol, 2.79 g), and I_2 (~~0.2~~2 mmol, 508 mg) were taken in a 100 mL standard test tube. After that, the reaction mixture was heated at 120°C for 0.5 h. Then, the mixture was cooled and diluted with ethyl acetate and the reaction was quenched with 0.5 mL of saturated sodium thiosulfate. It was concentrated under reduced pressure. The crude product was then purified by column chromatography column chromatography (elution: petroleum ether/ethyl acetate = 3/1).

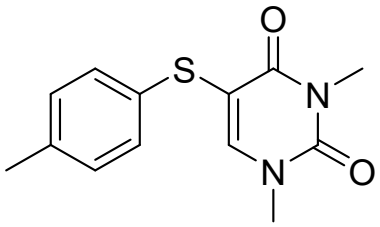
4. Experimental details for the synthesis of 4a

1,3-dimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione **5a** (26 mg, 0.1 mmol) and m-CPBA (3-Chloroperoxybenzoic acid) (52 mg, 0.3 mmol) were dissolved in dichloromethane(5 mL). The mixture was kept at 20℃ for 9 h, and the dichloromethane was removed in vacuo. The crude product was then purified using column chromatography to afforded 6 (0.091 mmol, 27 mg, 90% yield).

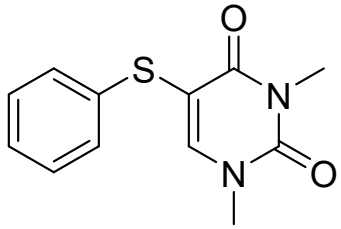
5. Control experiment

Uracil (0.5 mmol, 70 mg), S-(p-tolyl) 4-methylbenzenesulfonothioate (0.375 mmol, 104.5mg) or P-Tolyl Disulfide (0.375 mmol, 92 mg) and I_2 (0.1 mmol, 25 mg) were taken in a 10 mL standard test tube. After that, the reaction mixture was heated at 120°C for 0.5 h. Then, the mixture was cooled and diluted with ethyl acetate and the reaction was quenched with 0.5 mL of saturated sodium thiosulfate. It was concentrated under reduced pressure. The crude product was then purified by column chromatography column chromatography (elution: petroleum ether).

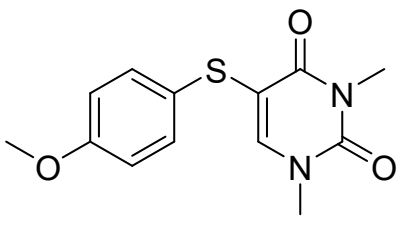
6. Characterization data of the products



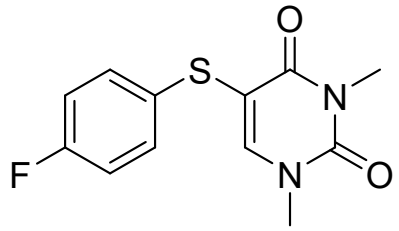
1,3-dimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3a)： White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (130mg). m.p. 119.6-119.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.26 (d, *J* = 0.9 Hz, 1H), 7.25 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.40 (s, 3H), 3.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.74, 151.50, 146.30, 137.29, 130.99, 129.94, 107.39, 37.18, 28.62, 21.03. HRMS: calcd for $C_{13}H_{14}N_2O_2S$ $(M+H)^+$: 263.0854, Found 263.0841.



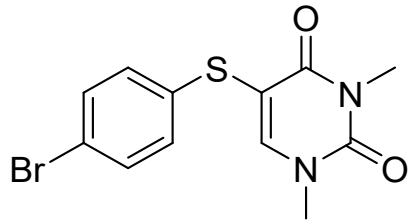
1,3-dimethyl-5-(phenylthio)pyrimidine-2,4(1H,3H)-dione (3b): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (123mg). m.p. 129.4-129.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.32 – 7.27 (m, 4H), 7.20 (t, *J* = 7.1 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H). HRMS: calcd for $C_{12}H_{12}N_2O_2SNa$ $(M+Na)^+$: 271.0517, Found 271.0527.



5-((4-methoxyphenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3c): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 94% isolated yield (130mg). m.p. 115.1-115.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.39 (s, 3H), 3.36 (s, 3H). HRMS calcd for $C_{13}H_{14}N_2O_3SNa$ $(M+Na)^+$: 301.0623, Found 301.0612.

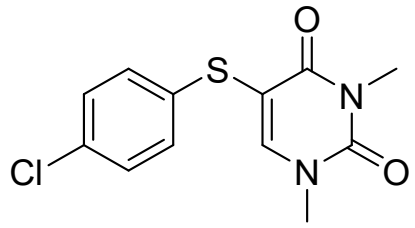


5-((4-fluorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3d): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (132mg). m.p. 88.0-89.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.35 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 3.42 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.92, 161.70, 161.28, 151.39, 147.00, 131.75, 129.77, 116.26, 116.11, 106.65, 37.23, 28.62. HRMS calcd for $C_{12}H_{11}N_2O_2SFNa$ $(M+Na)^+$: 289.0423, Found 289.0419.

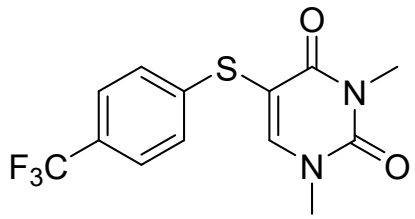


5-((4-bromophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3e): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (162mg). m.p. 161.0-162.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s,

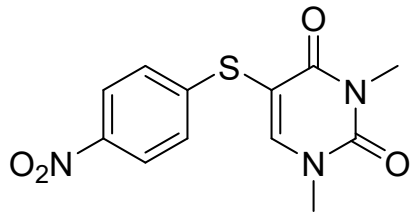
1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 3.44 (s, 3H), 3.36 (s, 3H). HRMS calcd for $C_{12}H_{11}N_2O_2SBrNa$ $(M+Na)^+$: 348.9622, Found 348.9617.



5-((4-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3f): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 85% isolated yield (120mg). m.p. 124.7-127.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.23 (d, *J* = 0.4 Hz, 4H), 3.44 (s, 3H), 3.36 (s, 3H). HRMS calcd for $C_{12}H_{11}N_2O_2SClNa$ $(M+Na)^+$: 305.0127, Found 305.0130.

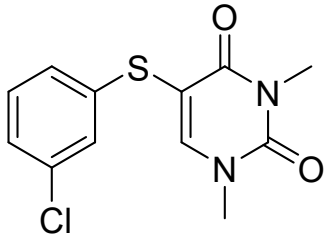


1,3-dimethyl-5-((4-(trifluoromethyl)phenyl)thio)pyrimidine-2,4(1H,3H)-dione (3g): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 83% isolated yield (131mg). m.p. 146.8-147.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.46 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.52, 151.39, 149.13, 140.87, 126.89, 125.79, 103.38, 37.36, 28.75. HRMS calcd for $C_{13}H_{11}N_2O_2SF_3Na$ $(M+Na)^+$: 339.0391, Found 339.0394.



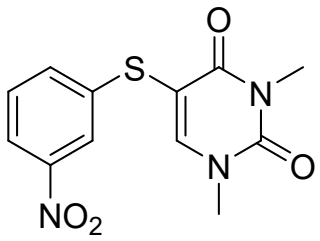
1,3-dimethyl-5-((4-nitrophenyl)thio)pyrimidine-2,4(1H,3H)-dione

(3h): Yellow solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 65% isolated yield (95mg). m.p. 166.0-167.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.85 (s, 1H), 7.28 (d, *J* = 10.6 Hz, 2H), 3.53 (s, 3H), 3.42 (s, 3H). HRMS calcd for $C_{12}H_{11}N_3O_4SNa$ $(M+Na)^+$: 316.0368, Found 316.0360.

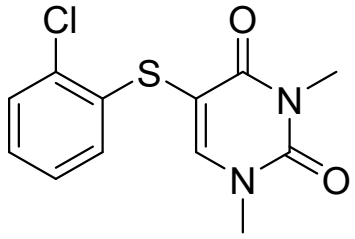


5-((3-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione

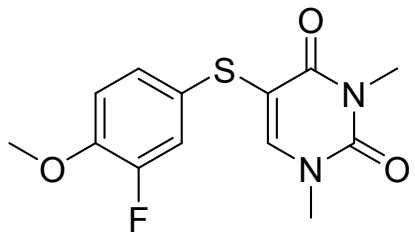
(3i): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 96% isolated yield (136mg). m.p. 116.7-119.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.20 – 7.12 (m, 4H), 3.45 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.59, 151.42, 148.63, 137.54, 134.78, 130.03, 127.48, 126.69, 126.07, 104.37, 37.34, 28.73. HRMS calcd for $C_{12}H_{11}N_2O_2SClNa$ $(M+Na)^+$: 305.0127, Found 305.0113.



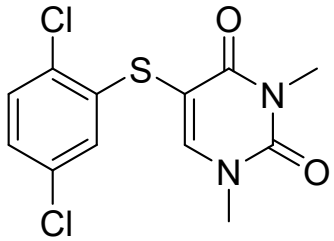
1,3-dimethyl-5-((3-nitrophenyl)thio)pyrimidine-2,4(1H,3H)-dione (3j): Light yellow solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 89% isolated yield (130mg). m.p. 133.0-133.8 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.07 – 8.02 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.62 (dd, *J* = 10.3, 6.4 Hz, 1H), 3.44 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 161.27, 152.18, 151.38, 148.22, 139.71, 132.42, 130.28, 120.44, 120.29, 99.24, 36.83, 28.28. HRMS calcd for $C_{12}H_{11}N_3O_4SNa$ $(M+Na)^+$: 316.0368, Found 316.0370.



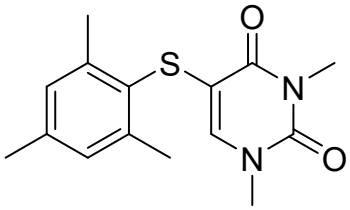
5-((2-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3k): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 98% isolated yield (138mg). m.p. 214.3-214.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.33 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.13 (dtd, *J* = 16.7, 7.4, 1.4 Hz, 2H), 7.05 (dd, *J* = 7.7, 1.6 Hz, 1H), 3.45 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.59, 151.48, 149.05, 134.55, 132.40, 129.75, 128.47, 127.29, 127.20, 103.39, 37.37, 28.74. HRMS calcd for $C_{12}H_{11}N_2O_2SClNa$ $(M+Na)^+$: 305.0127, Found 305.0130.



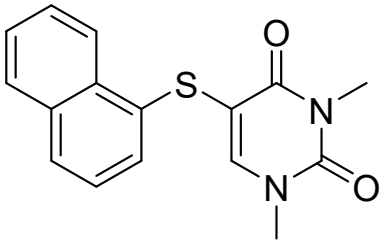
5-((3-fluoro-4-methoxyphenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3l): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (146mg). m.p. 132.8-133.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.20 – 7.08 (m, 2H), 6.87 (t, *J* = 8.6 Hz, 1H), 3.85 (s, 3H), 3.42 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.67, 152.96, 151.40, 147.34, 146.62, 126.83, 125.84, 118.37, 113.73, 107.01, 56.24, 37.24, 28.62. HRMS calcd for $C_{13}H_{13}N_2O_3SFNa$ $(M+Na)^+$: 319.0529, Found 319.0520.



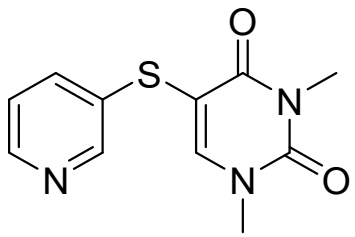
5-((2,5-dichlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3m): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 48% isolated yield (77mg). m.p. 202.4-203.3 ℃. ^{1}H NMR (600 MHz, DMSO-*d*^{6}) δ 8.40 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.22 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.12 (d, *J* = 2.2 Hz, 1H), 3.37 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 161.27, 152.88, 151.52, 138.61, 132.67, 130.76, 127.59, 126.45, 125.61, 97.51, 36.89, 28.31. HRMS calcd for $C_{12}H_{10}N_2O_2SCl_2Na$ $(M+Na)^+$: 338.9738, Found 338.9724.



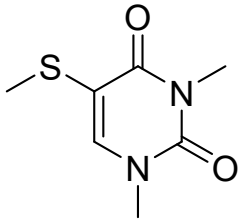
5-(mesitylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3n): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (143mg). m.p. 177.6-178.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.24 (s, 1H), 3.36 (s, 3H), 3.25 (s, 3H), 2.43 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.36, 151.11, 143.55, 139.78, 135.78, 129.72, 124.54, 111.21, 37.25, 28.38, 21.54, 21.12. HRMS calcd for $C_{15}H_{18}N_2O_2SNa$ $(M+Na)^+$: 313.0987, Found 313.1000.



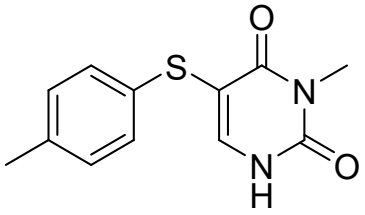
1,3-dimethyl-5-(naphthalen-1-ylthio)pyrimidine-2,4(1H,3H)-dione (3o): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (147mg). m.p. 197.4-197.6 ℃. ^{1}H NMR (600 MHz, DMSO-*d*^{6}) δ 8.38 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 3.37 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d*^{6}) δ 161.80, 151.91, 151.84, 133.87, 133.81, 130.75, 129.03, 126.96, 126.85, 126.52, 126.40, 125.00, 123.95, 100.85, 37.22, 28.72. HRMS calcd for $C_{16}H_{14}N_2O_2SNa$ $(M+Na)^+$: 321.0674, Found 321.0681.



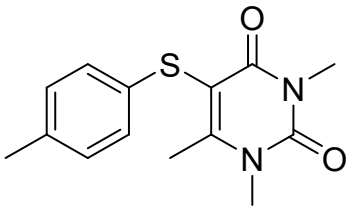
1,3-dimethyl-5-(pyridin-3-ylthio)pyrimidine-2,4(1H,3H)-dione (3p): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 65% isolated yield (81mg). m.p. 165.2-166.5 ℃. ^{1}H NMR (600 MHz, DMSO-*d*^{6}) δ 8.44 (s, 1H), 8.37 (d, *J* = 17.0 Hz, 2H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.32 – 7.22 (m, 1H), 3.36 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d*^{6}) δ 161.30, 151.58, 151.34, 147.19, 146.65, 134.31, 133.71, 123.86, 99.68, 36.73, 28.22. HRMS calcd for $C_{11}H_{11}N_3O_2SNa$ $(M+Na)^+$: 272.0470, Found 272.0454.



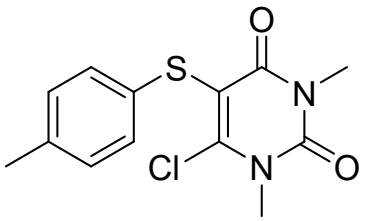
1,3-dimethyl-5-(methylthio)pyrimidine-2,4(1H,3H)-dione (3q): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 79% isolated yield (73mg). m.p. 92.1-93.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1H), 3.39 (s, 3H), 3.35 (s, 3H), 2.30 (s, 3H). HRMS calcd for $C_7H_{10}N_2O_2SNa$ $(M+Na)^+$: 209.0361, Found 209.0355.



3-methyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3r): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 95% isolated yield (118mg). m.p. 240.3-240.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.20 – 7.11 (m, 4H), 3.34 (s, 3H), 2.30 (s, 3H). HRMS calcd for $C_{12}H_{12}N_2O_2SNa$ $(M+Na)^+$: 271.0517, Found 271.0507.

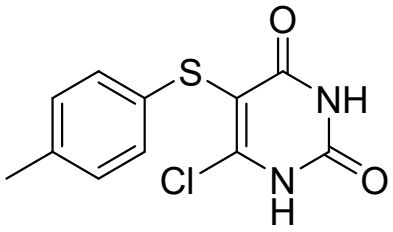


1,3,6-trimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3s): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 99% isolated yield (137mg). m.p. 109.2-110.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.51 (s, 3H), 3.37 (s, 3H), 2.66 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.37, 157.60, 151.65, 136.02, 132.58, 129.73, 127.66, 105.25, 33.32, 28.98, 20.90, 19.27. HRMS calcd for $C_{14}H_{16}N_2O_2SNa$ $(M+Na)^+$: 299.0830, Found 299.0835.

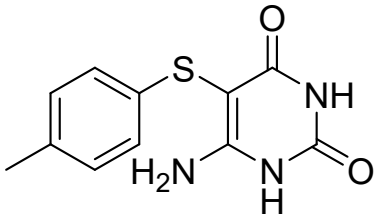


6-chloro-1,3-dimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3t): White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 3 : 1) in 84% isolated yield (124mg). m.p. 129.6-130.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.67 (d, *J* = 0.6 Hz, 3H), 3.37 (d, *J*

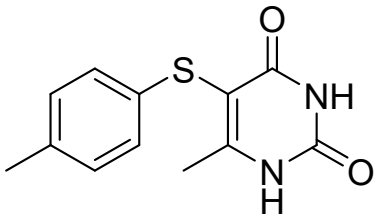
= 0.5 Hz, 3H), 2.30 (s, 3H). HRMS calcd for $C_{13}H_{13}N_2O_2SClNa$ $(M+Na)^+$: 319.0284, Found 319.0273.



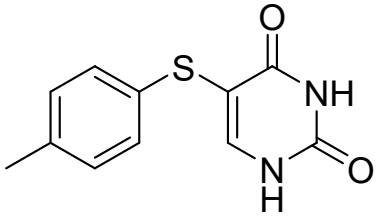
6-chloro-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3u): White solid was obtained by column chromatography on silica gel (eluent: dichloromethane/methanol = 20 : 1) in 53% isolated yield (71mg). m.p. 266.1-268.0 ℃. ^{1}H NMR (600 MHz, DMSO) δ 12.58 (s, 1H), 11.58 (s, 1H), 7.09 (s, 4H), 2.24 (s, 3H). HRMS calcd for $C_{11}H_9N_2O_2SClNa$ $(M+Na)^+$: 290.9971, Found 290.9971.



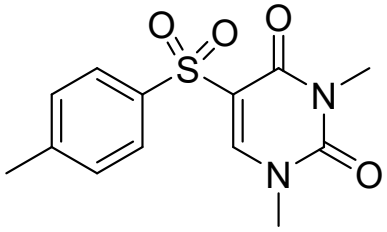
6-amino-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3v): White solid was obtained by column chromatography on silica gel (eluent: dichloromethane/methanol = 20 : 1) in 79% isolated yield (98mg). m.p. ＞300 ℃. ^{1}H NMR (600 MHz, DMSO-d^6) δ 10.57 (s, 1H), 10.42 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 6.61 (s, 2H), 2.22 (s, 3H). HRMS calcd for $C_{11}H_{11}N_3O_2SNa$ $(M+Na)^+$: 272.0470, Found 272.0465.



6-methyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3w): White solid was obtained by column chromatography on silica gel (eluent: dichloromethane/methanol = 20 : 1) in 71% isolated yield (88mg). m.p. ＞300 ℃. ^{1}H NMR (600 MHz, DMSO-d^6) δ 11.28 (s, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 2.29 (s, 3H), 2.23 (s, 3H). HRMS calcd for $C_{12}H_{12}N_2O_2SNa$ $(M+Na)^+$: 271.0517, Found 271.0510.

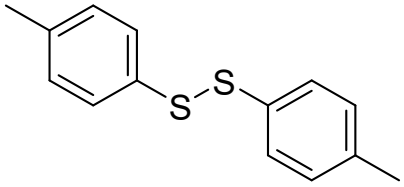


5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3x): White solid was obtained by column chromatography on silica gel (eluent: dichloromethane/methanol = 20 : 1) in 50% isolated yield (58mg). m.p. 284.9-285.6 ℃. ^{1}H NMR (600 MHz, DMSO-d^6) δ 11.36 (s, 2H), 7.84 (s, 1H), 7.10 (s, 4H), 2.24 (s, 3H). HRMS calcd for $C_{11}H_{10}N_2O_2SNa$ $(M+Na)^+$: 257.0361, Found 257.0352.

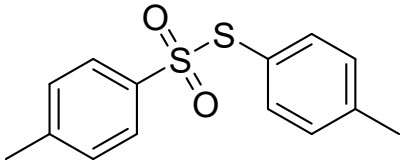


1,3-dimethyl-5-tosylpyrimidine-2,4(1H,3H)-dione (4a) [1]**:** White solid was obtained by column chromatography on silica gel (eluent:

dichloromethane/methanol = 50 : 1) in 90% isolated yield (27mg). m.p. 175.0-176.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 3.53 (s, 3H), 3.27 (s, 3H), 2.42 (s, 3H).



1,2-di-p-tolyldisulfane (5a) [2]**:** White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 50 : 1) in 43% isolated yield (53mg). m.p. 46.1-47.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 4H), 7.09 (d, J = 8.0 Hz, 4H), 2.30 (s, 6H).



S-(p-tolyl) 4-methylbenzenesulfonothioate (6a) [2]**:** White solid was obtained by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 30 : 1) in 46% isolated yield (64mg). m.p. 75.2-76.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

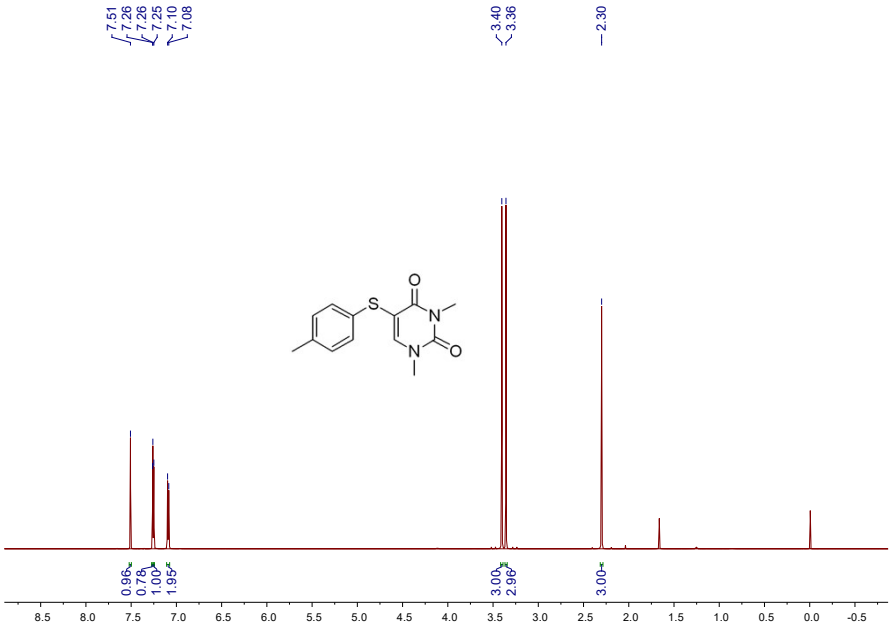
7. References

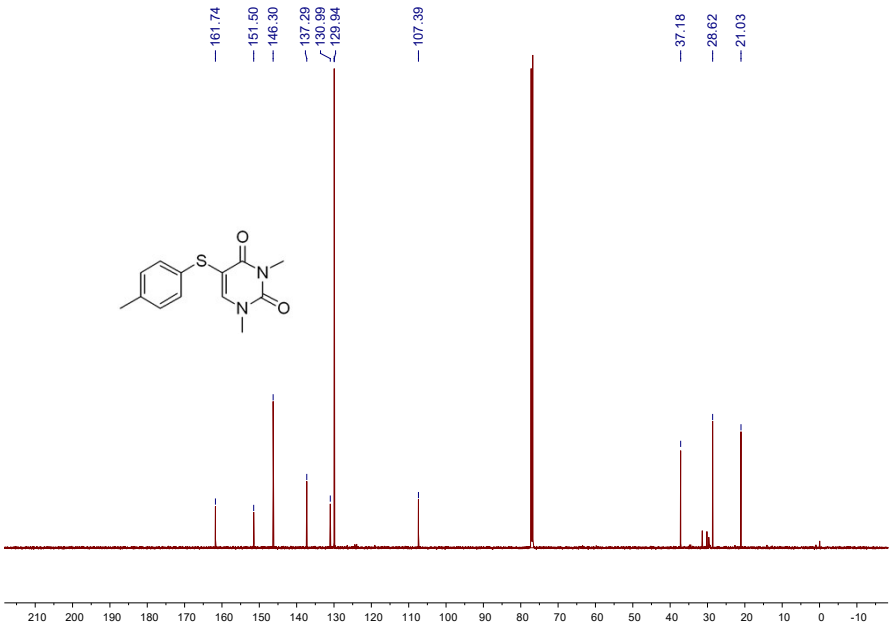
[1] D. Beukeaw, M. Noikham and S. Yotphan, *Tetrahedron*, 2019, **75**, 130537.

[2] F. L. Yang and S. K. Tian, *Angew. Chem. Int. Ed*. 2013, **52**, 4929–4932.

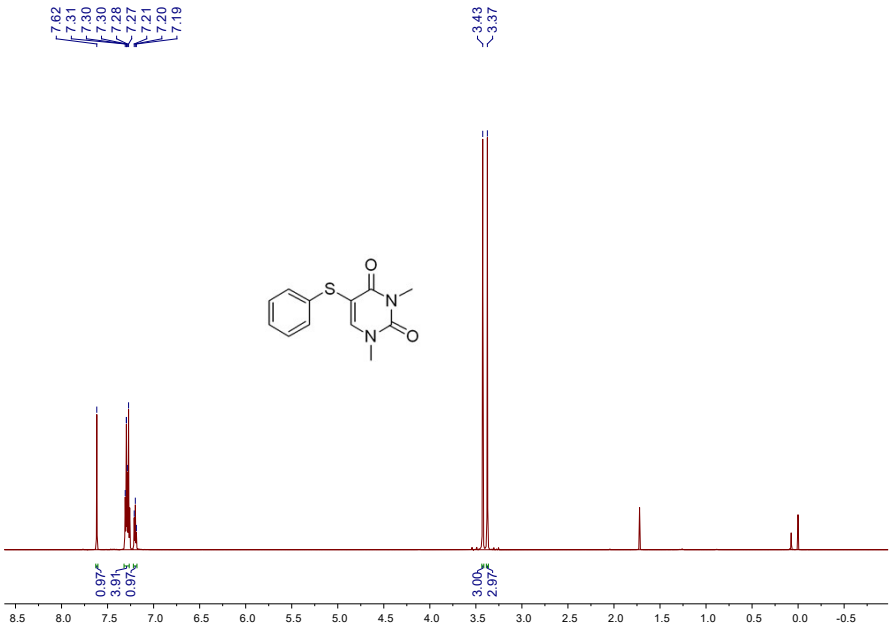
8. NMR spectra

1,3-dimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3a)：

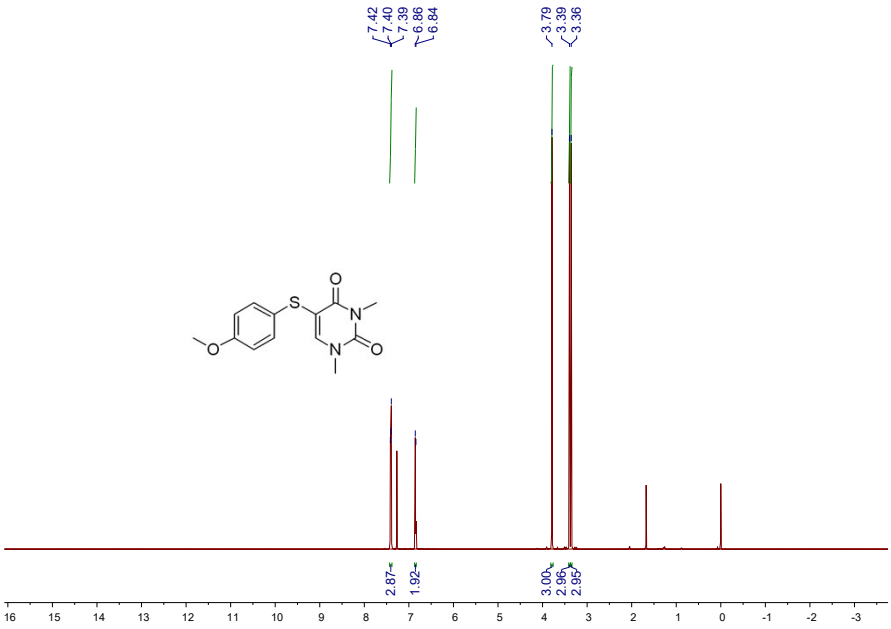




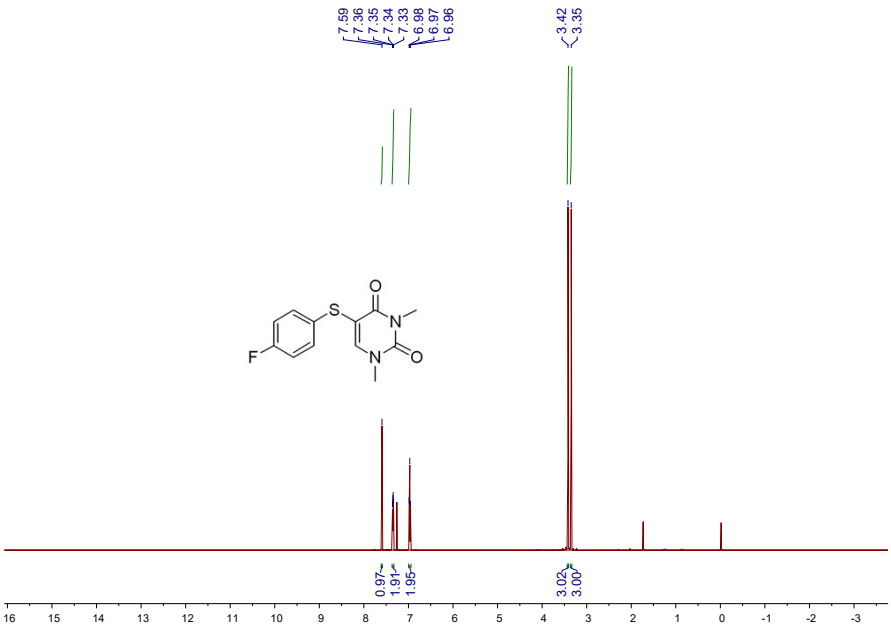
1,3-dimethyl-5-(phenylthio)pyrimidine-2,4(1H,3H)-dione (3b):

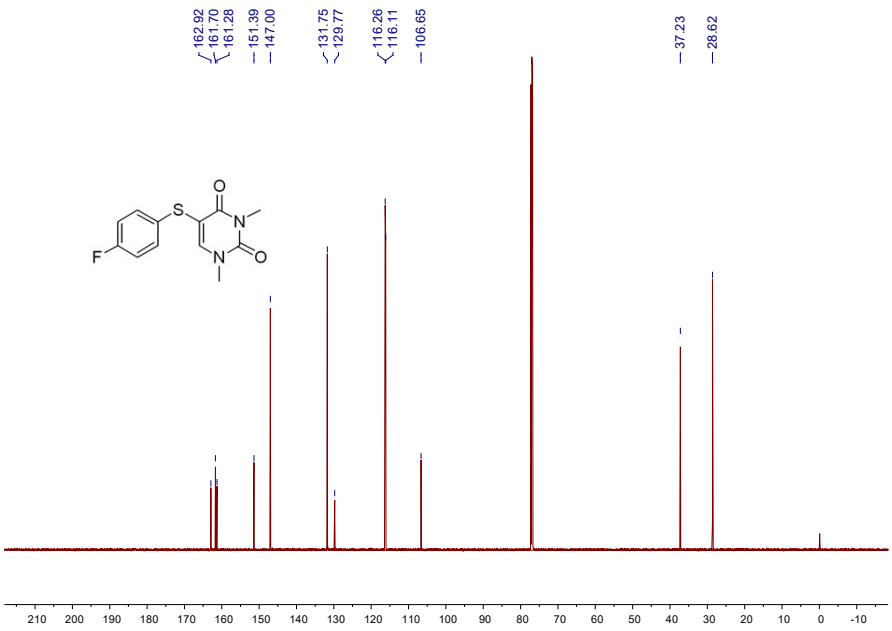


5-((4-methoxyphenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3c):

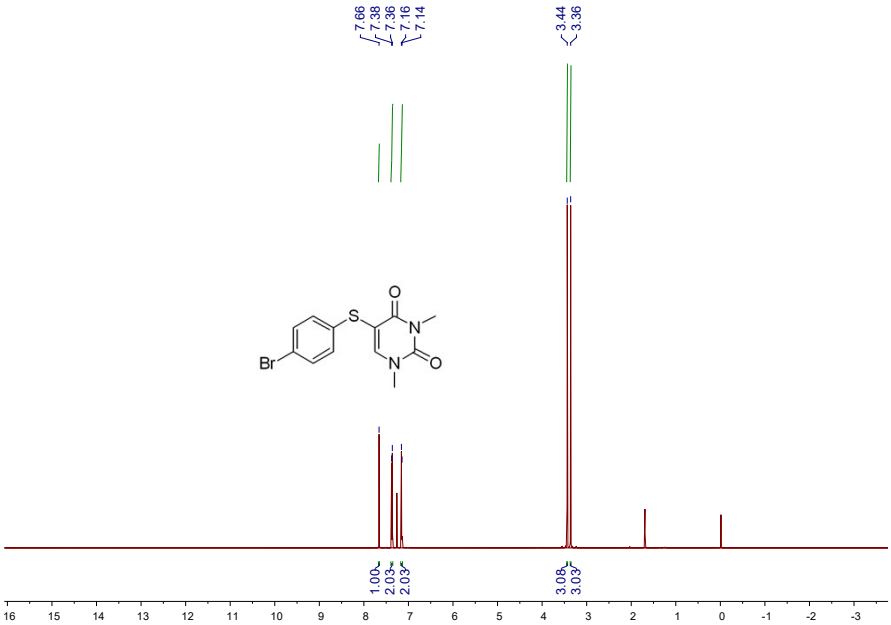


5-((4-fluorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3d):

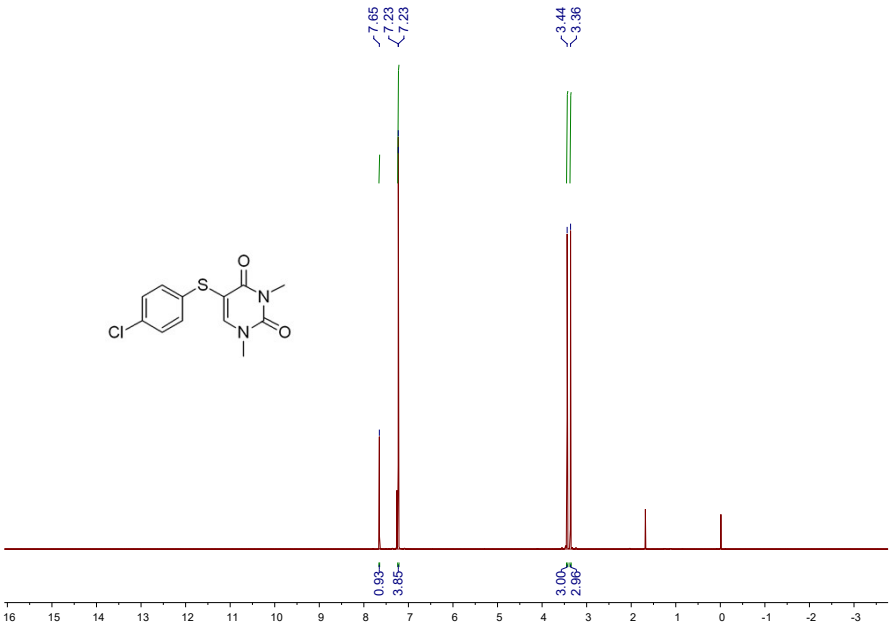




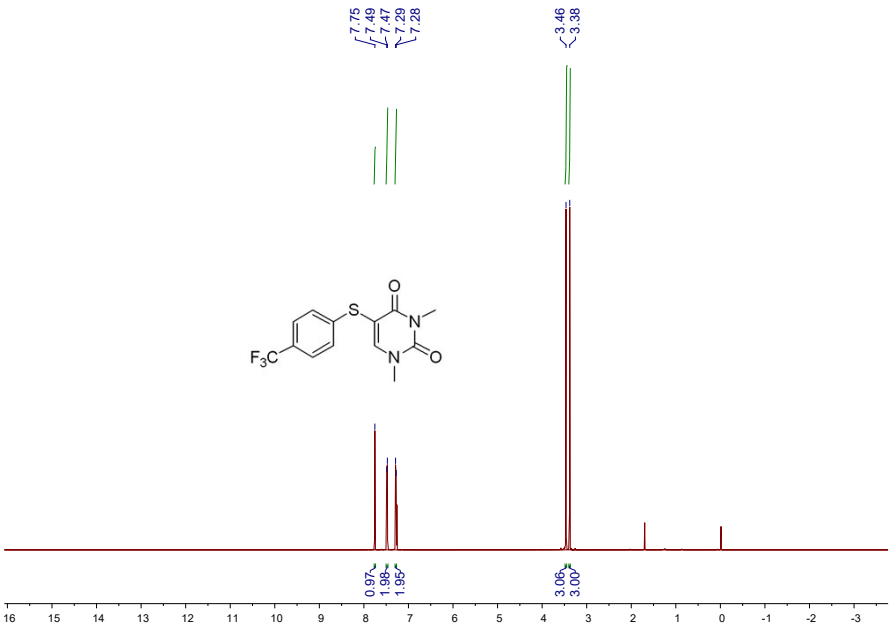
5-((4-bromophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3e):

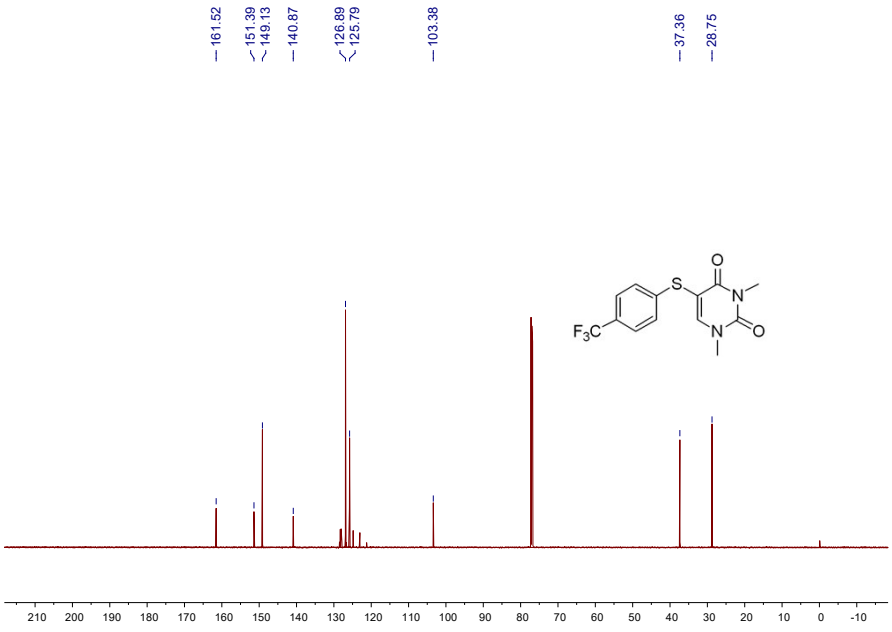


5-((4-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3f):

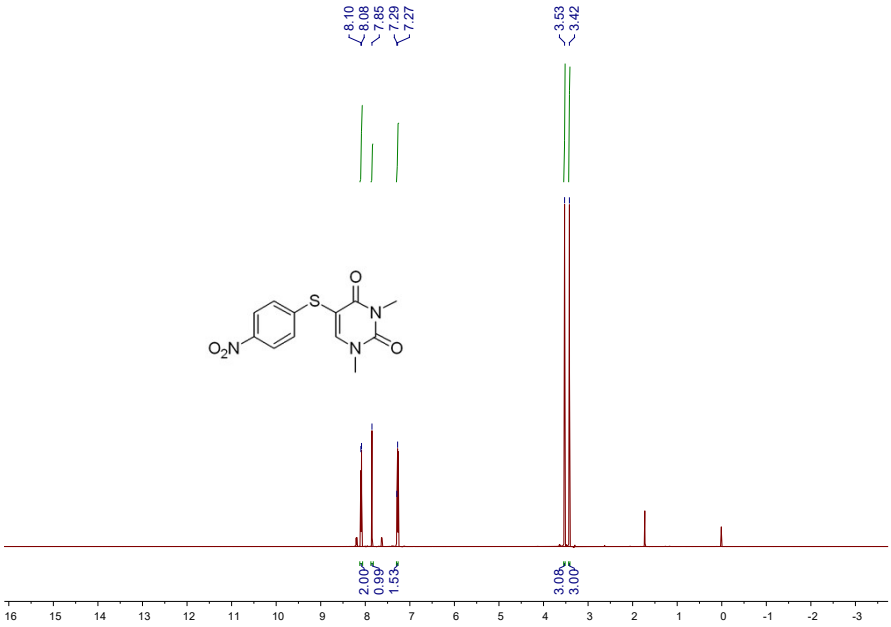


1,3-dimethyl-5-((4-(trifluoromethyl)phenyl)thio)pyrimidine-2,4(1H,3H)-dione (3g):

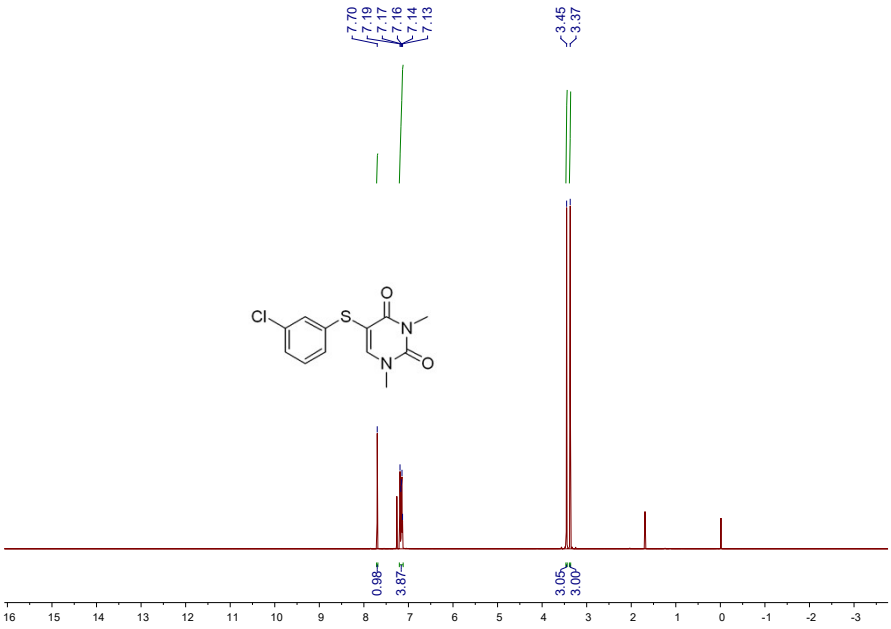


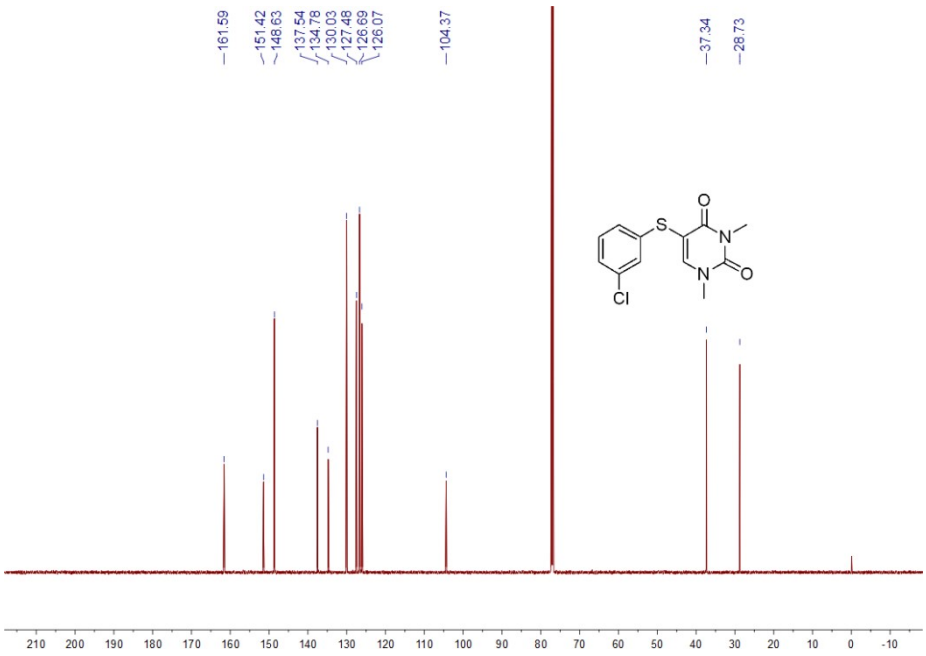


1,3-dimethyl-5-((4-nitrophenyl)thio)pyrimidine-2,4(1H,3H)-dione (3h):

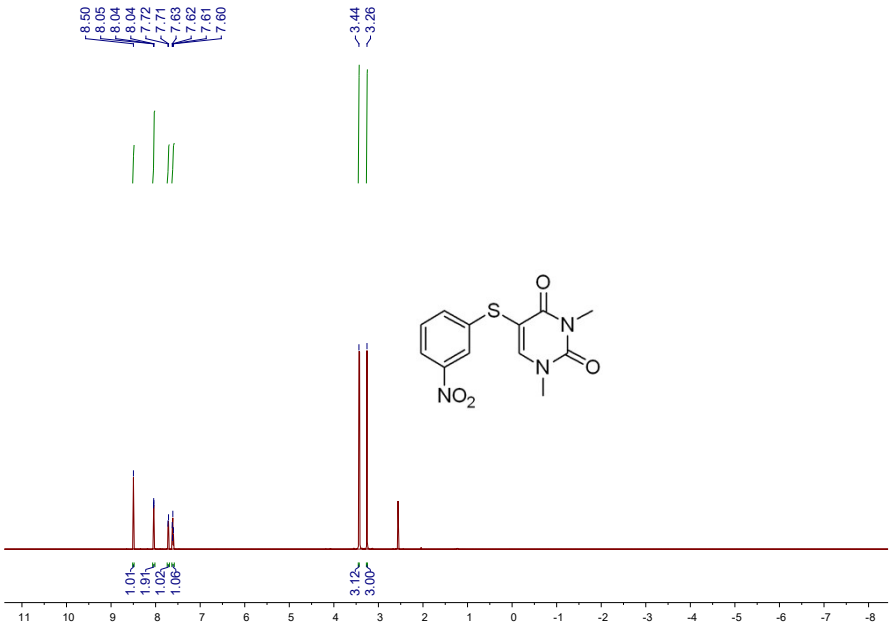


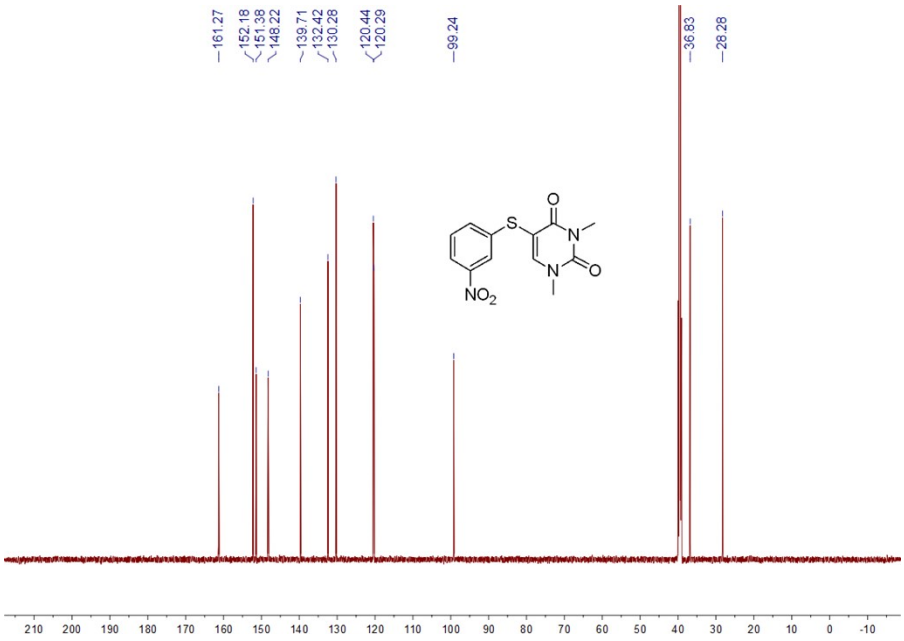
5-((3-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3i):



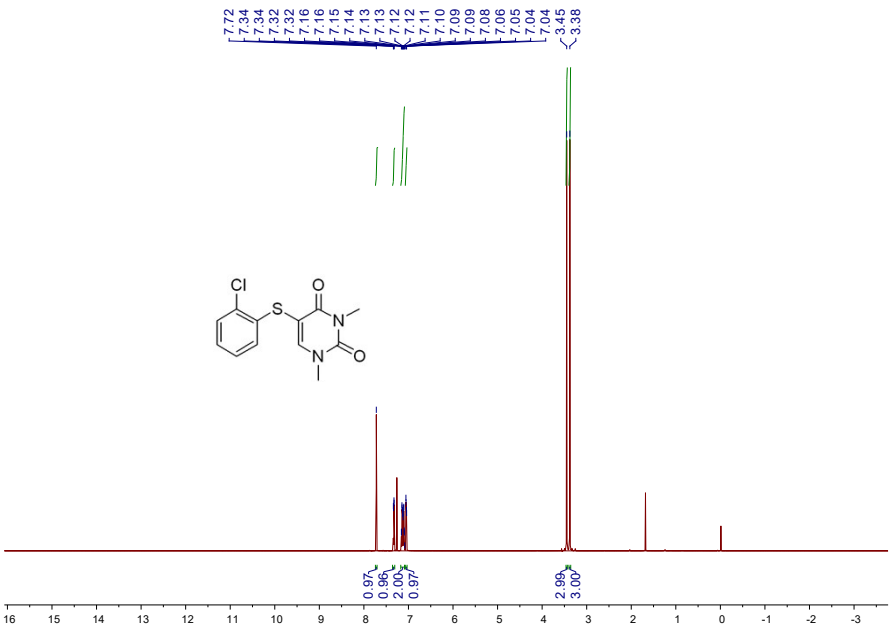


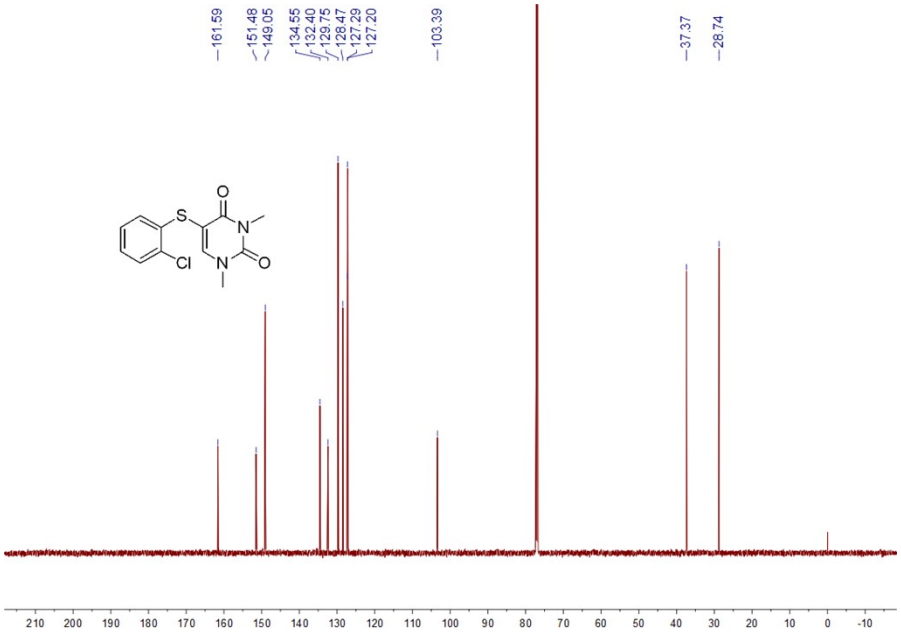
1,3-dimethyl-5-((3-nitrophenyl)thio)pyrimidine-2,4(1H,3H)-dione (3j):



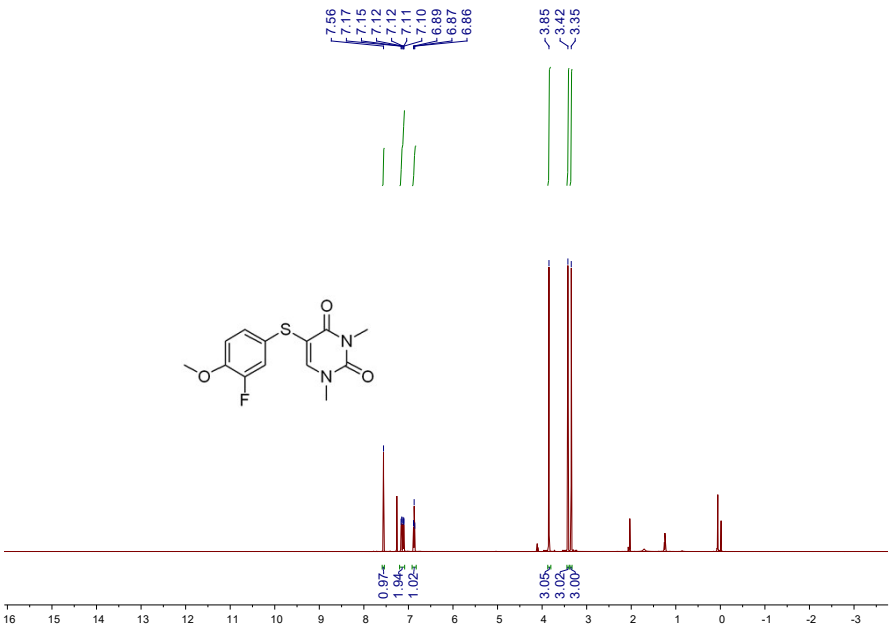


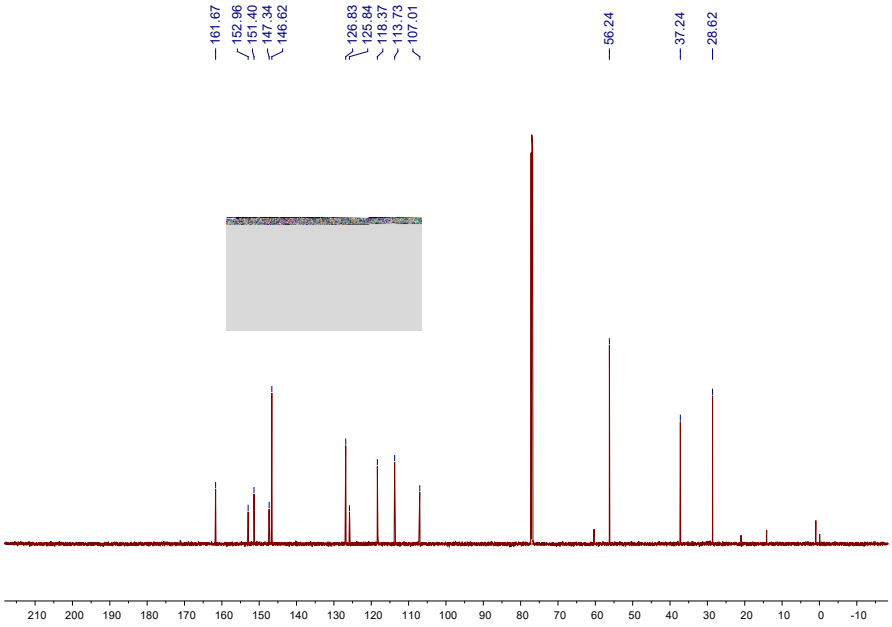
5-((2-chlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3k):



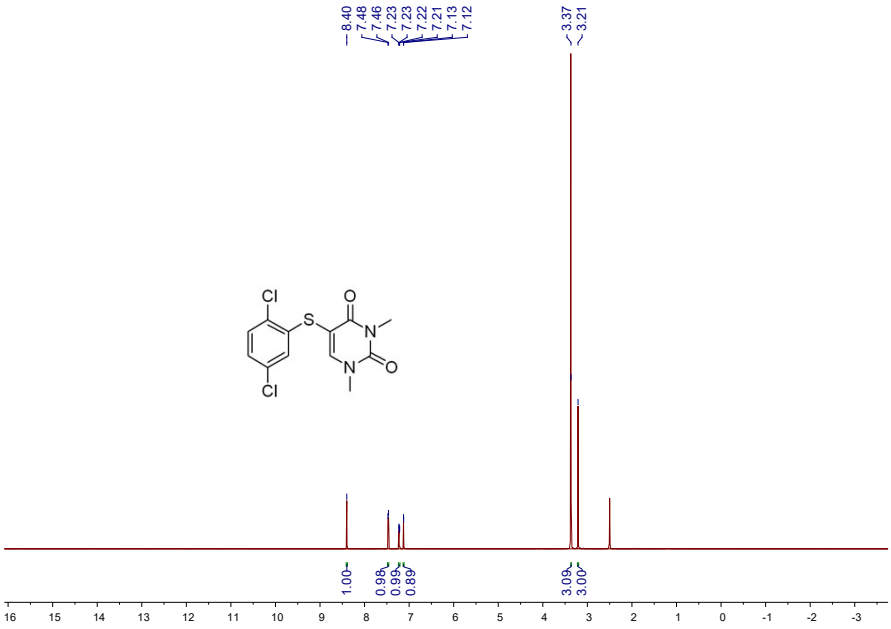


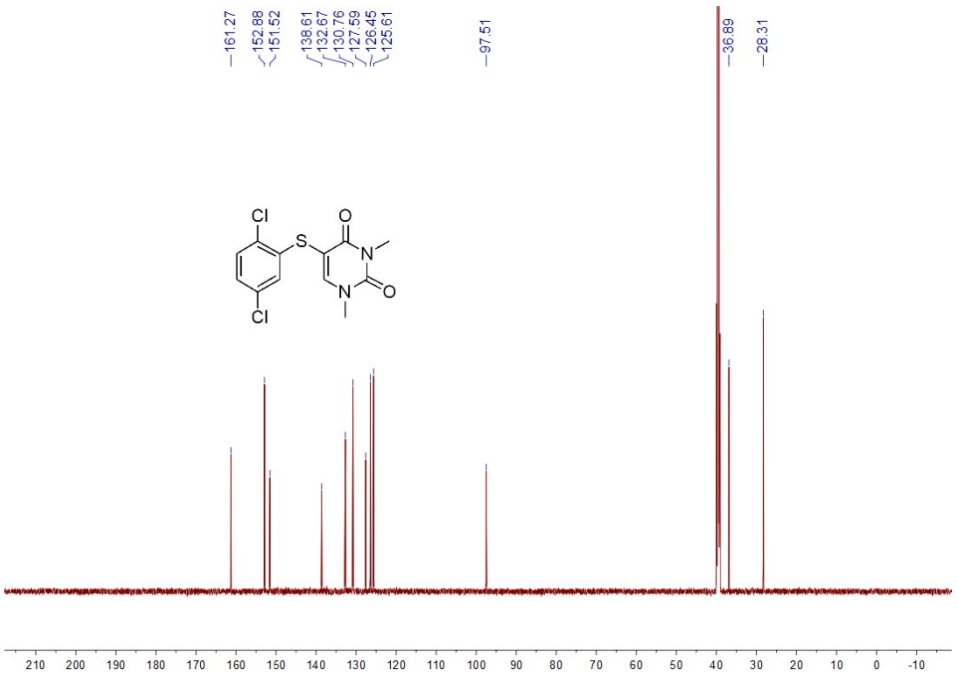
5-((3-fluoro-4-methoxyphenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3l):



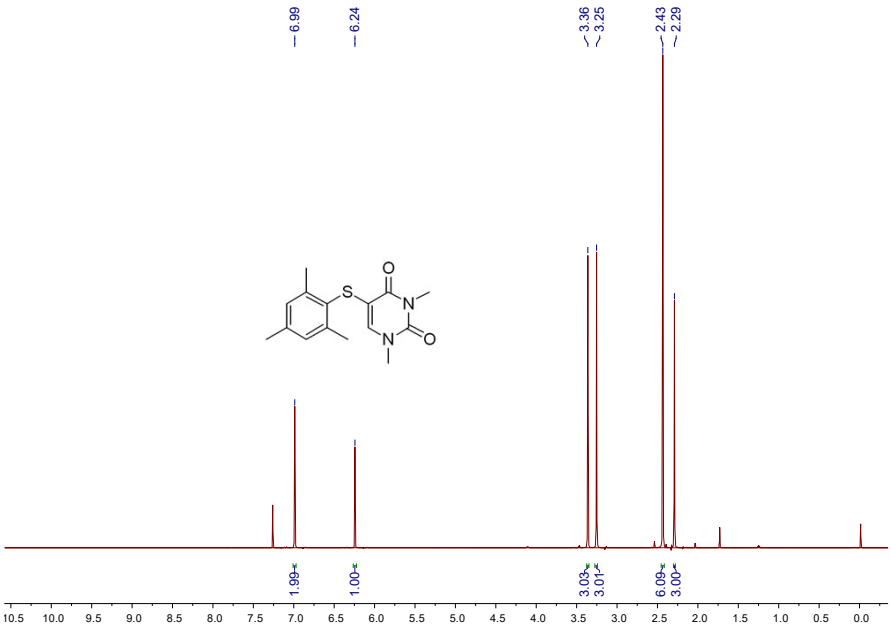


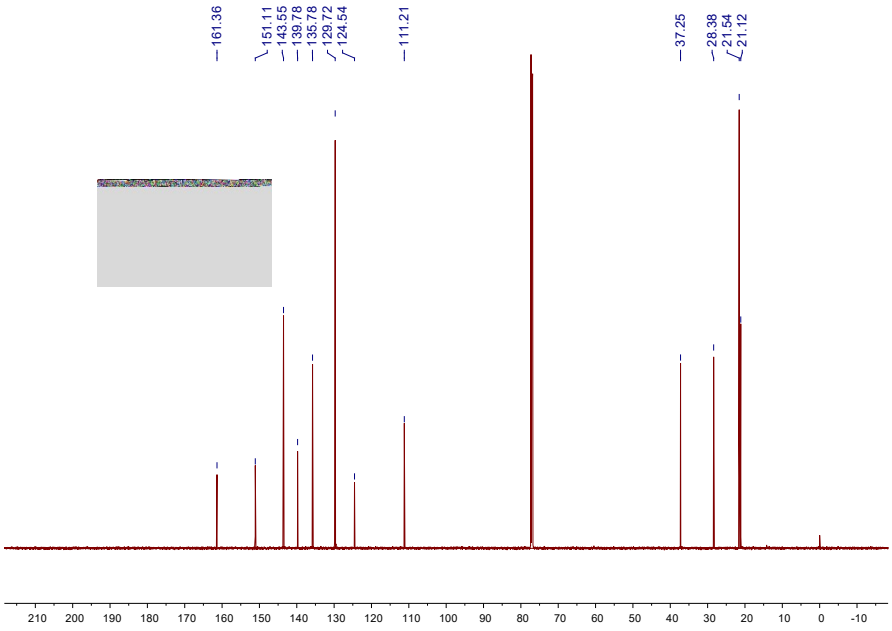
5-((2,5-dichlorophenyl)thio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3m):



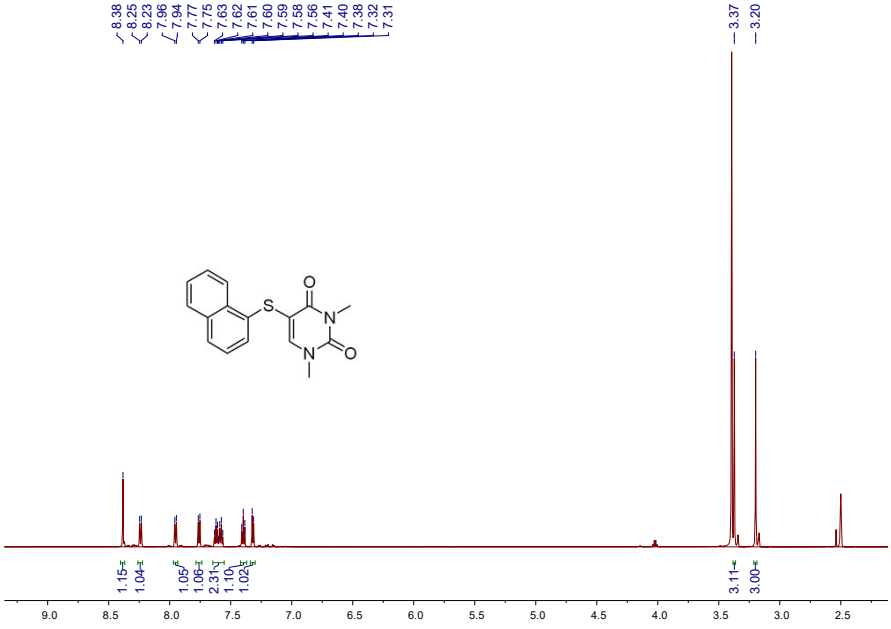


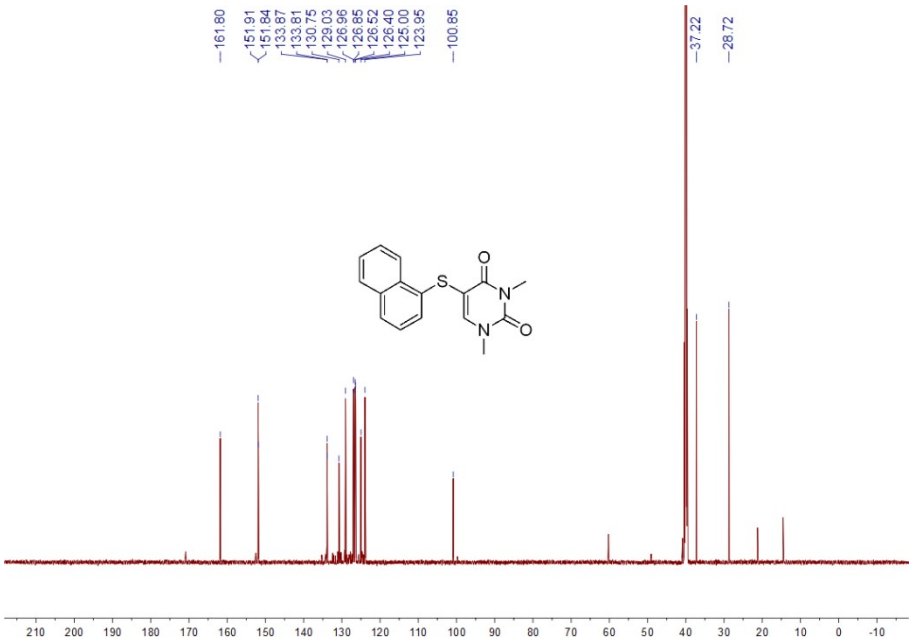
5-(mesitylthio)-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3n):



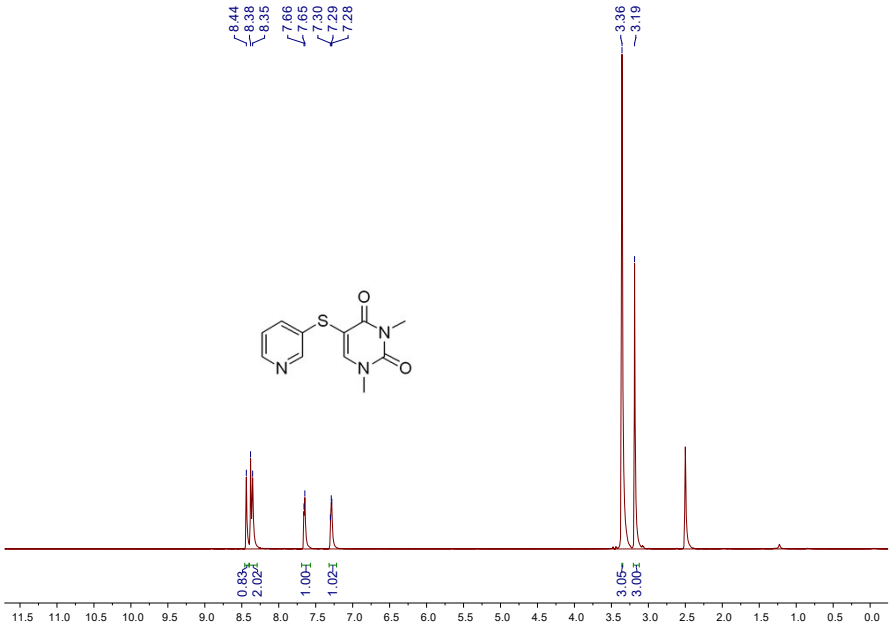


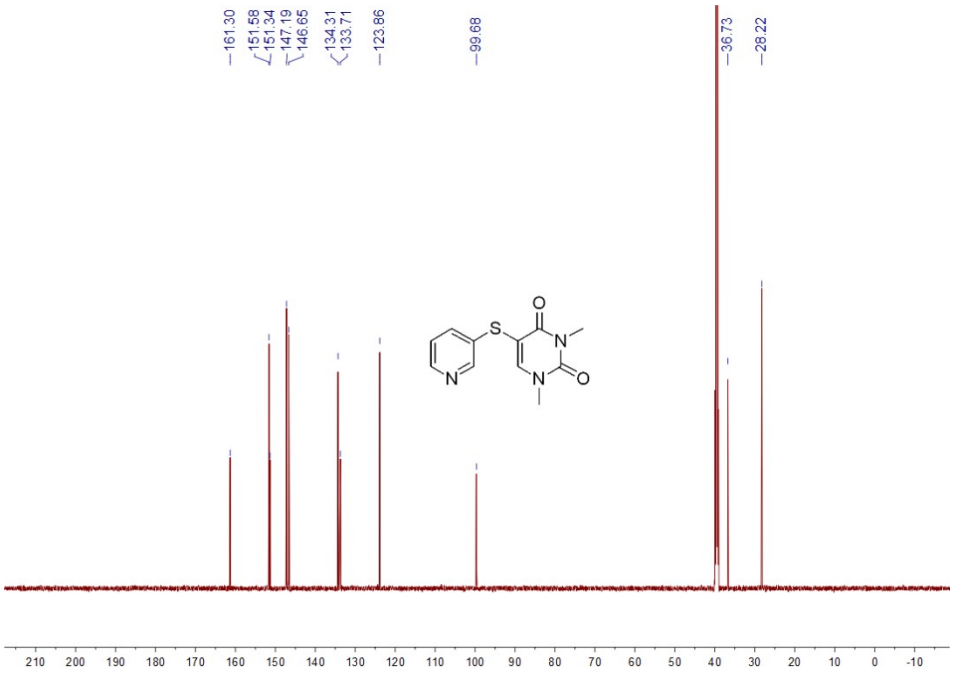
1,3-dimethyl-5-(naphthalen-1-ylthio)pyrimidine-2,4(1H,3H)-dione (3o):



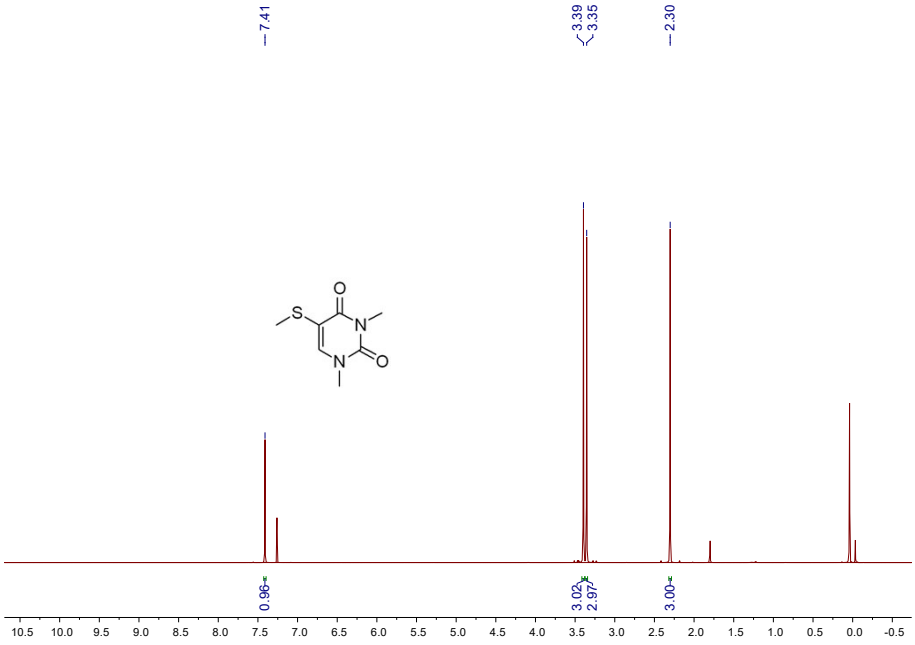


1,3-dimethyl-5-(pyridin-3-ylthio)pyrimidine-2,4(1H,3H)-dione (3p):

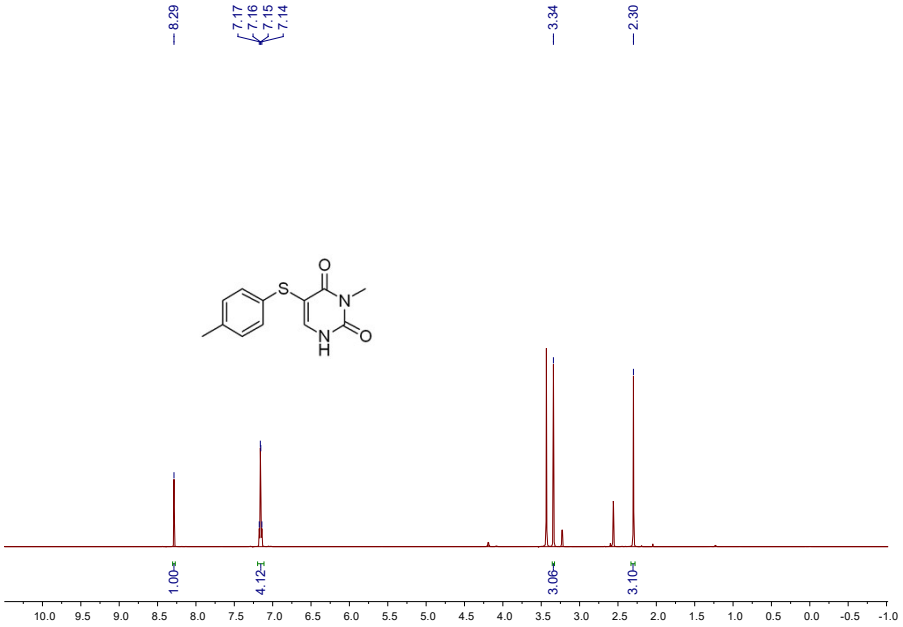




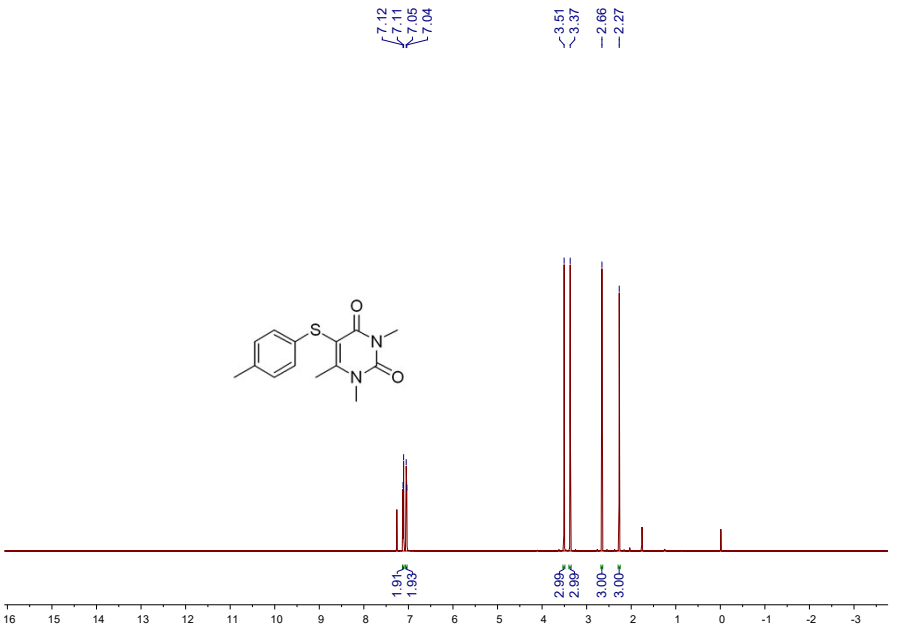
1,3-dimethyl-5-(methylthio)pyrimidine-2,4(1H,3H)-dione (3q):

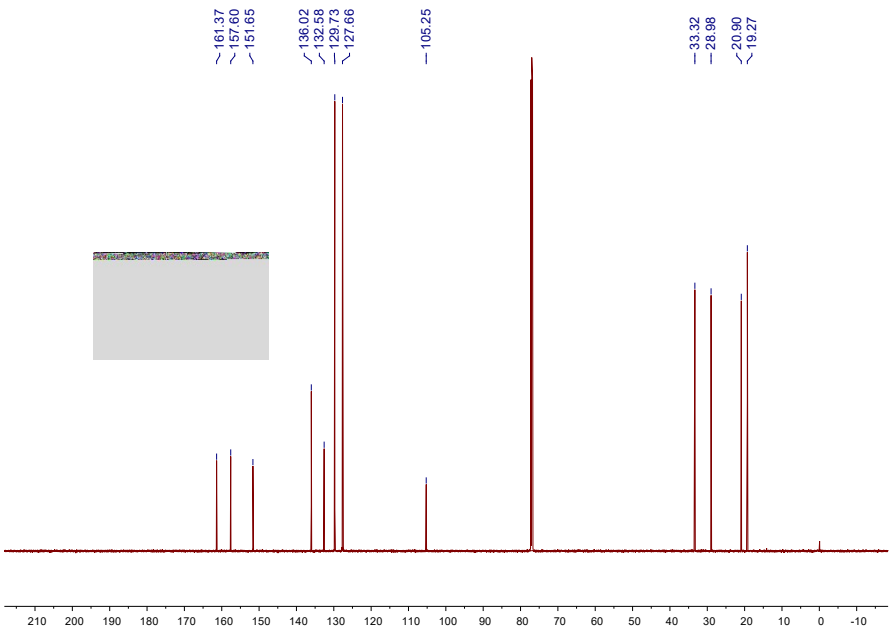


3-methyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3r):

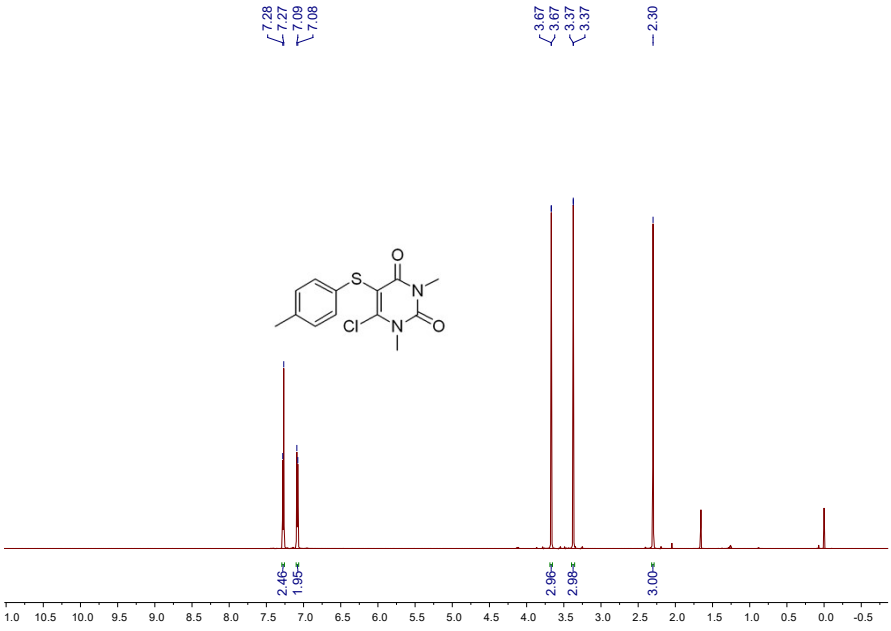


1,3,6-trimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3s):

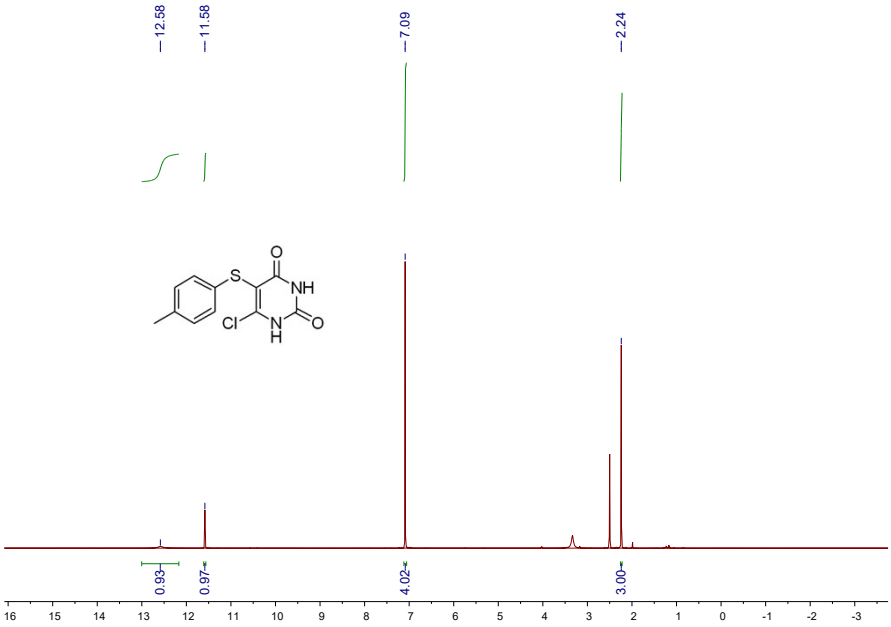




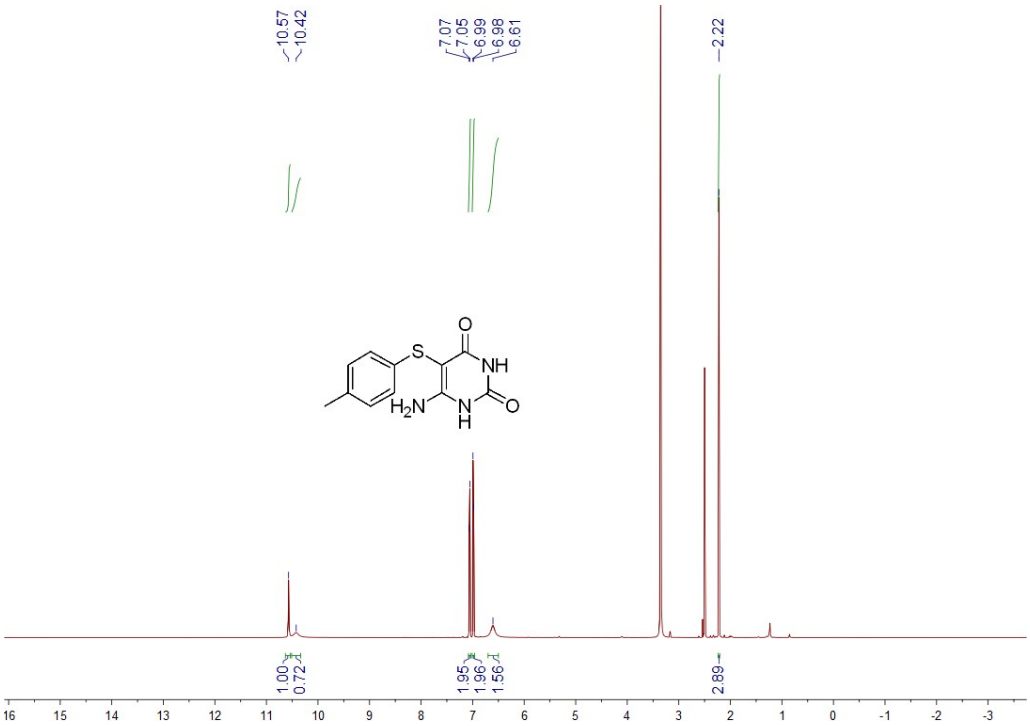
chloro-1,3-dimethyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3t):



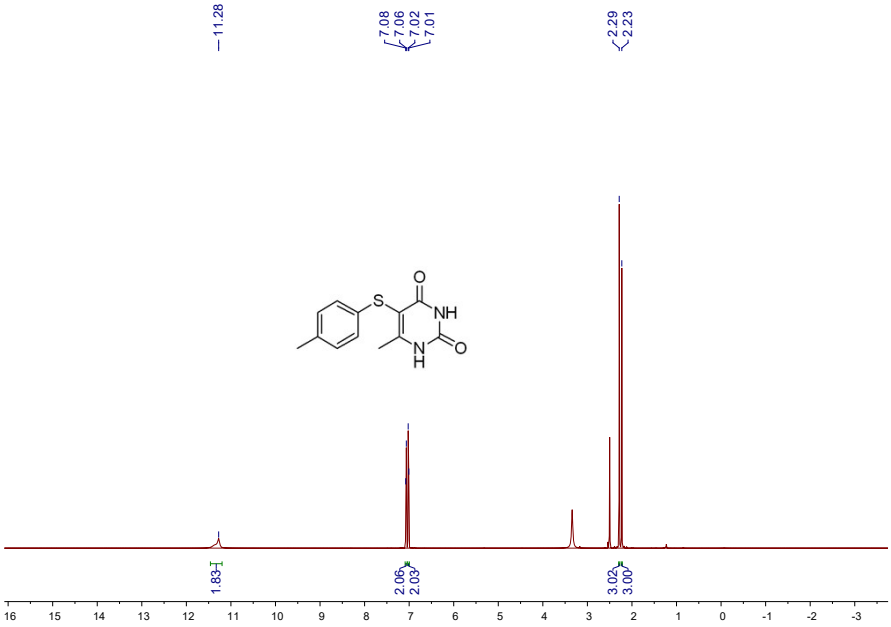
6-chloro-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3u):



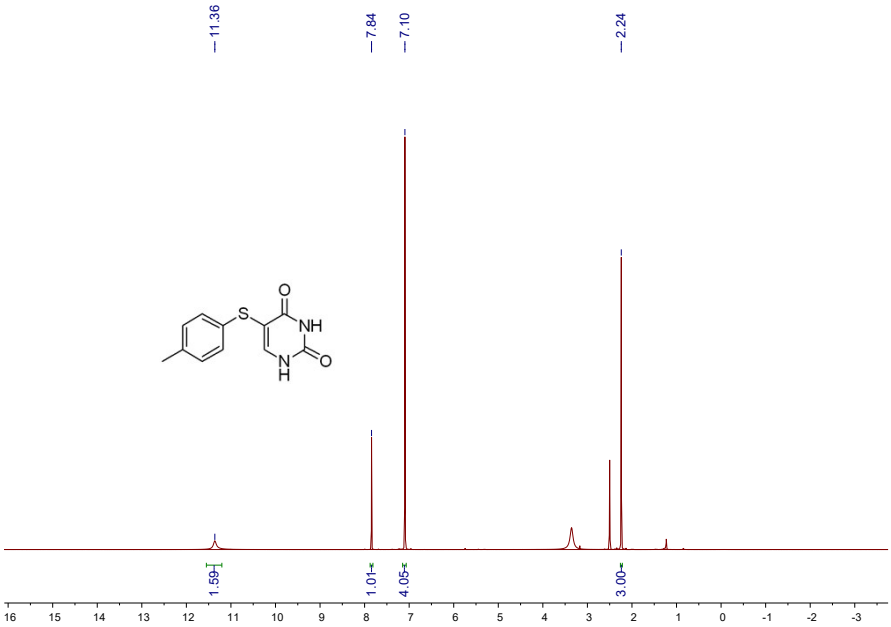
6-amino-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3v):



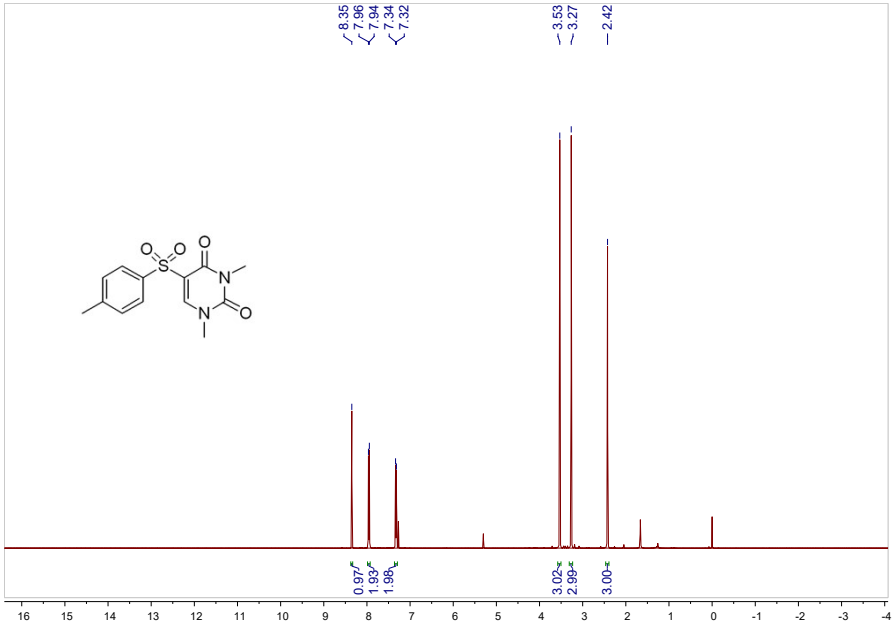
6-methyl-5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3w):



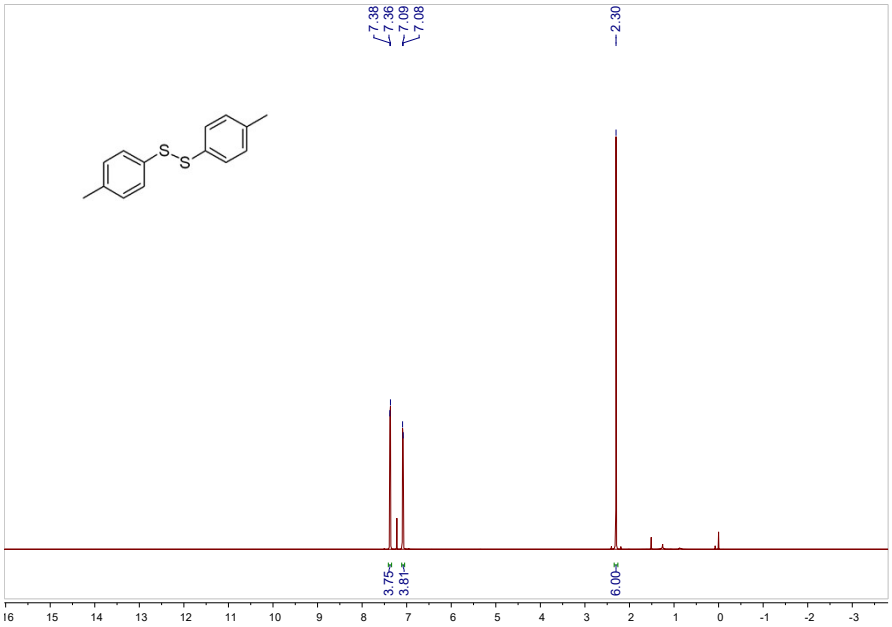
5-(p-tolylthio)pyrimidine-2,4(1H,3H)-dione (3x):



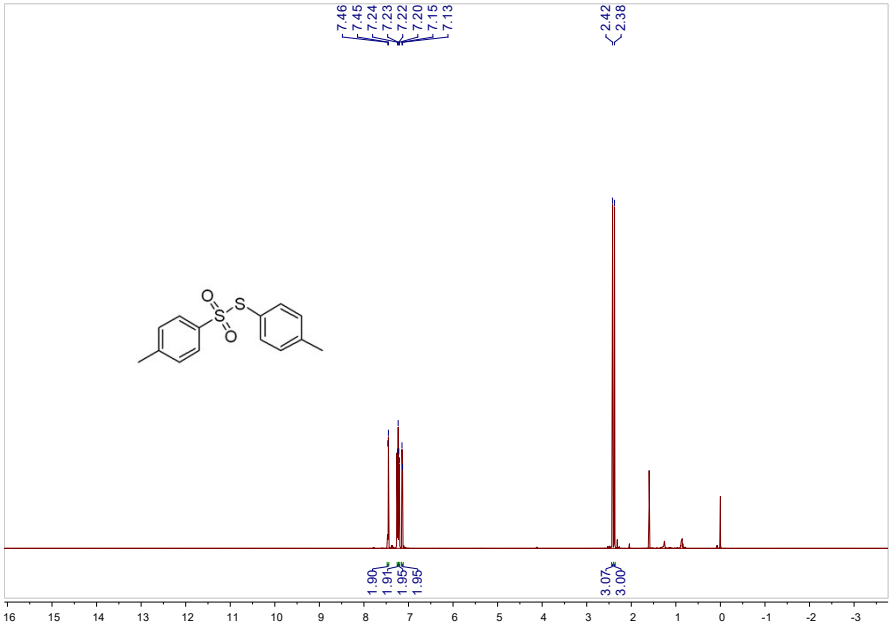
1,3-dimethyl-5-tosylpyrimidine-2,4(1H,3H)-dione (4a):



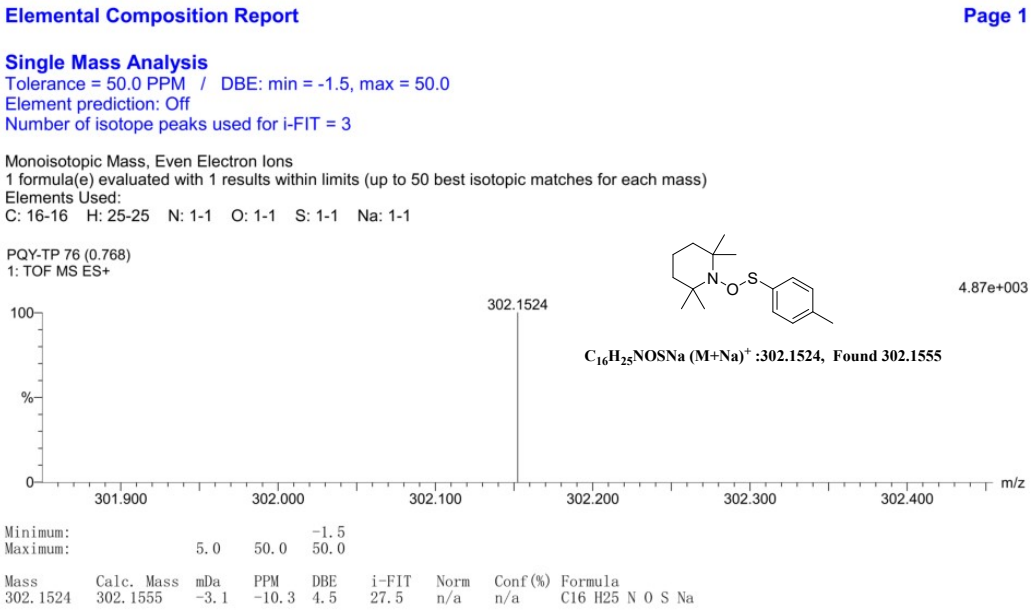
1,2-di-p-tolyldisulfane (5a):



S-(p-tolyl) 4-methylbenzenesulfonothioate (6a):



9. Mass Spectrometry

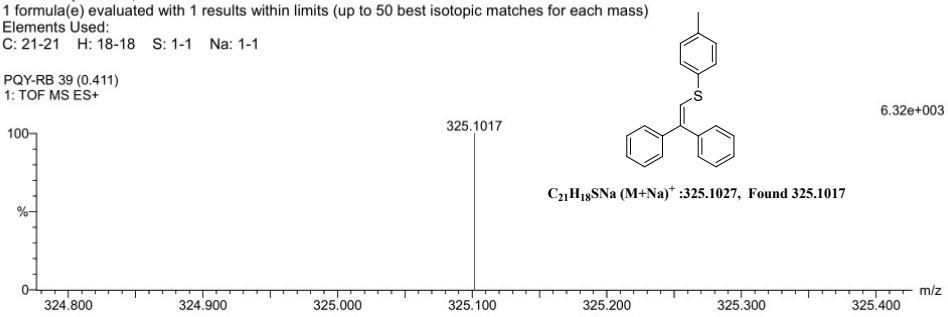


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 21-21 H: 18-18 S: 1-1 Na: 1-1

PQY-RB 39 (0.411)
1: TOF MS ES+



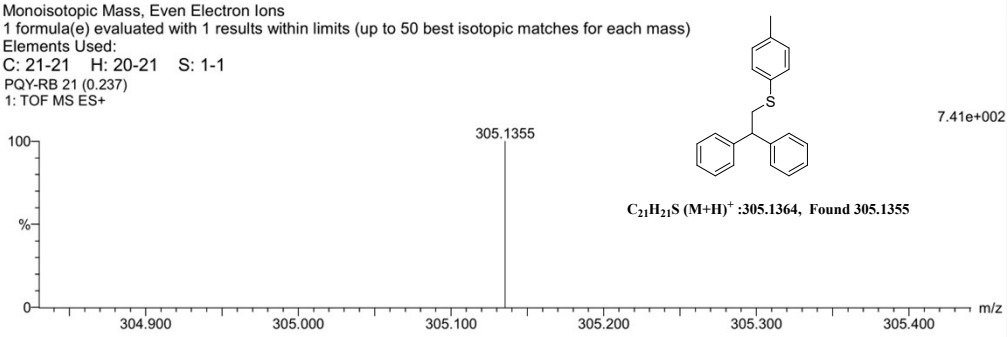
$C_{21}H_{18}SNa\ (M+Na)^+$:325.1027, Found 325.1017

Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
325.1017	325.1027	-1.0	-3.1	12.5	28.3	n/a	n/a	C21 H18 S Na

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 21-21 H: 20-21 S: 1-1
PQY-RB 21 (0.237)
1: TOF MS ES+



$C_{21}H_{21}S\ (M+H)^+$:305.1364, Found 305.1355

Minimum:				-1.5				
Maximum:		5.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
305.1355	305.1364	-0.9	-2.9	11.5	22.8	n/a	n/a	C21 H21 S