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Supporting Information

1, 1'-sulfinyldipyridinium bis (hydrogen sulfate) ionic liquid: synthesis and its application towards temperature influenced synthesis of novel pyranopyrimidinediones and pyranopyrimidinetriones

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A) General Information

IR spectra were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer. NMR spectra were recorded on a BrukerAC-300 spectrometer in DMSO-d_6 and $CDCl_3$ using tetramethylsilane as internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS.

B) Typical procedure for preparation of ionic liquid:

Step I: Synthesis of ionic liquid $[(Py)_2SO]Cl_2$:

A three necked flask (100 ml) equipped with a condenser was charged with pyridine (0.79 g, 10mmol) in dry dichloromethane (50 ml). Then under rigorous stirring, 3.65 ml (5mmol) of thionyl chloride was added drop wise over a period of 30 min. After the addition was completed, the reaction was stirred for 12 h at room temperature. The ionic liquid $[(Py)_2SO]Cl_2$ was obtained by distillation of dichloromethane. The ionic liquid was washed with dry dichloromethane (3×10 ml) and purified through drying in a vacuum at 80 ^{0}C to remove the residual dichloromethane.

Step II: Synthesis of ionic liquid $[(Py)_2SO][HSO_4]_2$:

A round bottom flask (50 ml) was charged with $[(Py)_2SO]Cl_2$ (10 g, 36 mmol), then sulphuric acid (3.53 g, 36 mmol) was added over a period of 5 min at 0-5 ^{0}C. Afterward, the reaction mixture was stirred for 12 h at 120 ^{0}C to give $[(Py)_2SO]$ $[HSO_4]_2$ in 98% yield.

C) a) Typical procedure for synthesis of Pyranopyrimidinedione :

A mixture of salicyldehyde (1mmol) and 6-amino uracil (2 mmol) in bronsted acidic ionic liquid $[(Py)_2SO][HSO_4]_2$ (20 mol%) was stirred in ethanol at ambient temperature for the time indicated in Table 3. The progress of the reaction was monitored by TLC. After completion of reaction, the precipitated product was filtered and washed with water and cooled ethanol.

b) Typical procedure for synthesis of Pyranopyrimidinetrione:

A mixture of salicylaldehyde (1 mmol) and uracil (2 mmol) in bronsted acidic ionic liquid $[(Py)_2SO][HSO_4]_2$ (20 mol%) was refluxing in ethanol (5 mL) for 5 h. After completion of the reaction confirmed by TLC, the reaction mixture was cooled to room temperature. Then, the precipitated product was filtered and washed with water (10 mL) and methanol (5 mL) to afford the pure product.

D) Reusability of $[(Py)_2SO][HSO_4]_2$ ionic liquids as catalyst for synthesis of pyranopyrimidinedione:

Recycling of catalyst is one of the most significant criteria of green chemical reaction, hence recovery and reuse of the ionic liquid catalyst was examined in the reaction of salicylaldehyde and 6-amino uracil in ehanol. After completion of reaction, the product was separated by simple filtration. Then ionic liquid was conveniently recovered and reused after heat treatment under vacuum at 70^{0}C for 2 hours. As shown in **table 1.** Ionic liquid

$[(Py)_2SO][HSO_4]_2$ was reused at least five times without significant decrease in the reaction yield.

Table 1. Reusability of catalyst for synthesis of pyranopyrimidinedione[a]

Run	Cycle	Time (h)	Yield (%)[b]
1	0	1	96
2	I	1	93
3	II	1	90
4	III	1	89
5	IV	1	88

[a] Salicylaldehyde (1mmol), 6-amino uracil (2-mmol) and 20 mol% catalyst in ethanol at room temperature.
[b] Yield refers to pure, isolated product.

E) Infrared Spectra:

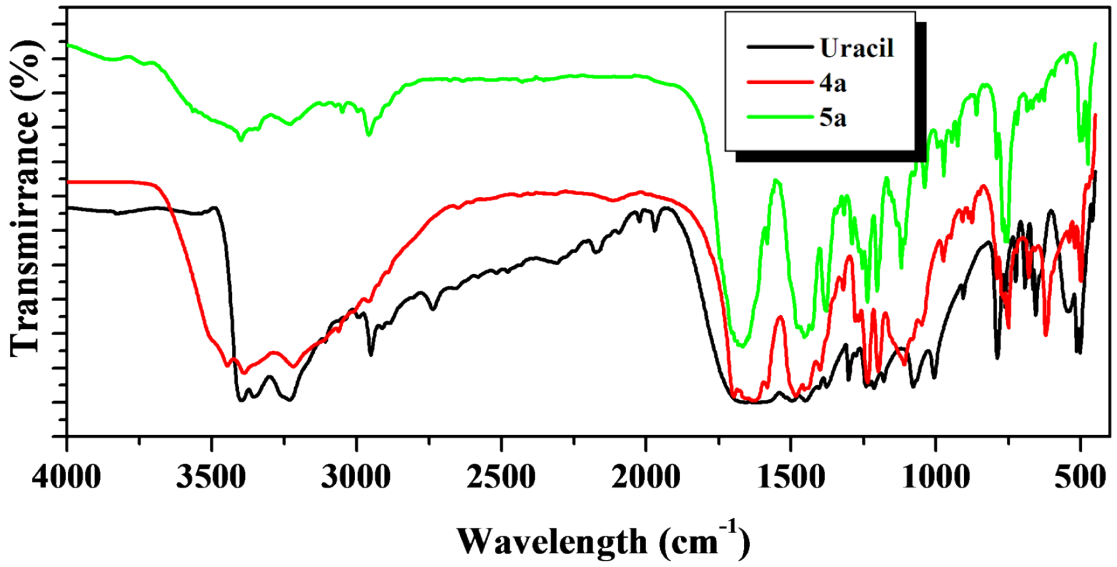
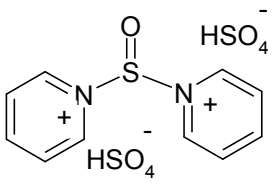


Fig. 1 IR spectra of uracil, pyranopyrimidinedione **(4a)**, pyranopyrimidinetrione **(5a)**.

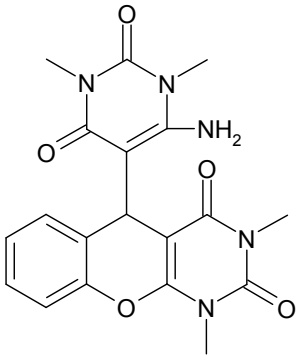
F) Spectral data of $[(Py)_2SO][HSO_4]_2$ ionic liquid:



^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.08-8.12 (t, 2H, *J*= 10 Hz), 8.51-8.66 (m, 4H), 8.91-8.93 (d, 2H, *J*= 10 Hz), (DMSO-d_6, 125 MHz): 127.78, 141.97, 146.98, MS (ESI): 257 m/z and 159 m/z (+ ve mode), 97 m/z (- ve mode).

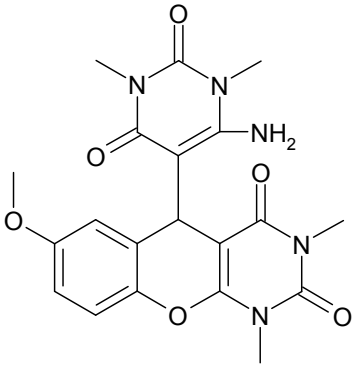
G) Spectral data of synthesized Pyranopyrimidinedione compounds:

Entry a, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



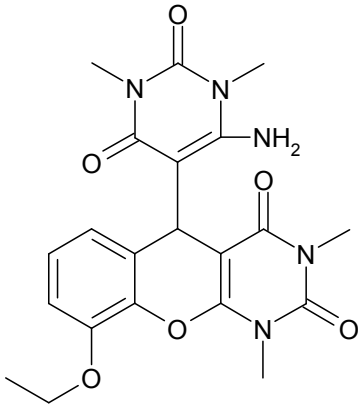
White solid; M.P. 278 ^{0}C; IR (KBr): 3445, 3388, 3218, 1695, 1634, 1583, 1484, 1199, 1109, 1050, 974, 875, 789, 749, 679, 631 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 3.10 (s, 3H), 3.33 (s, 3H), 3.51 (s, 3H), 3.61 (s, 3H), 4.81 (s, 1H), 5.77 (s, 2H, -NH_2, D_2O exchangeable), 7.07-7.11 (t, 3H, *J*= 6 Hz), 7.18-7.21 (dd, 1H, *J*= 3,3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 27.62, 28.12, 29.05, 29.20, 30.31, 87.78, 93.52, 115.51, 123.52, 125.13, 127.75, 128.32, 150.17, 150.72, 151.10, 151.47, 160.95, 164.01; MS (EI): 397 (m/z).

Entry b, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-methoxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



White solid; M.P. 255-258 ^{0}C; IR (KBr): 3400, 3253, 2955, 1704, 1614, 1486, 1421, 1279, 1222, 1081, 1034, 977, 851, 809, 786, 767, 753, 689, 653 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 3.12 (s, 3H), 3.33 (s, 3H), 3.48-3.49 (d, 3H, *J*= 3 Hz), 3.57 (s, 3H), 3.78 (s, 3H), 4.82 (s, 1H), 5.78 (s, 2H, -NH_2, D_2O exchangeable), 6.59-6.60 (d, 1H, *J*= 3 Hz), 6.73-6.77 (dd, 1H, *J*= 3,3 Hz), 7.04-7.07 (d, 1H, *J*= 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 18.72, 27.33, 27.90, 29.01, 30.08, 55.46, 56.79, 87.25, 91.11, 112.57,113.36, 116.17, 125.45, 144.51, 150.34, 151.23, 152.29, 154.02, 156.46, 160.78, 162.49; MS (EI): 427 (m/z).

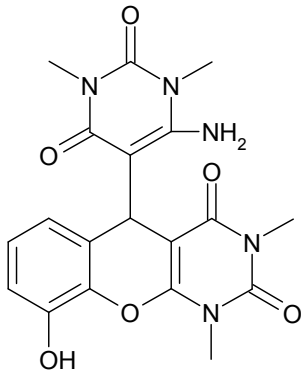
Entry c, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-9-ethoxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



White solid; M.P. 258-260 ^{0}C; IR (KBr): 3467, 3382, 3238, 1676, 1646, 1602, 1495, 1452, 1277, 1215, 1139, 1055, 924, 857, 836, 791, 776, 753, 683, 645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.44-1.49 (t, 3H, *J*= 6 Hz), 3.12 (s, 3H), 3.33 (s, 3H), 3.48 (s, 3H), 3.60 (s, 3H), 4.07-4.13 (m, 2H), 4.84 (s, 1H), 5.75 (s, 2H, -NH_2, D_2O exchangeable), 6.62-6.65 (d, 1H, *J*= 9 Hz), 6.76-6.79 (d, 1H, *J*= 9 Hz), 6.95-7.00 (t, 1H, *J*= 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 14.81, 27.69, 28.08, 29.22, 30.54, 64.37,

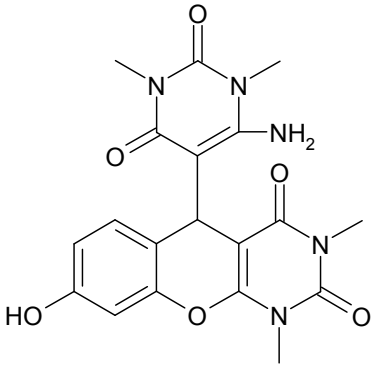
87.58, 93.17, 111.41,119.44, 124.41, 124.70, 140.38, 146.59, 150.51, 151.51, 154.29, 161.20, 164.04; MS (EI): 441 (m/z).

Entry d, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-9-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



White solid; M.P. 248-250 ^{0}C; IR (KBr): 3521, 3461, 3372, 3234, 2950, 1692,1622, 1476, 1332, 1216, 1145, 1087, 1049, 964, 858, 791, 770, 754, 725, 686, 638 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.91 (s, 3H), 3.14 (s, 3H), 3.34 (s, 3H), 3.45 (s, 3H), 5.02 (s, 1H), 6.51-6.54 (d, 1H, *J*= 9 Hz), 6.71-6.74 (d, 1H, *J*= 9 Hz), 6.82-6.88 (t, 1H, *J*= 9 Hz) 7.06 (s, 2H, -NH_2, D_2O exchangeable), 9.68 (s, 1H, -OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.39, 27.98, 29.37, 30.36, 87.51, 90.77, 114.88, 118.75, 124.87, 125.90, 139.08, 139.84, 144.82, 150.62, 151.28, 152.09, 153.75, 160.58, 161.83; MS (EI): 413 (m/z).

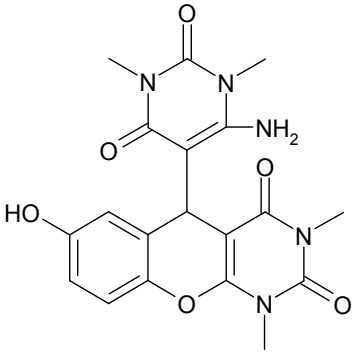
Entry e, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-8-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



White solid; M.P. 233-235 ^{0}C; IR (KBr): 3568, 3415, 3231, 2950, 1658, 1632, 1587, 1493, 1460, 1371, 1253, 1219, 1197, 1102, 1046, 970, 789, 750, 679, 629 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.90 (s, 3H), 3.14 (s, 3H), 3.34 (s, 3H), 3.42 (s, 3H),

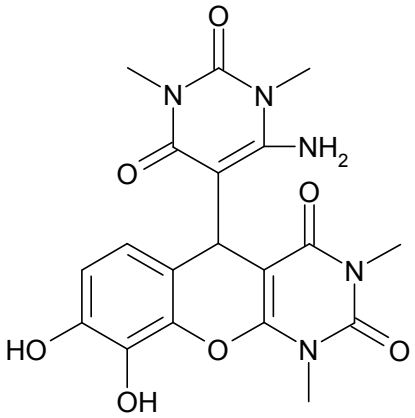
4.93 (s, 1H), 6.49-6.52 (d, 2H, *J*= 9 Hz), 6.87-6.90 (d, 1H, *J*= 9 Hz), 7.01 (s, 2H, -NH_2, D_2O exchangeable), 9.60 (s, 1H, -OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.37, 28.00, 28.60, 29.26, 30.34, 88.03, 90.93, 102.52, 112.94, 115.13, 129.35, 150.42, 150.58, 151.30, 152.02, 153.79, 156.91, 160.51, 161.83; MS (EI): 413 (m/z).

Entry f, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



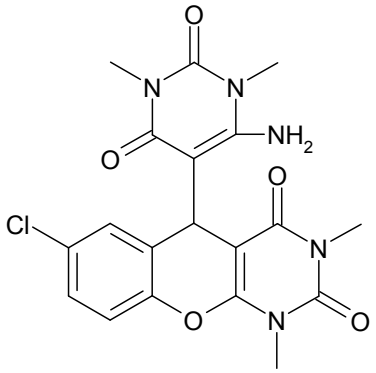
White solid; M.P. 220-224 ^0C; IR (KBr): 3444, 3333, 1681, 1615, 1486, 1448, 1399, 1352, 1323, 1285, 1223, 1200, 1115, 976, 894, 806, 790, 767, 752, 672, 618 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.19 (s, 3H), 3.13 (s, 3H), 3.35 (s, 3H), 3.41 (s, 3H), 4.99 (s, 1H), 6.48-6.49 (d, 1H, *J*= 3 Hz), 6.55-6.59 (dd, 1H, *J*= 3,3 Hz), 6.93-6.96 (d, 1H, *J*= 9 Hz) 7.06 (s, 2H, -NH_2, D_2O exchangeable), 9.27 (s, 1H, -OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.40, 27.97, 29.17, 29.53, 30.39, 87.05, 90.64, 114.39, 114.61, 116.69, 125.66, 143.09, 150.60, 151.29, 152.13, 153.98, 154.48, 160.52, 161.81; MS (EI): 413 (m/z).

Entry g, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-8,9-dihydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



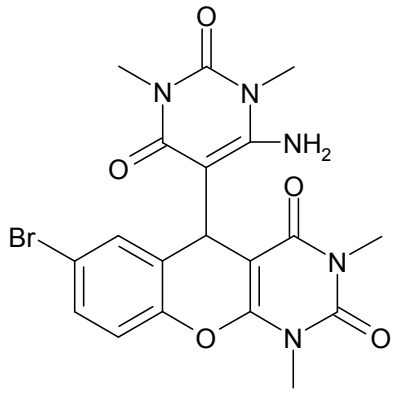
White solid; M.P. 242-2345 ^{0}C; IR (KBr): 3474, 3412, 3313, 3219, 1684, 1630, 1492, 1323, 1275, 1217, 1194, 1059, 997, 968, 817, 781, 792, 756, 689, 617 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.91 (s, 3H), 3.14 (s, 3H), 3.33 (s, 3H), 3.47 (s, 3H), 4.93 (s, 1H), 6.36-6.39 (d, 1H, *J*= 9 Hz), 6.49-6.52 (d, 1H, *J*= 9 Hz), 6.99 (s, 2H, -NH_2, D_2O exchangeable), 8.80 (s, 1H, -OH, D_2O exchangeable), 9.19 (s, 1H, -OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.37, 27.98, 28.95, 29.42, 30.33, 87.78, 91.14, 112.25, 116.23, 117.77, 132.69, 140.01, 145.36, 150.64, 151.30, 151.89, 153.76, 161.90; MS (EI): 274 (m/z) (base peak).

Entry h, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-chloro-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



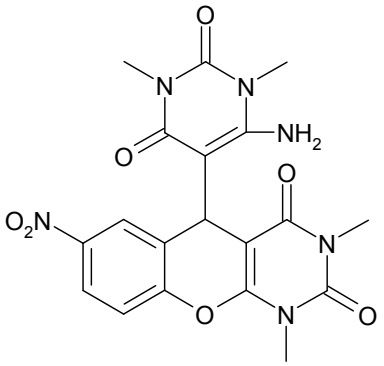
White solid; M.P. 255-258 ^{0}C; IR (KBr): 3423, 3371, 3065, 2950, 1698, 1644, 1471, 1443, 1264, 1241, 1192, 1124, 1080, 1042, 977, 867, 851, 787, 766, 748, 664 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.90 (s, 3H), 3.14 (s, 3H), 3.35 (s, 3H), 3.43 (s, 3H), 5.08 (s, 1H), 7.08-7.09 (d, 1H, *J*= 3 Hz), 7.13 (s, 2H, -NH_2, D_2O exchangeable), 7.22-7.28 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.44, 28.05, 29.32, 30.41, 87.26, 90.25, 118.00, 127.19, 127.72, 128.22, 128.65, 148.97, 150.51, 151.26, 152.36, 153.62, 160.70, 161.66; MS (EI): 431 (m/z).

Entry i, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-bromo-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



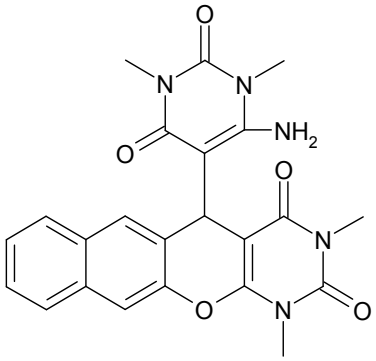
White solid; M.P. 285-287 ^{0}C; IR (KBr): 3395, 3251, 2952, 1709, 1634, 1497, 1471, 1404, 1239, 1182, 1115, 1048, 977, 781, 765, 752, 687, 618 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.91 (s, 3H), 3.14 (s, 3H), 3.35 (s, 3H), 3.43 (s, 3H), 5.08 (s, 1H), 7.13 (s, 2H, -NH_2, D_2O exchangeable), 7.16 (s, 1H), 7.21-7.22 (d, 1H, *J*= 3 Hz), 7.36-7.40 (dd, 1H, *J*= 3,3 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 27.43, 28.04, 29.10, 29.31, 30.41, 49.06, 79.62, 87.33, 90.25, 116.38, 118.38, 127.64, 130.57, 131.13, 149.46, 150.50, 151.25, 152.34, 153.57, 160.68, 161.63; MS (EI): 475 (m/z).

Entry j, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-7-nitro-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



Yellow solid; M.P. 224-226 ^{0}C; IR (KBr): 3411, 3230, 2956, 1697, 1639, 1523, 1475, 1375, 1339, 1242, 1198, 1122, 1087, 977, 935, 891, 845, 766, 754, 635 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.90 (s, 3H), 3.16 (s, 3H), 3.37 (s, 3H), 3.47 (s, 3H), 5.21 (s, 1H), 7.22 (s, 2H, -NH_2, D_2O exchangeable), 7.42-7.45 (d, 1H, *J*= 9 Hz), 7.96-7.97 (d, 1H, *J*= 3 Hz), 8.08-8.12 (dd, 1H, *J*= 3,3 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 28.39, 30.50, 32.41, 115.15, 123.89, 124.24, 128.77, 139.74, 150.82, 154.08, 162.39, 163.04; MS (EI): 442 (m/z).

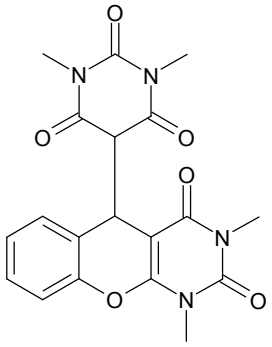
Entry k, Table 3:



White solid; M.P. 256-258 ^{0}C; IR (KBr): 3424, 3204, 2956, 1674, 1634, 1459, 1324, 1279, 1235, 1118, 993, 925, 806, 783, 754, 617 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.81 (s, 3H), 3.21 (s, 3H), 3.37 (s, 3H), 3.49 (s, 3H), 5.48 (s, 1H), 7.31 (s, 2H, -NH_2, D_2O exchangeable), 7.39-7.51 (m, 2H), 7.83-7.90 (m, 3H), 8.31 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): Due to insufficient solubility of compound we are unable to scan its ^{13}C NMR; MS (EI): 447 (m/z).

Spectral data of synthesized Pyranopyrimidinetrione compounds:

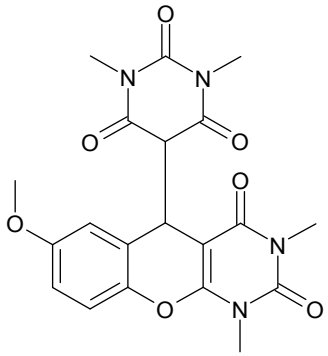
Entry a, Table 4: 5-(1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3 *d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



Yellow solid; M.P. 226 ^{0}C; IR (KBr): 3399, 3225, 2957, 1668, 1583, 1455, 1379, 1317, 1290, 1253, 1236, 1203, 1119, 1039, 973, 925, 860, 791, 760, 753, 684 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 3.08 (s, 3H), 3.27 (s, 3H), 3.36 (s, 3H), 3.56 (s, 3H), 4.08-4.09 (d, 1H, *J*= 3 Hz), 5.09-5.10 (d, 1H, *J*= 3 Hz), 7.09-7.18 (m, 3H), 7.30-7.33 (dd, 1H, *J*= 3,3 Hz);^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 28.13, 28.29, 28.54, 29.16, 36.16, 54.18, 86.24, 116.78, 120.18, 126.11, 127.85, 129.47, 149.71, 150.56, 151.18, 154.59,

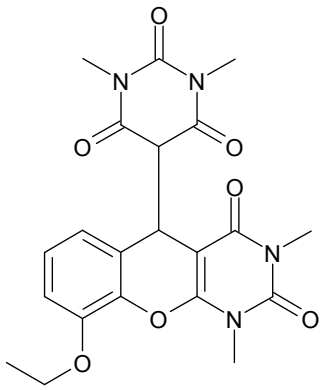
161.99, 166.92, 167.08; MS (EI): [M^+] 398 (m/z) and Base peak 243 (m/z).

Entry b, Table 4: 5-(7-methoxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



White solid; M.P. 194 ^{0}C; IR (KBr): 3509, 3405, 3255, 2957, 2919, 2888, 1679, 1659, 1635, 1485, 1379, 1276, 1237, 1038, 815, 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 3.10 (s, 3H), 3.28 (s, 3H), 3.36 (s, 3H), 3.54 (s, 3H), 3.77 (s, 3H), 4.13-4.14 (d, 1H, *J*= 3 Hz), 5.10-5.11 (d, 1H, *J*= 3 Hz), 6.66-6.67 (d, 1H, *J*= 3 Hz), 6.81-6.85 (dd, 1H, *J*= 3,3 Hz), 7.05-7.08 (d, 1H, *J*= 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 28.09, 28.34, 28.53, 29.10, 36.47, 54.06, 55.71, 85.60, 111.86, 115.24, 117.67, 121.01, 143.65, 150.57, 151.22, 154.75, 157.32, 162.06, 166.92, 167.12; MS (EI): [M^+] 426 (m/z) and Base peak 273 (m/z).

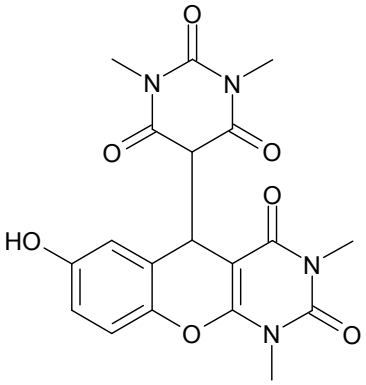
Entry c, Table 4: 5-(7-ethoxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



White solid; M.P. 206-208 ^{0}C; IR (ZnSe): 2878, 1680, 1658, 1636, 1588, 1468, 1443, 1415, 1378, 1343, 1269, 1230, 1144, 1098, 1005, 970, 893, 780, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm): 1.45-1.50 (t, 3H, *J*= 6 Hz), 3.09 (s, 3H), 3.28 (s, 3H), 3.38 (s, 3H), 3.58 (s, 3H), 4.08-4.13 (m, 3H), 5.12-5.13 (d, 1H, *J*= 3 Hz), 6.68-6.71 (d, 1H, *J*= 9

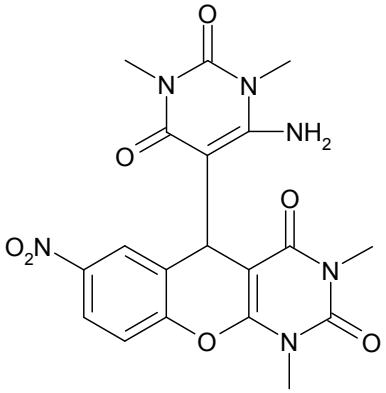
Hz), 6.86-6.88 (t, 1H, *J*= 6 Hz), 7.05-7.10 (t, 1H, *J*= 6 Hz): ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 14.73, 28.09, 28.30, 28.50, 29.11, 36.68, 54.09, 64.64, 85.97, 112.77, 118.59, 121.06, 125.78, 139.60, 147.48, 150.65, 151.28, 154.60, 162.05, 166.94, 167.11; MS (EI): [M^+] 442 (m/z) and Base peak 288 (m/z).

Entry d, Table 4: 5-(7-hydroxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



White solid; M.P. 230 ^{0}C; IR (KBr): 3406, 3196, 2961, 1681, 1455, 1381, 1318, 1277, 1225, 1120, 1049, 994, 979, 888, 866, 829, 810, 755, 677, 640 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.85 (s, 3H), 3.12 (s, 3H), 3.20 (s, 3H), 3.38 (s, 3H), 3.93-3.94 (d, 1H, *J*= 3 Hz), 4.68 (s,1H), 6.44 (s,1H), 6.69-6.72 (d, 1H, *J*= 9 Hz), 7.07-7.10 (d, 1H, *J*= 9 Hz), 9.67 (s, 1H, -OH); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 28.14, 28.18, 28.44, 29.24, 37.14, 54.31, 85.30, 91.37, 113.31, 116.64, 118.09, 120.52, 142.45, 150.47, 151.65, 154.88, 155.36, 161.72, 167.44, 168.06; MS (EI): [M^+] 414 (m/z) and Base peak 259 (m/z).

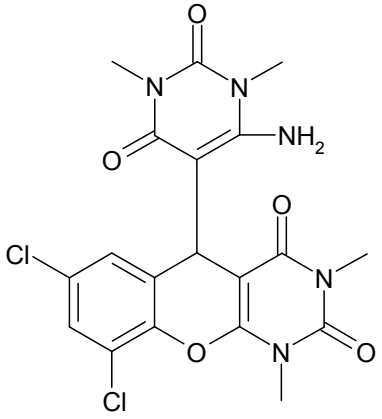
Entry e, Table 4: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-7-nitro-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



Yellow solid; M.P. 224-226 ^{0}C; IR (KBr): 3409, 3159, 2950, 1697, 1674, 1636, 1448,

1400, 1338, 1241, 1198, 1121, 891, 844, 753, 618 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ (ppm): 3.11 (s, 6H), 3.53 (s, 6H), 5.51 (s, 1H), 6.81-6.82 (d, 1H, *J*= 3 Hz) 7.90 (s, 2H, -NH_2), 7.89-7.90 (d, 1H, *J*= 3 Hz), 7.95-7.96 (d, 1H, *J*= 3 Hz); MS (EI): 442 (m/z).

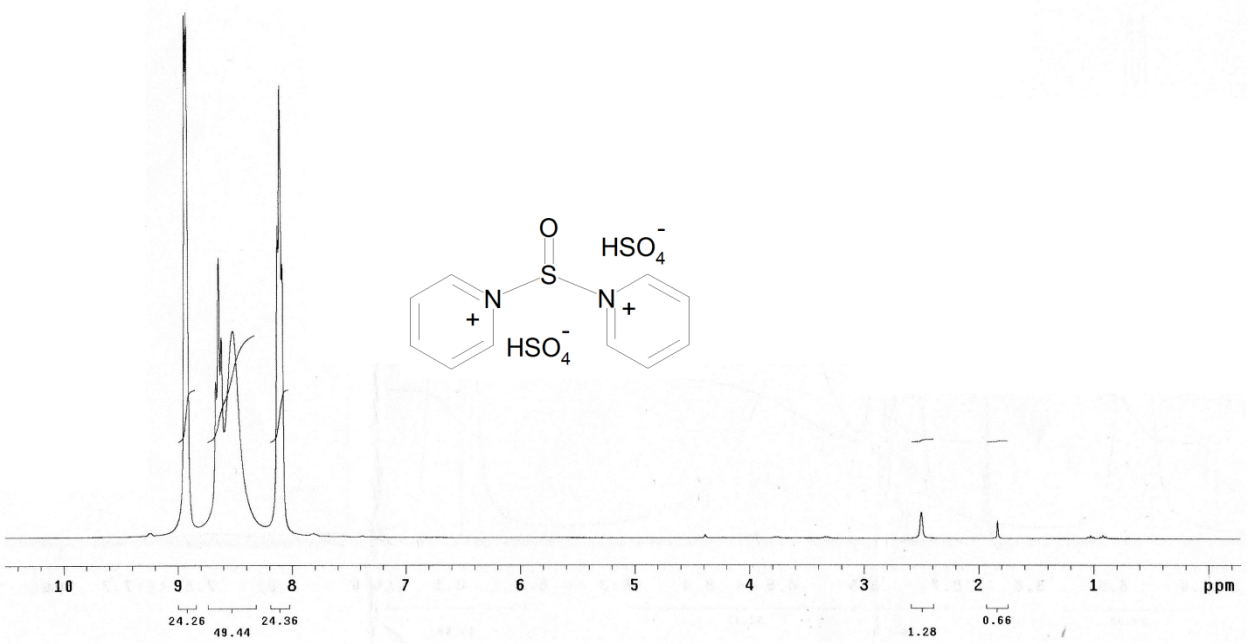
Entry f, Table 4: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7,9-dichloro-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



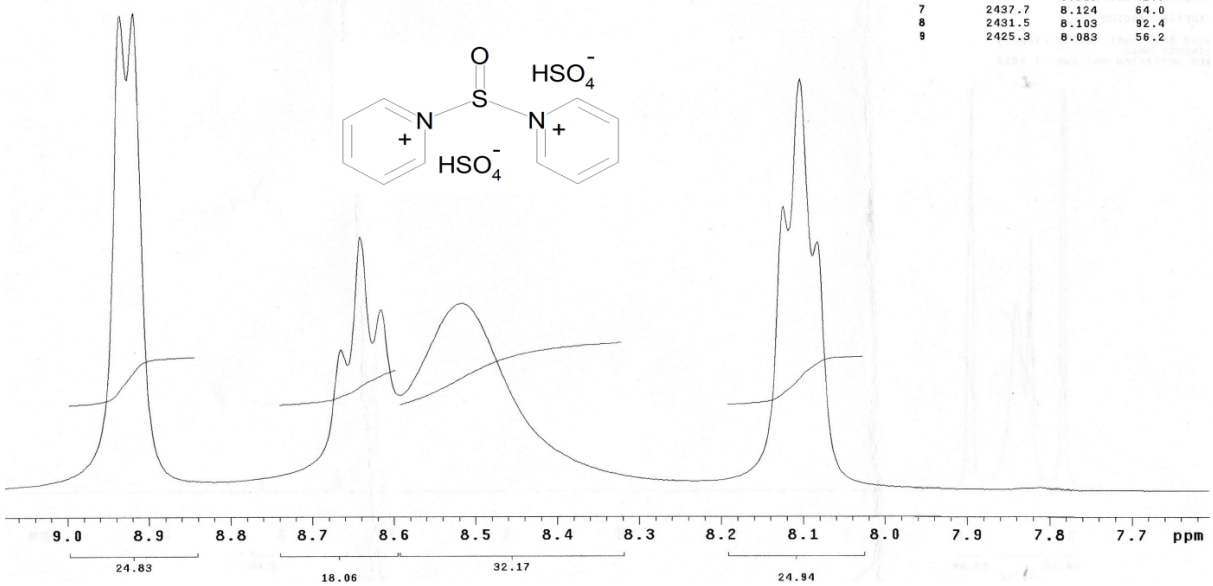
White solid; M.P. 264-266 ^0C; IR (KBr): 3456, 3159, 1719, 1695, 1639, 1490, 1451, 1402, 1253, 1183, 1114, 985, 921, 858, 789, 753, 618 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ (ppm): 2.92 (s, 3H), 3.15 (s, 6H), 3.46 (s, 6H), 5.13 (s, 1H), 7.07 (s, 1H), 7.17 (s, 2H, -NH_2), 7.57-7.58 (d, 1H, *J*= 3 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 28.09, 28.34, 28.53, 29.31, 30.09, 79.60, 87.35, 90.31, 116.63, 118.39, 127.63, 130.58, 131.13, 149.47, 150.51, 151.27, 152.37, 153.59, 160.73, 161.67.

^{1}H, ^{13}C and MS (ESI) Spectra of ionic liquid:

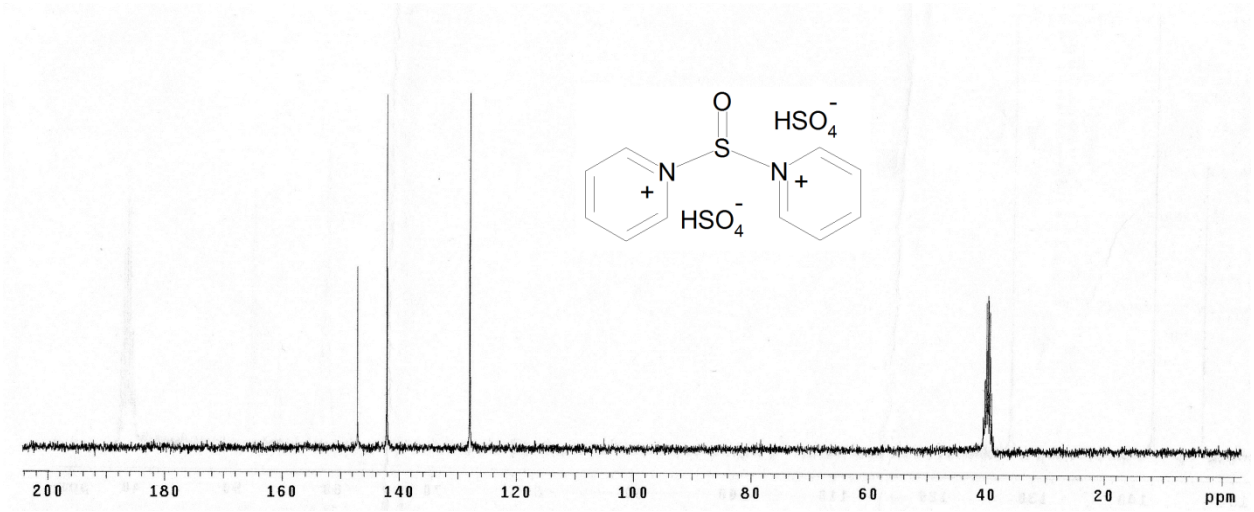
^{1}H NMR spectrum of ionic liquid



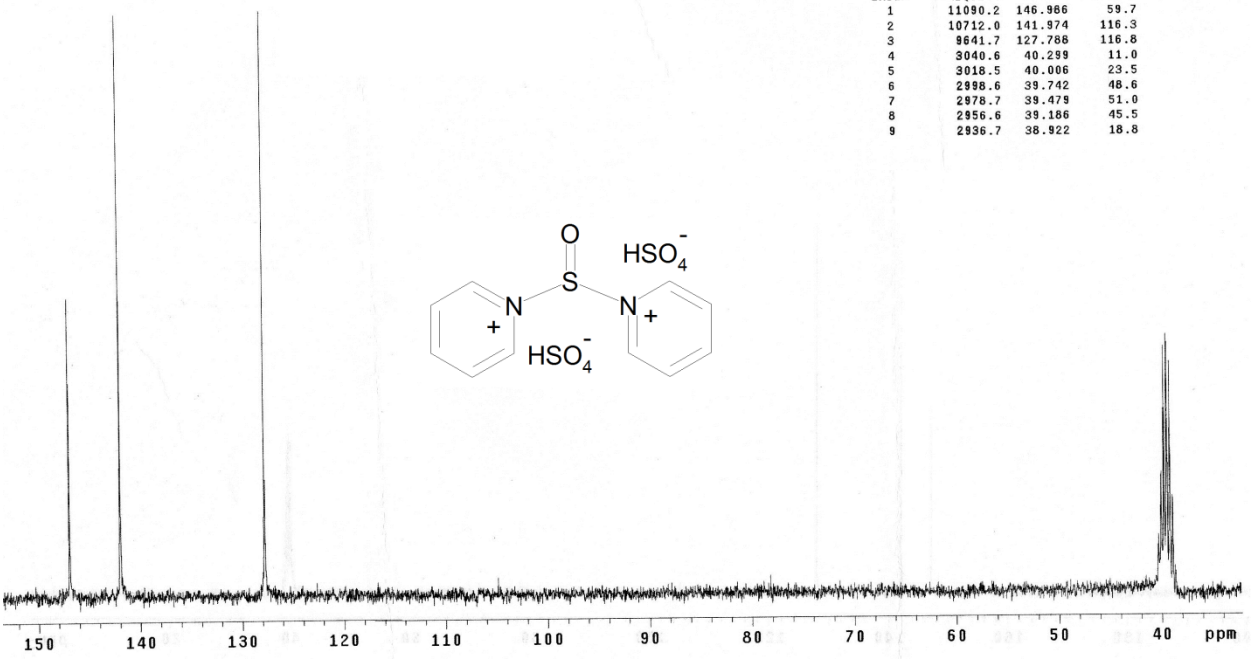
INDEX	FREQUENCY	PPM	HEIGHT
1	2680.4	8.933	106.7
2	2675.6	8.917	107.3
3	2599.8	8.664	32.2
4	2592.7	8.640	57.5
5	2585.0	8.615	41.2
6	2555.5	8.516	42.6
7	2437.7	8.124	64.0
8	2431.5	8.103	92.4
9	2425.3	8.083	56.2



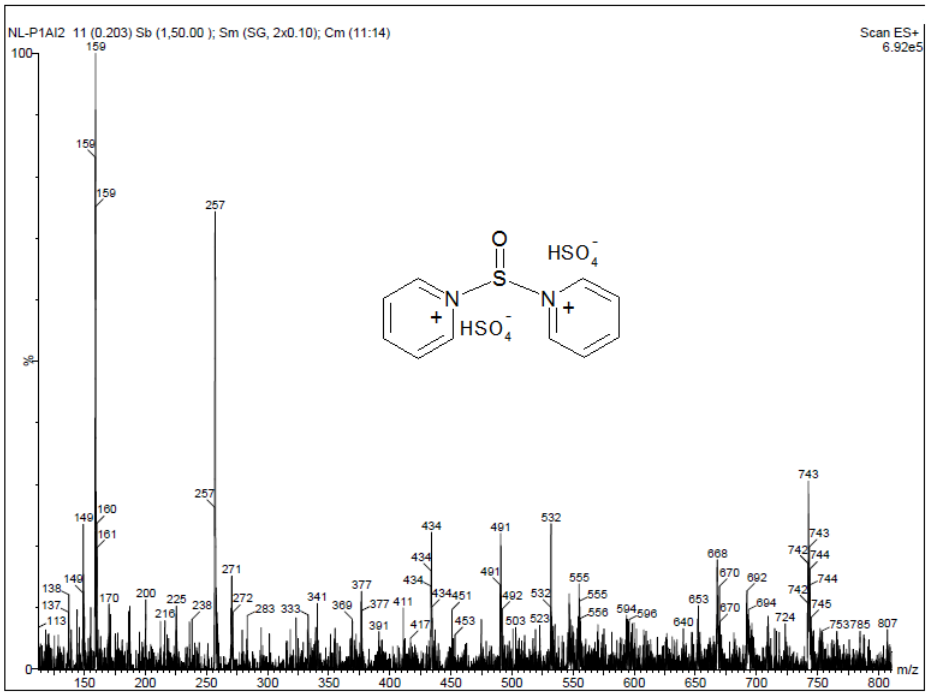
^{13}C NMR spectrum of ionic liquid



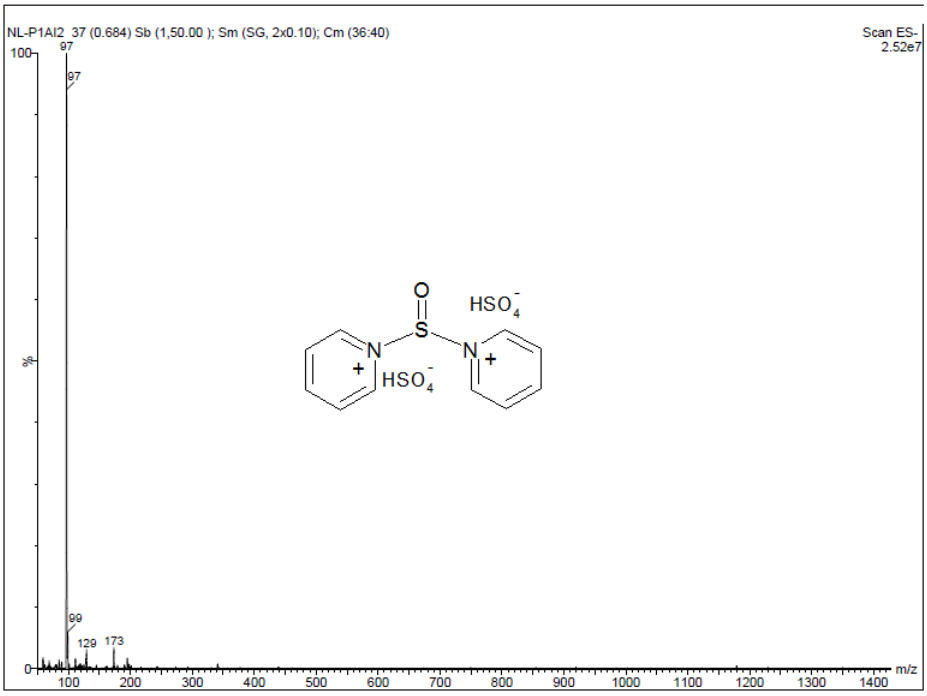
INDEX	FREQUENCY	PPM	HEIGHT
1	11090.2	146.986	59.7
2	10712.0	141.974	116.3
3	9641.7	127.788	116.8
4	3040.6	40.299	11.0
5	3018.5	40.006	23.5
6	2998.6	39.742	48.6
7	2978.7	39.479	51.0
8	2956.6	39.186	45.5
9	2936.7	38.922	18.8



MS (ESI) spectrum of ionic liquid in '+ve' mode

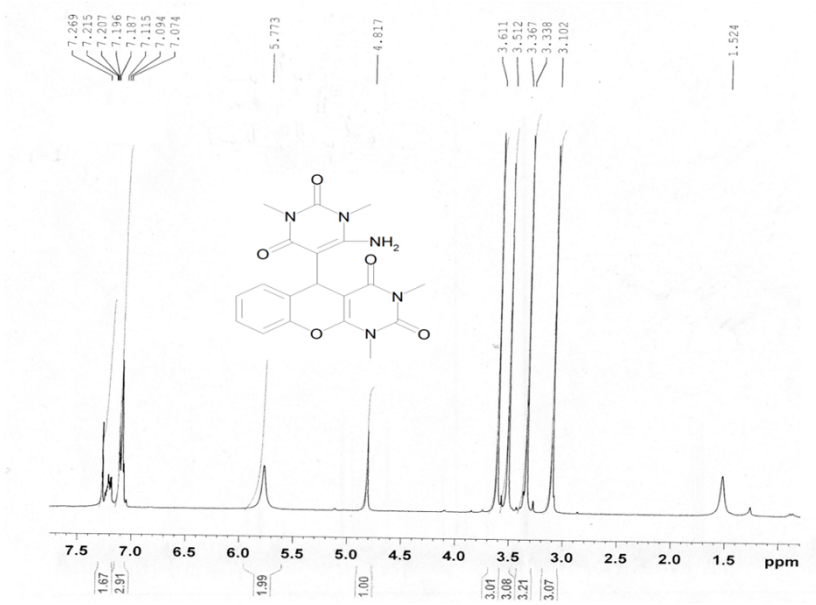


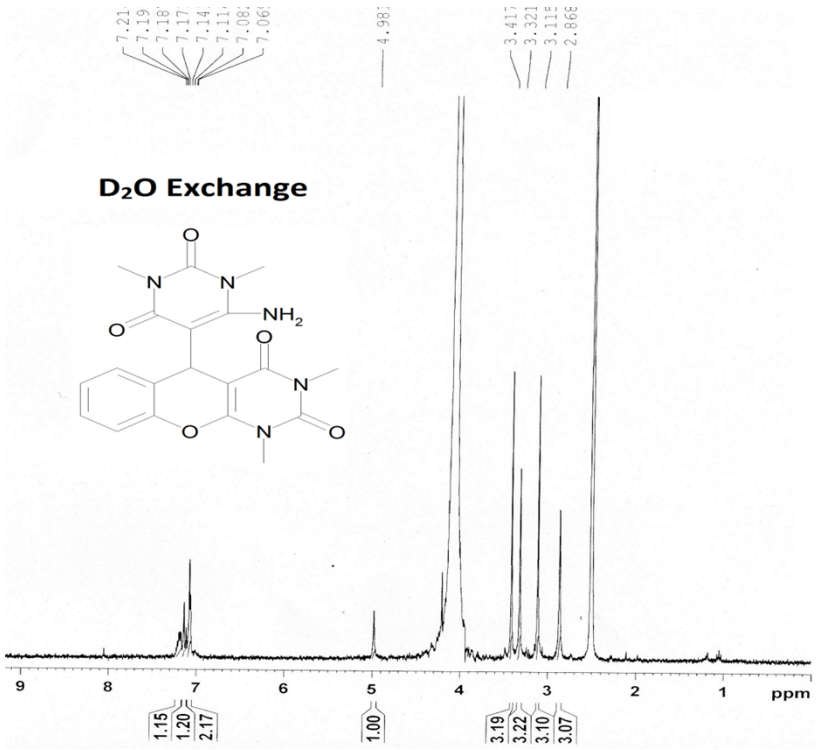
MS (ESI) spectrum of ionic liquid in '-ve' mode

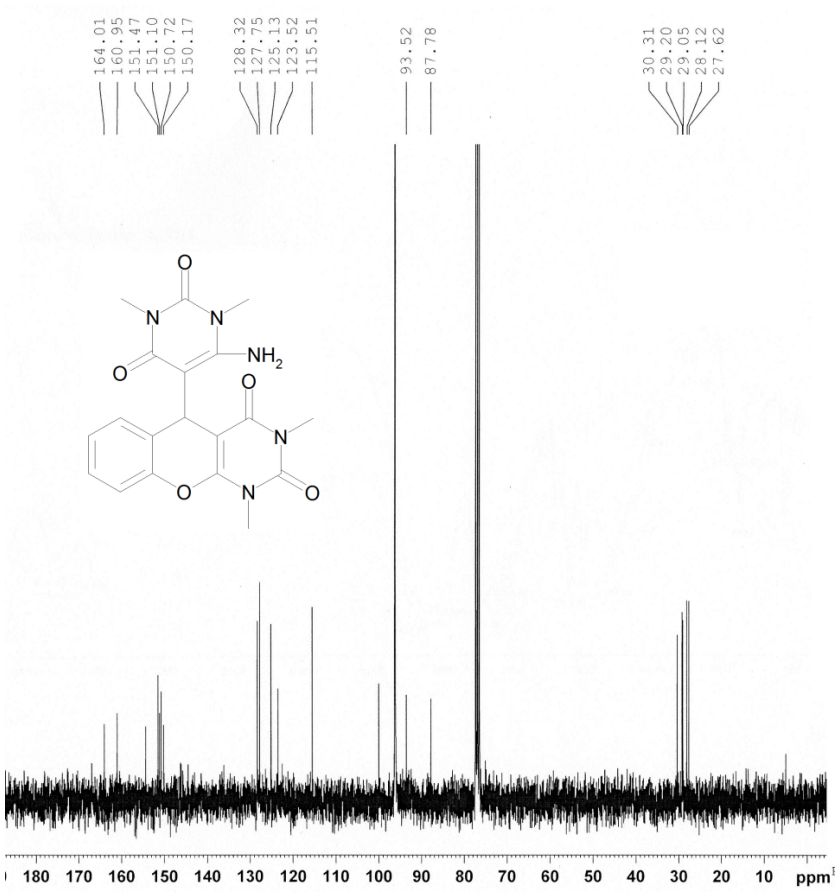


^{1}H NMR, ^{13}C NMR, IR and MS (EI) spectra of Synthesized Pyranopyrimidinedione products

Entry a, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione



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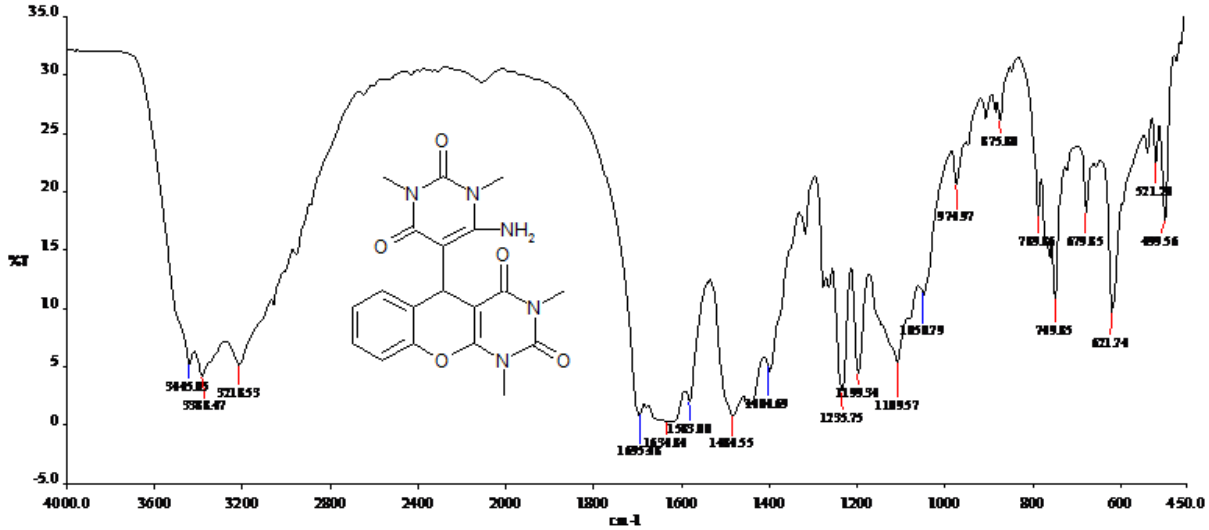
151.47
151.10
150.72
150.17
128.32
127.75
125.13
123.52
115.51
93.52
87.78
30.31
29.20
29.05
28.12
27.62
O
N
N
NH2
O
O
N
O
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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30
25
20
15
10
5
0
-5.0
%T
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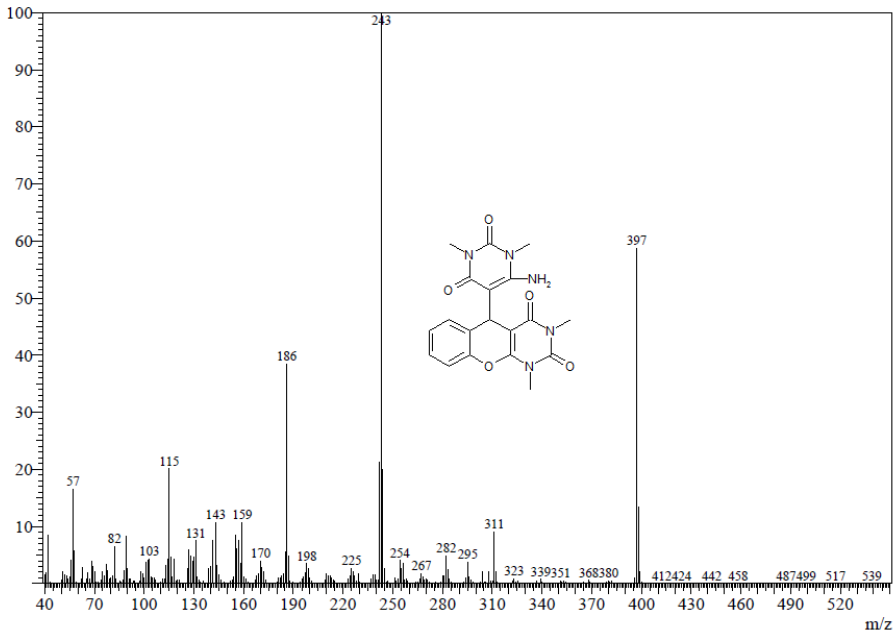
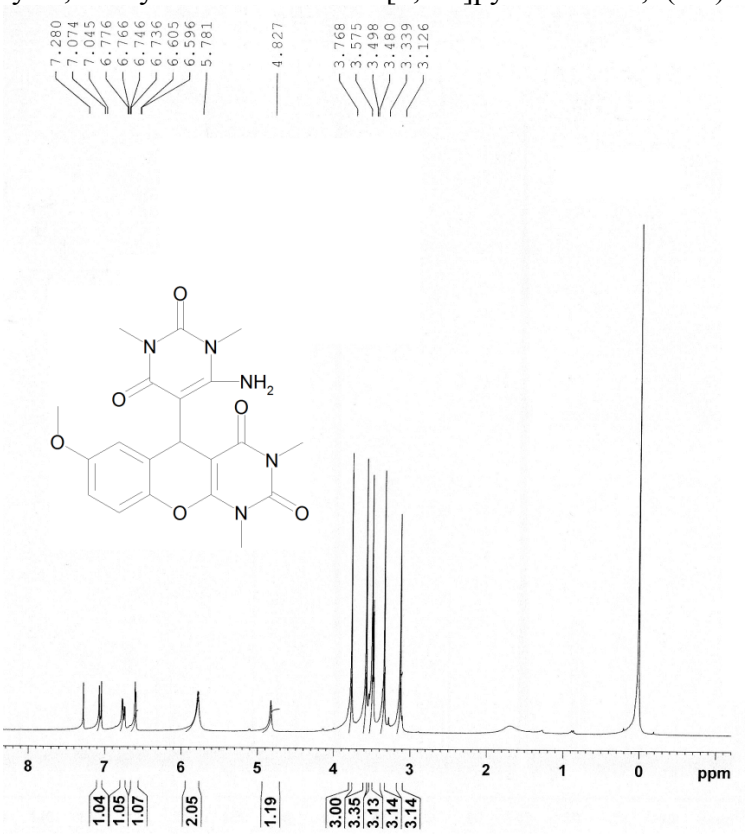
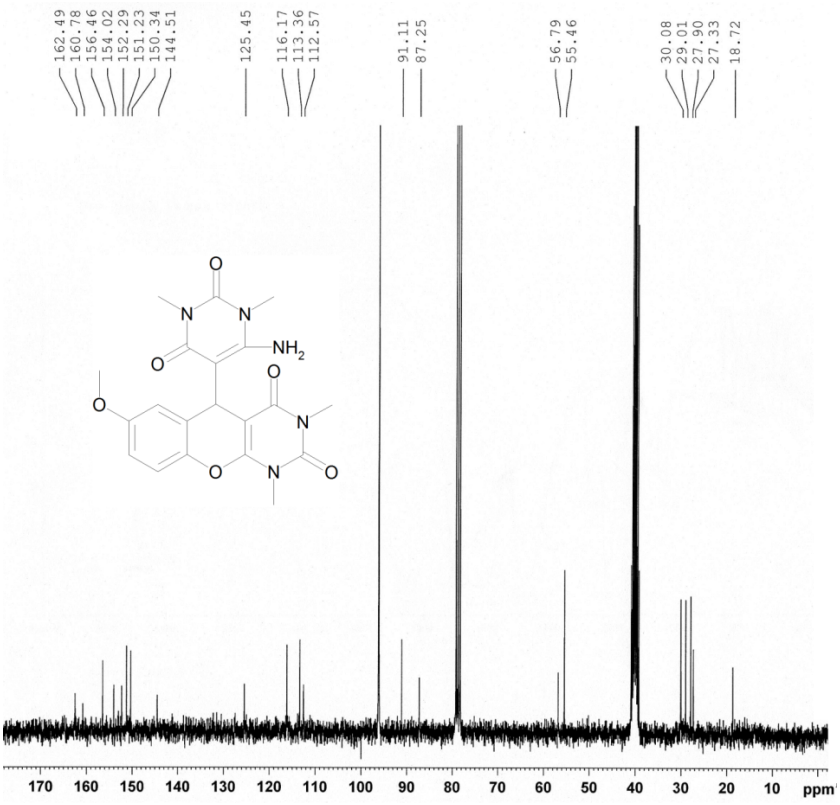
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
O
N
N
NH2
O
O
N
O
N
O



Entry b, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-methoxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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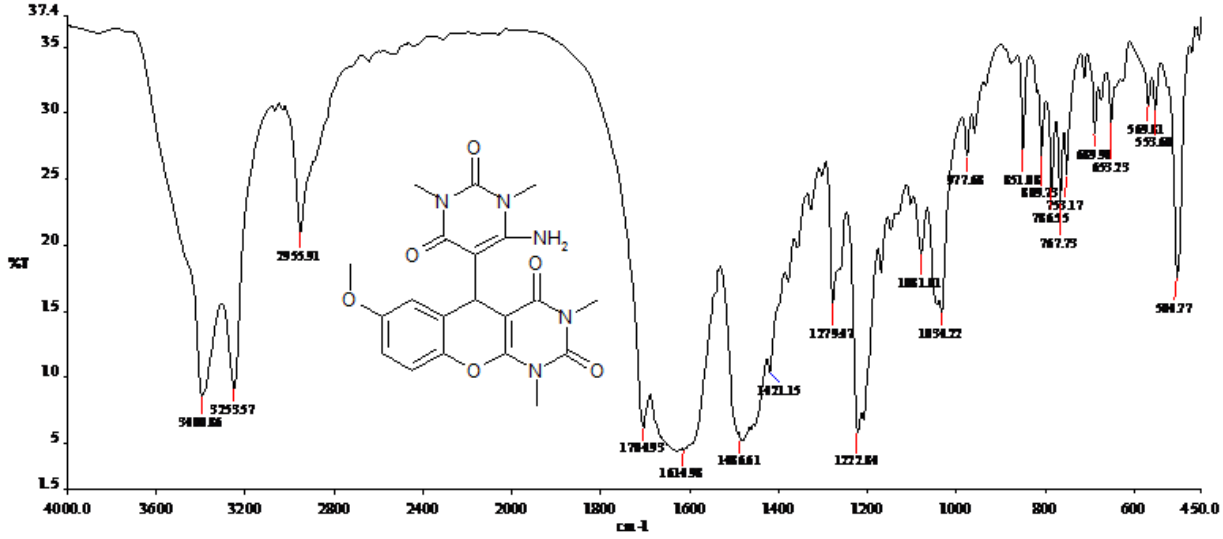
160.78
156.46
154.02
152.29
151.23
150.34
144.51
125.45
116.17
113.36
112.57
91.11
87.25
56.79
55.46
30.08
29.01
27.90
27.33
18.72
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


%T
cm-1
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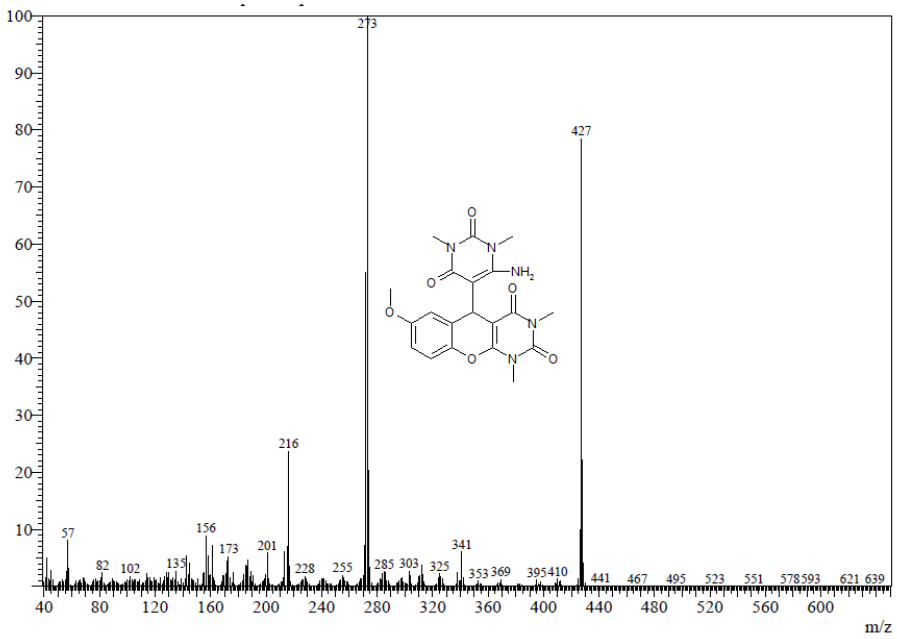
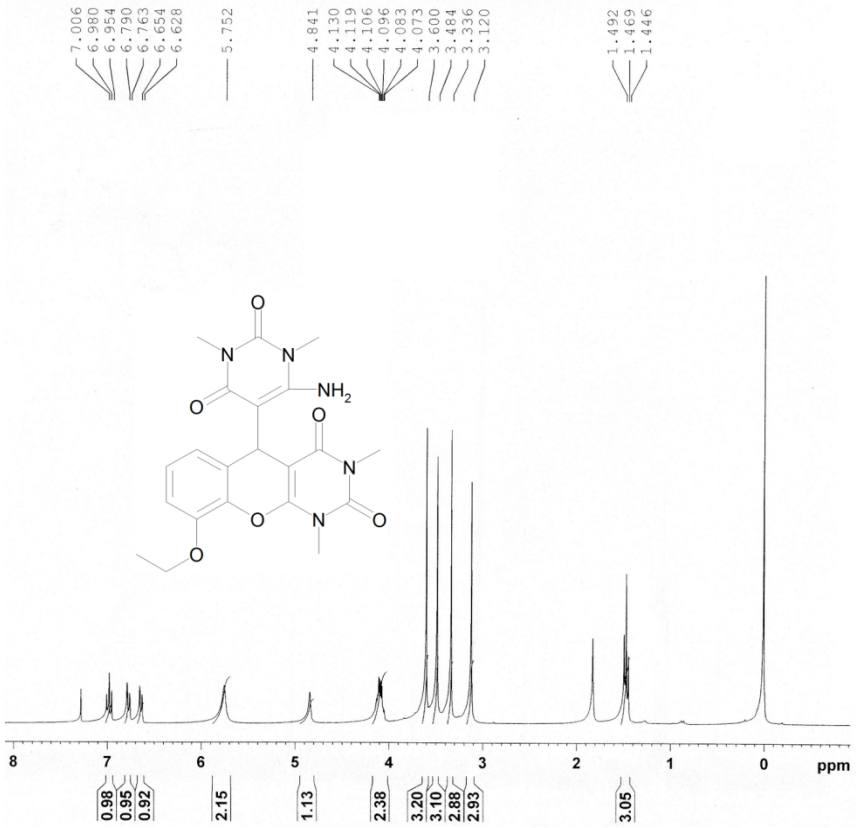
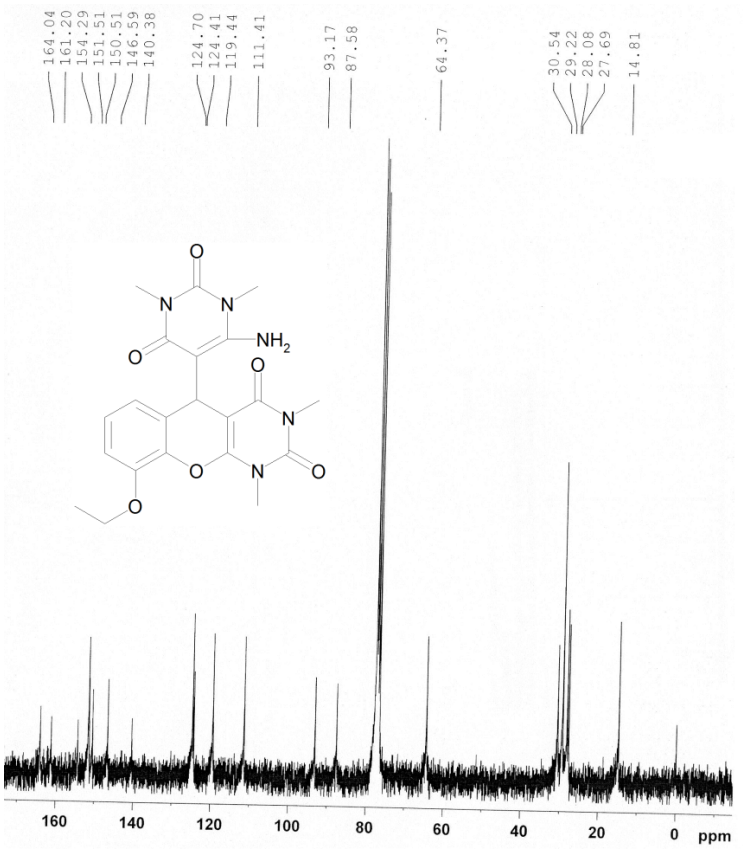
1222.84
1034.22
977.68
767.75
584.77



Entry c, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-9-ethoxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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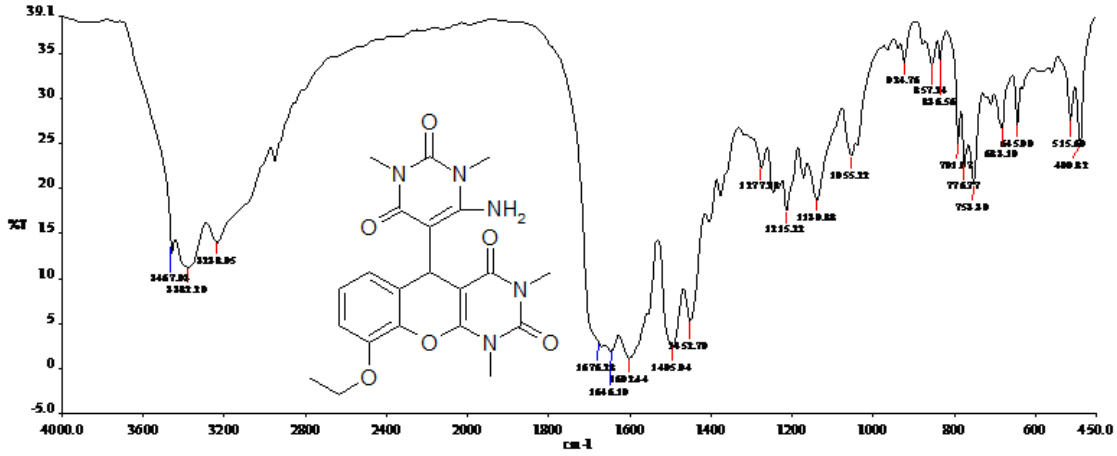
151.51
150.51
146.59
140.38
124.70
124.41
119.44
111.41
93.17
87.58
64.37
30.54
29.22
28.08
27.69
14.81
NH2
160
140
120
100
80
60
40
20
0
ppm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15
10
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2000
1800
1600
1400
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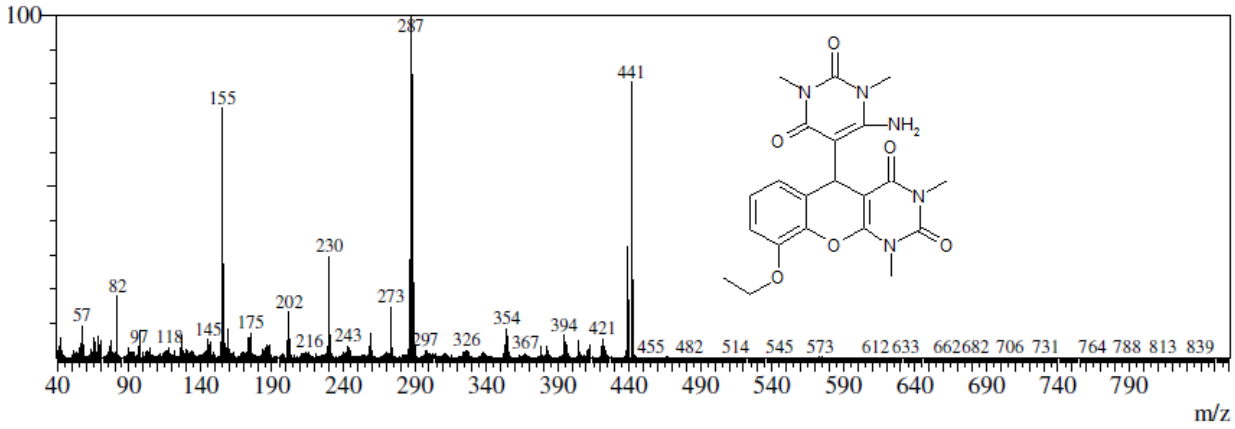
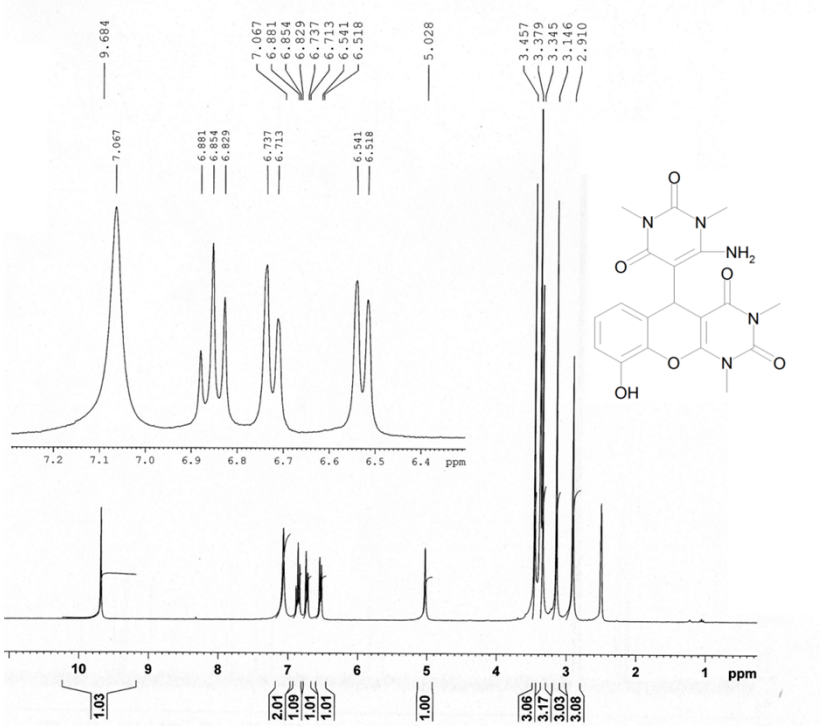
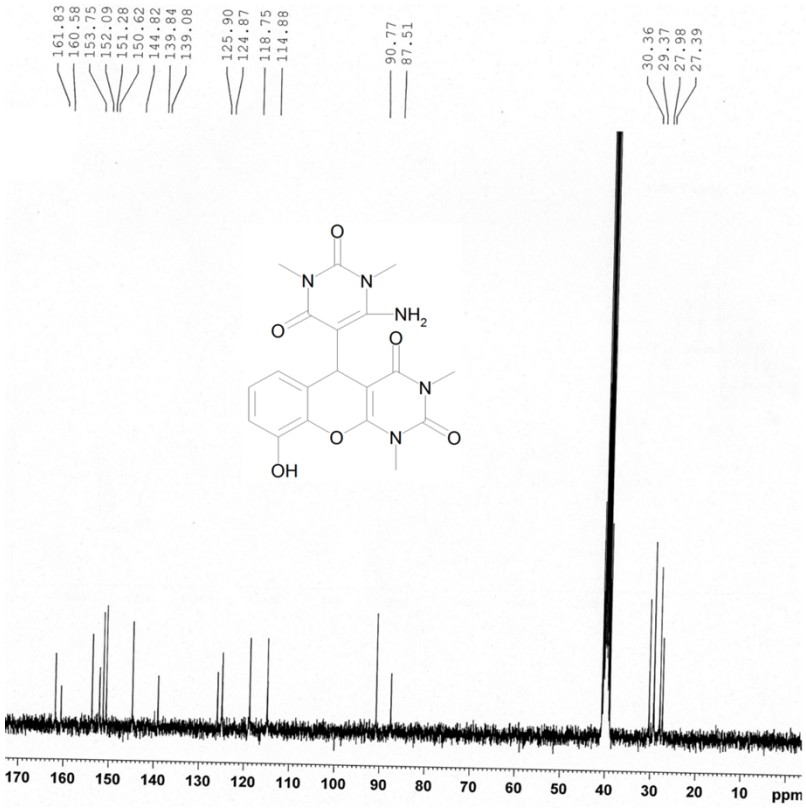
1000
800
600
450.0
cm-1
NH2



Entry d, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-9-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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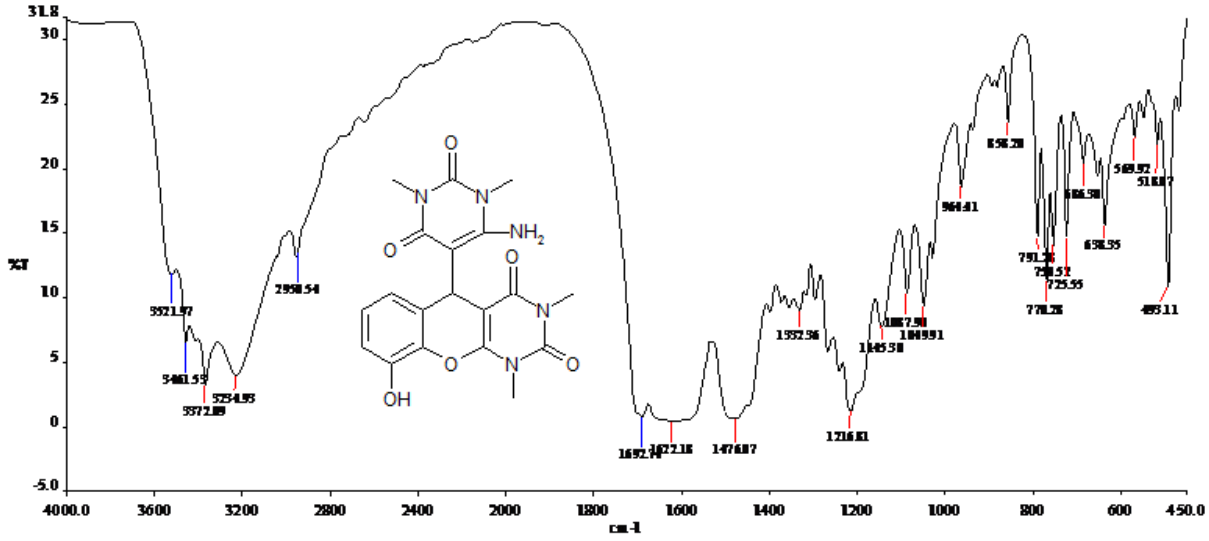
139.84
139.08
125.90
124.87
118.75
114.88
90.77
87.51
30.36
29.37
27.98
27.39
NH2
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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30
25
20
15
10
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0
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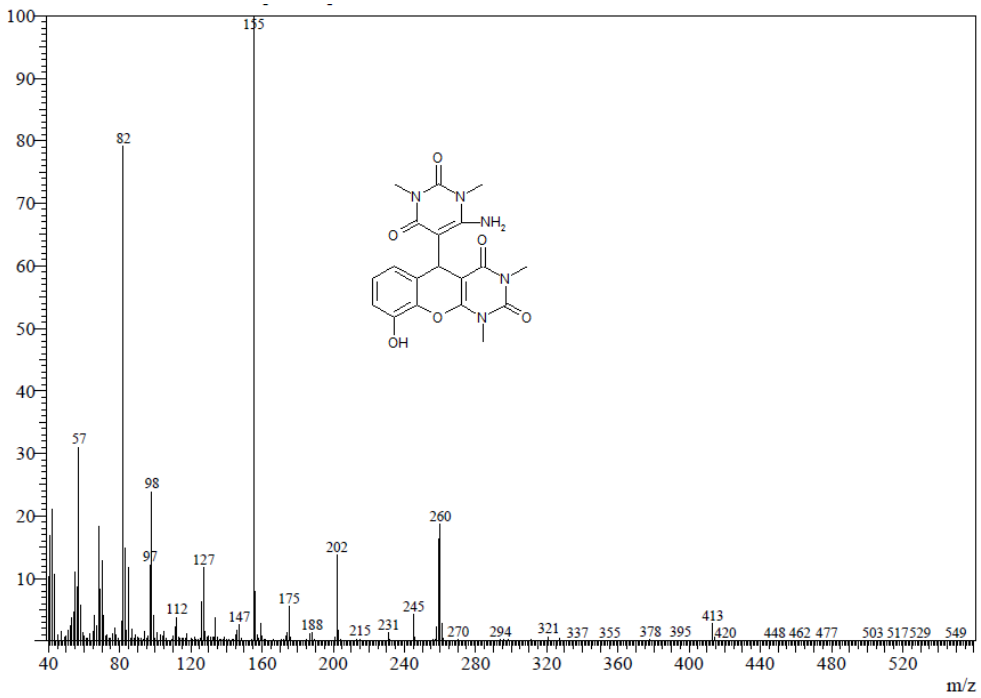
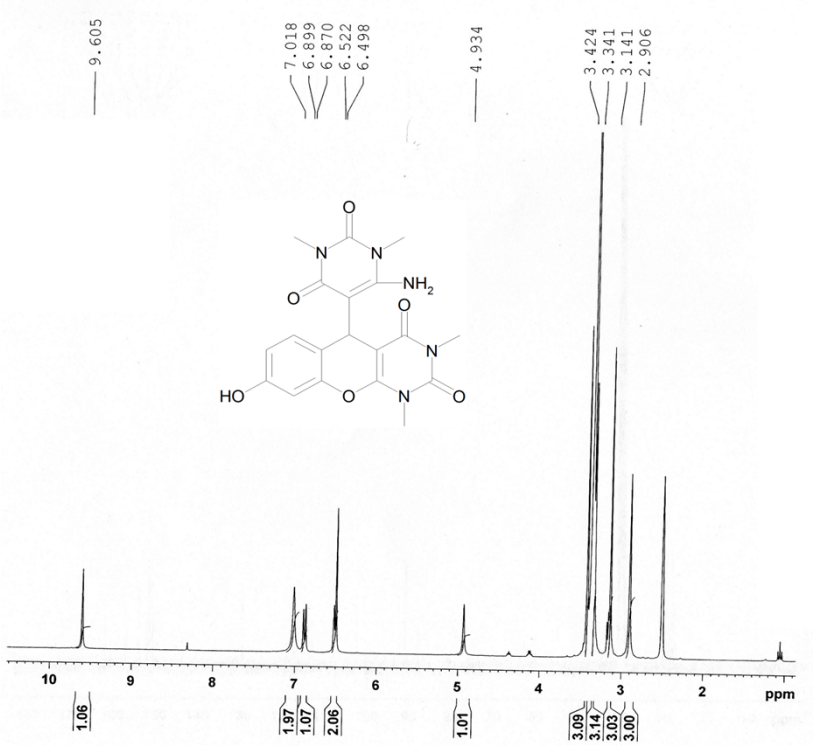
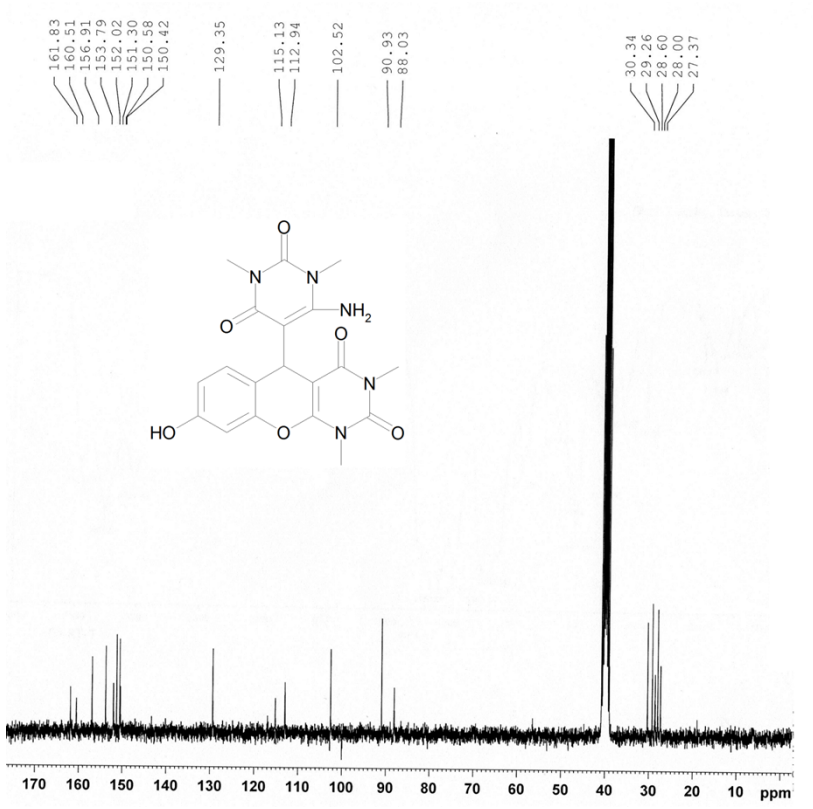
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 450.0
cm-1
NH2
OH

\



Entry e, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-8-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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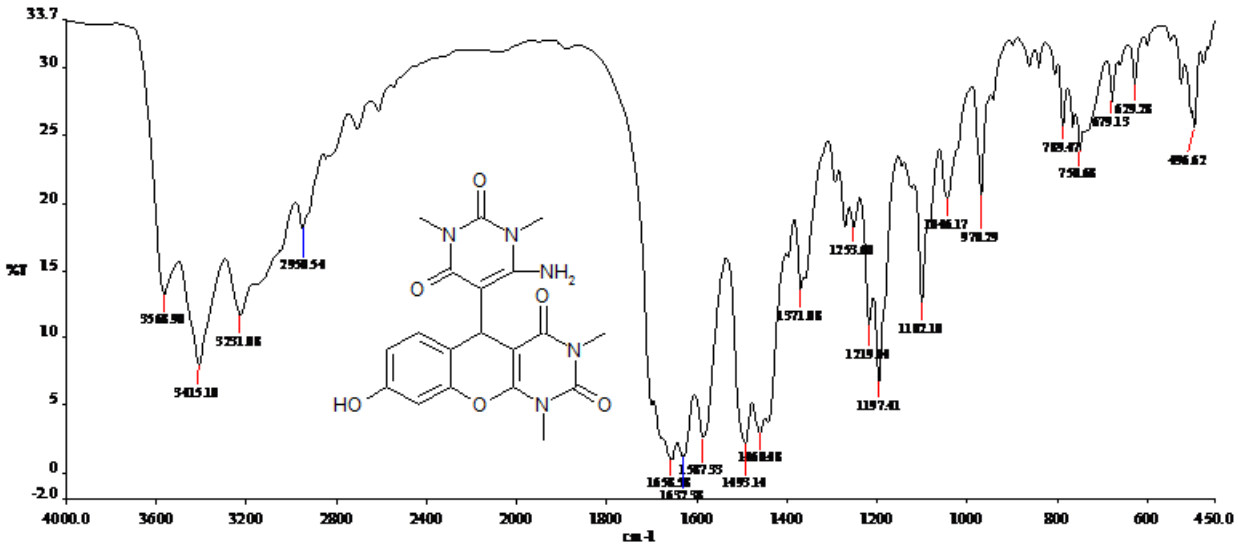
115.13
112.94
102.52
90.93
88.03
30.34
29.26
28.60
28.00
27.37
O
N
N
NH2
O
O
N
HO
O
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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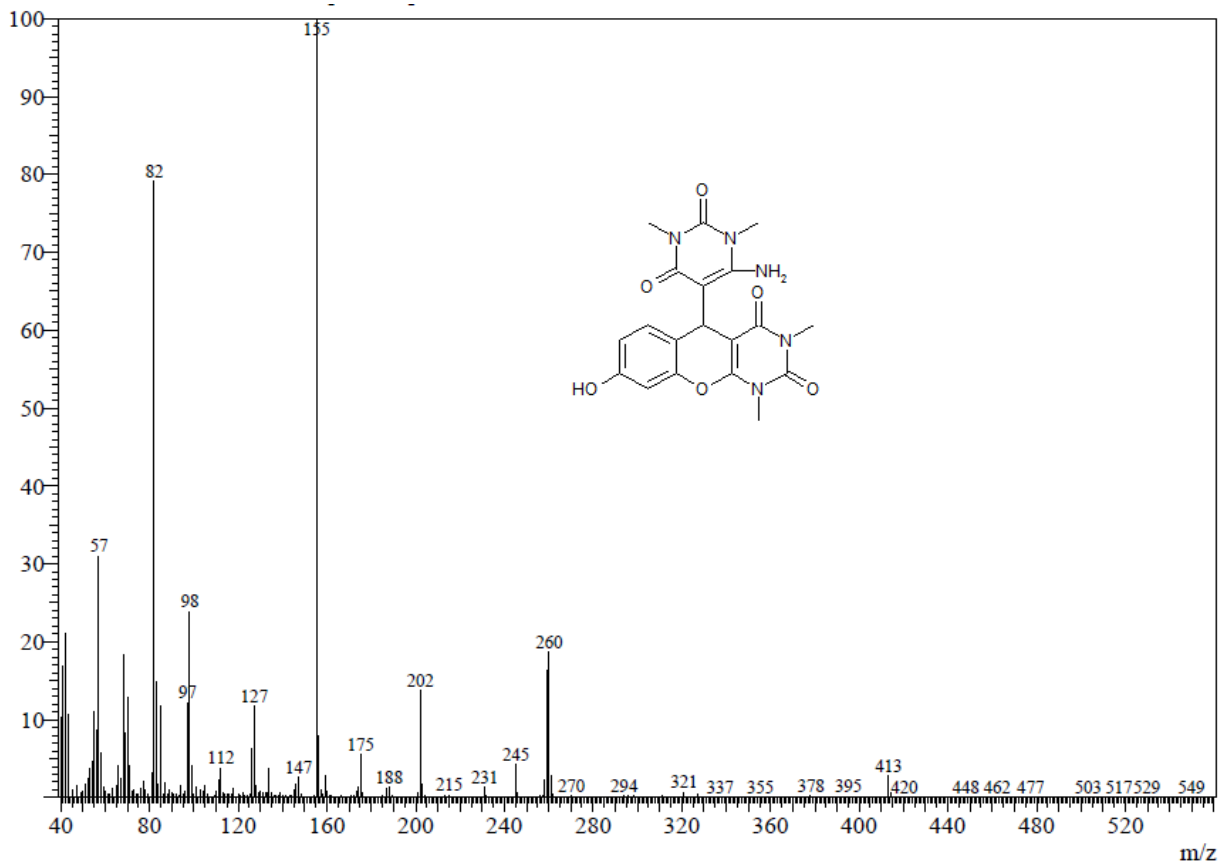
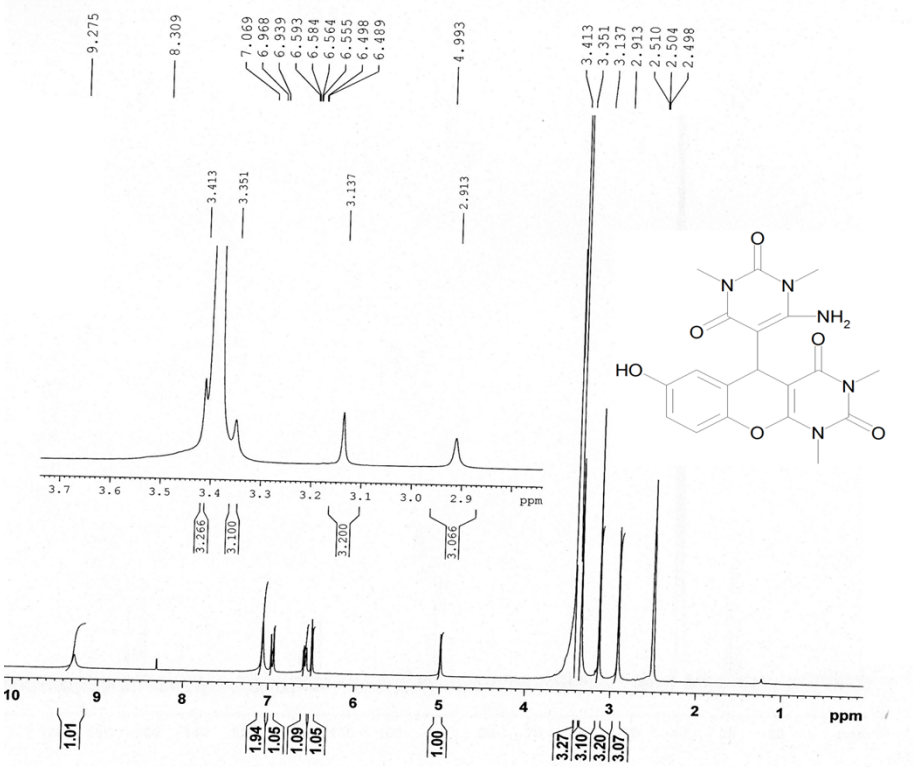
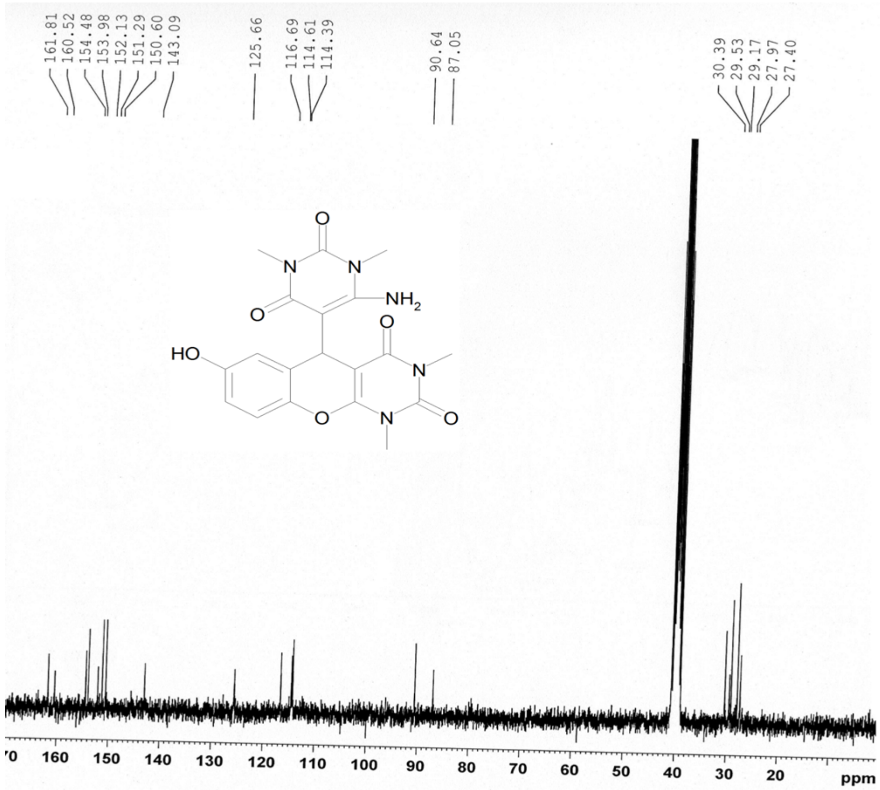
33.7
30
25
20
15
10
5
0
-2.0
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 450.0
cm-1
O
N
N
NH2
O
O
N
HO
O
N
O



Entry f, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-hydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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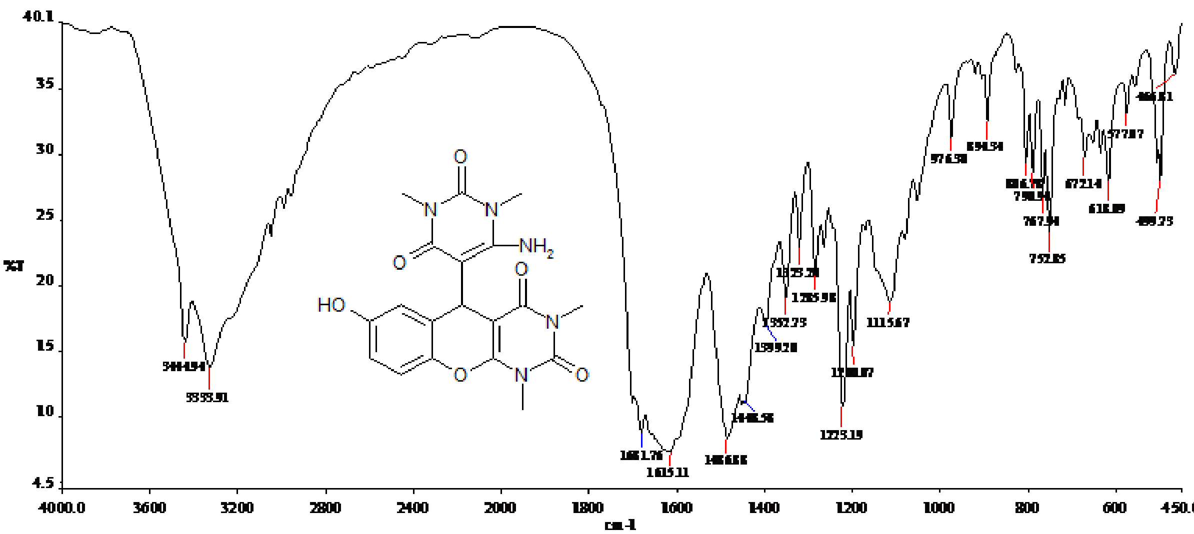
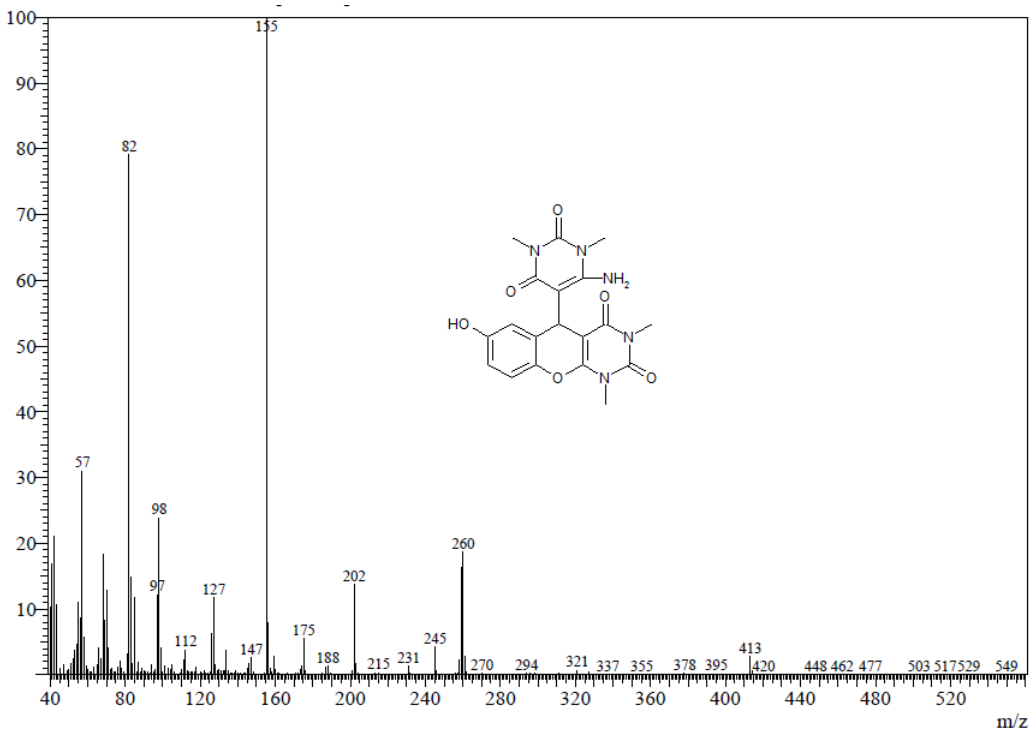
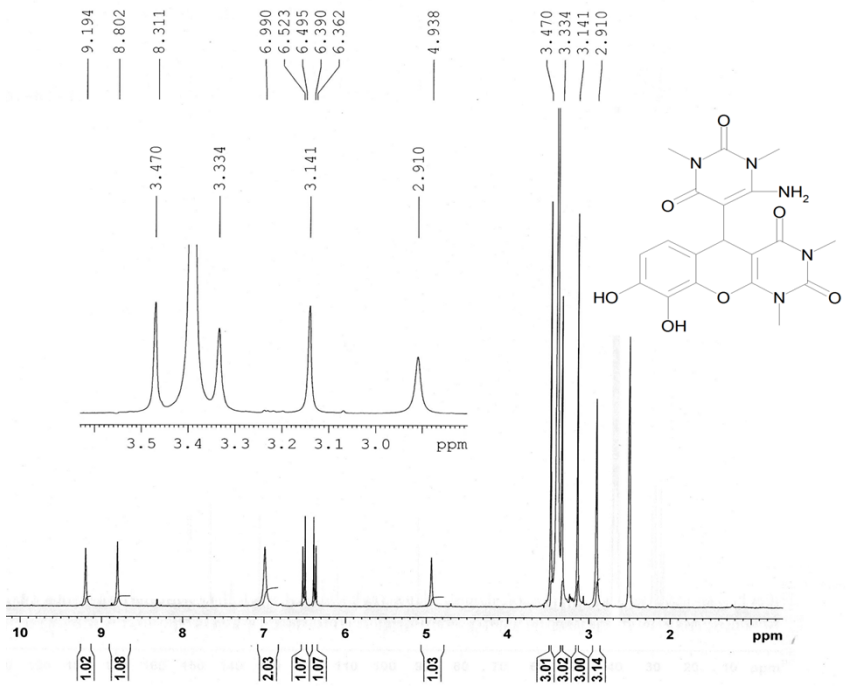
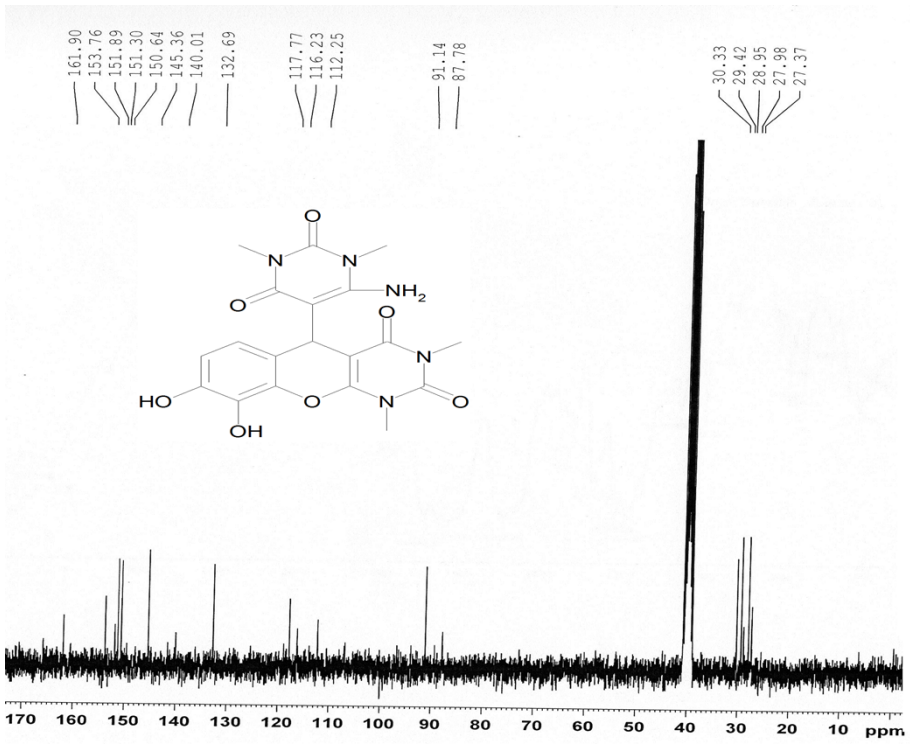
160.52
154.48
153.98
152.13
151.29
150.60
143.09
125.66
116.69
114.61
114.39
90.64
87.05
30.39
29.53
29.17
27.97
27.40
HO
O
N
NH2
ppm


%T
cm-1
HO
O
N
NH2



Entry g, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-8,9-dihydroxy-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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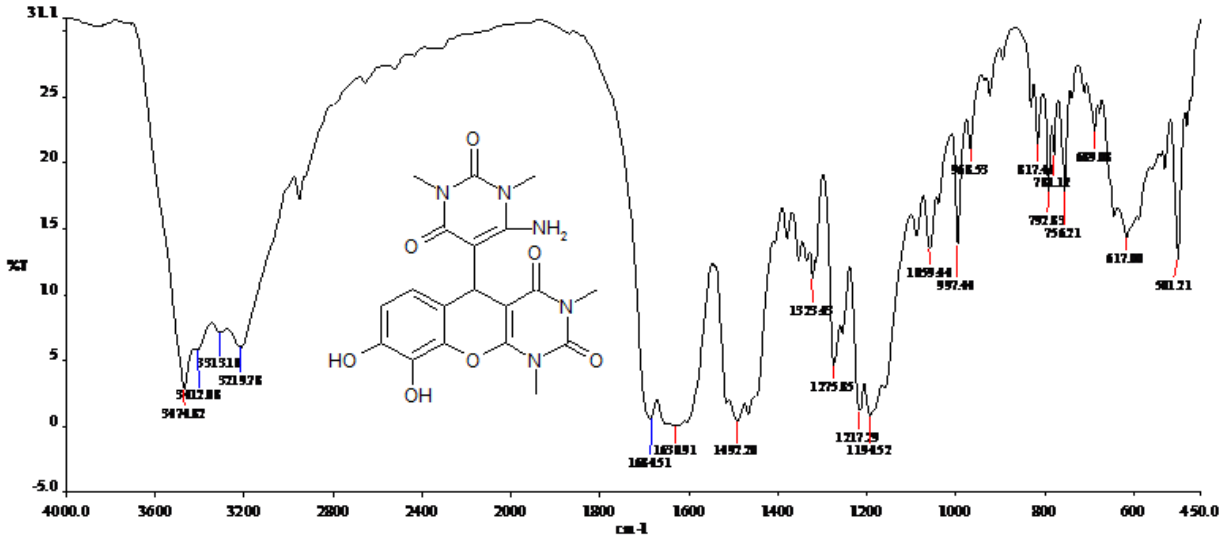
153.76
151.89
151.30
150.64
145.36
140.01
132.69
117.77
116.23
112.25
91.14
87.78
30.33
29.42
28.95
27.98
27.37
O
N
N
NH2
O
O
N
HO
O
N
O
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


%T
31.1
25
20
15
10
5
0
-5.0
4000.0
3600
3200
2800
2400
2000
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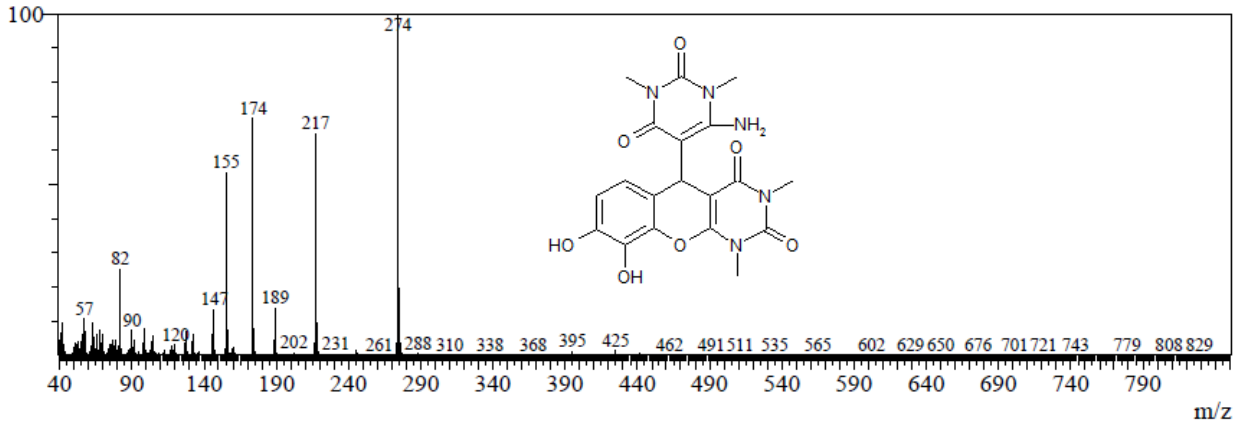
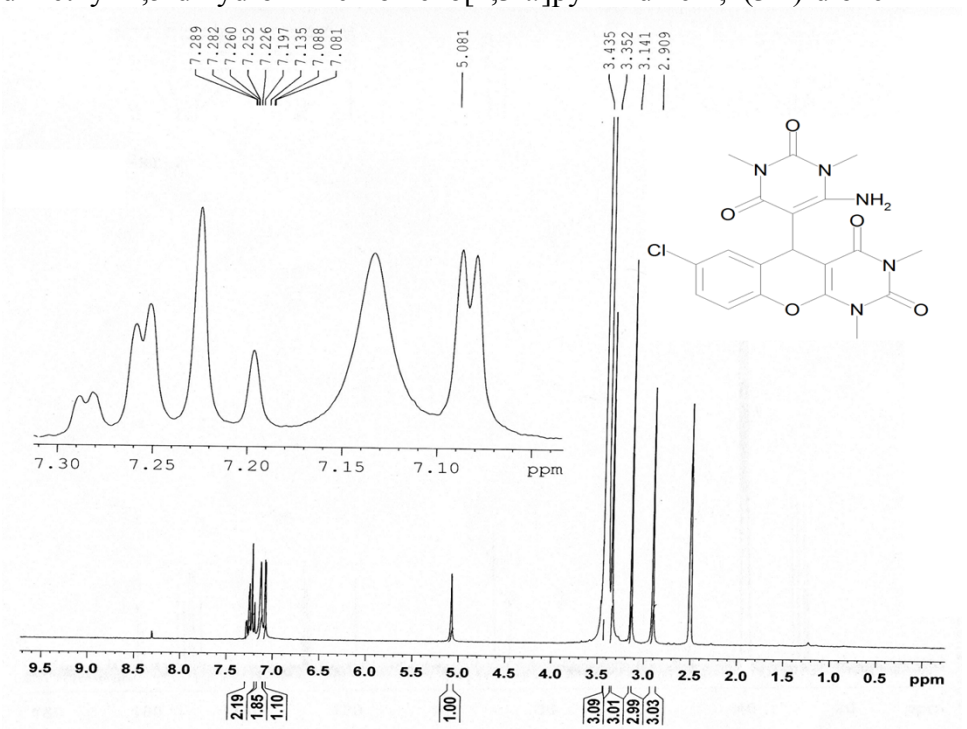
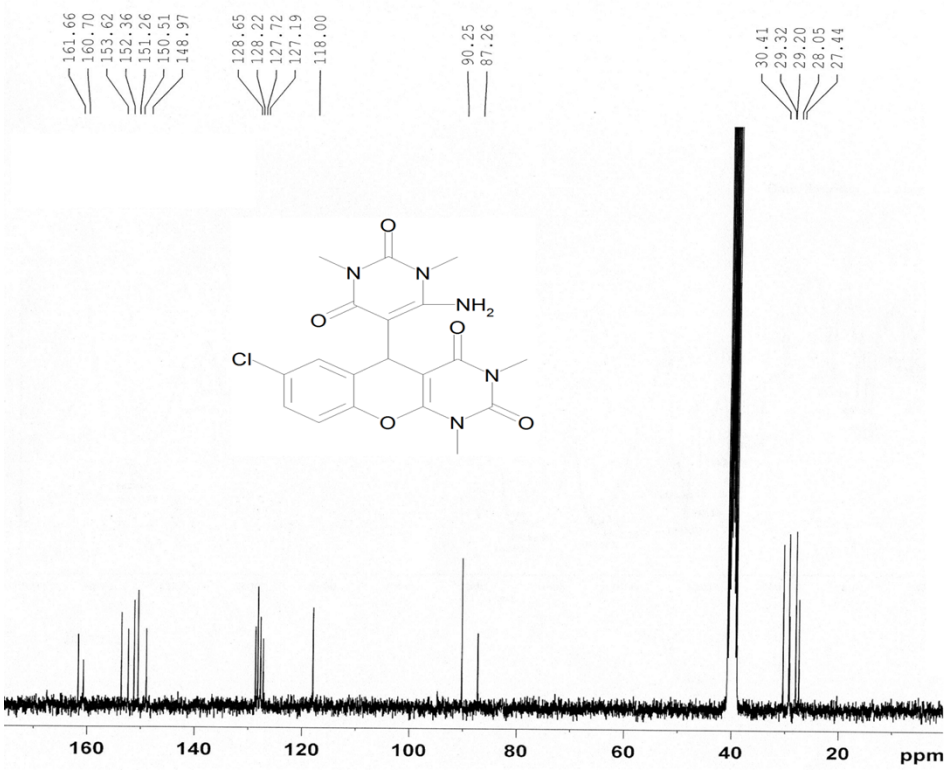
1600
1400
1200
1000
800
600
450.0
cm-1
O
N
N
NH2
O
O
N
HO
O
N
O
OH



Entry h, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-chloro-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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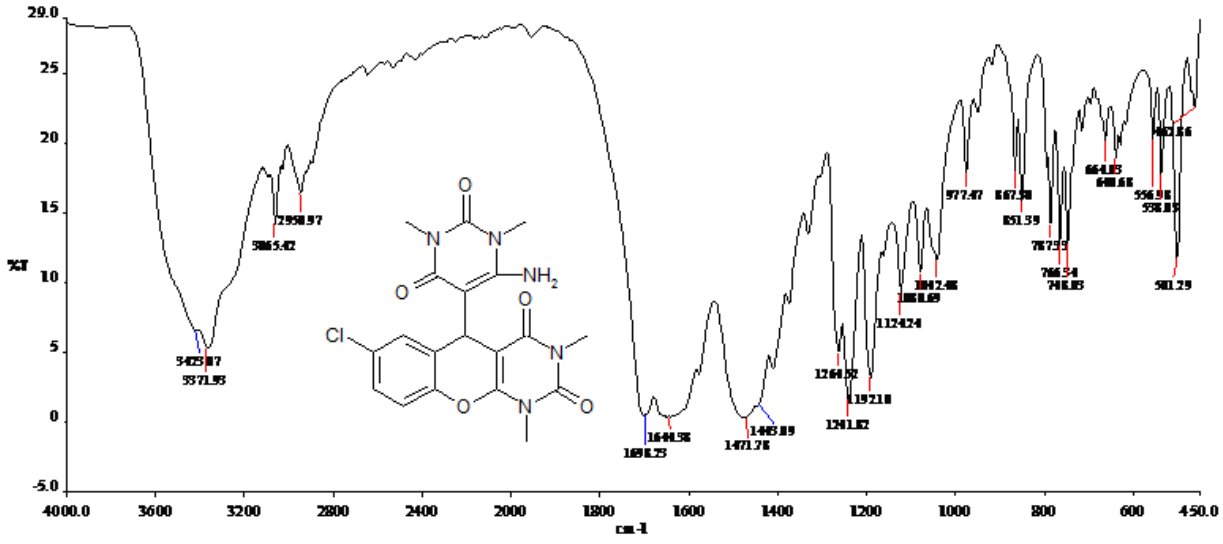
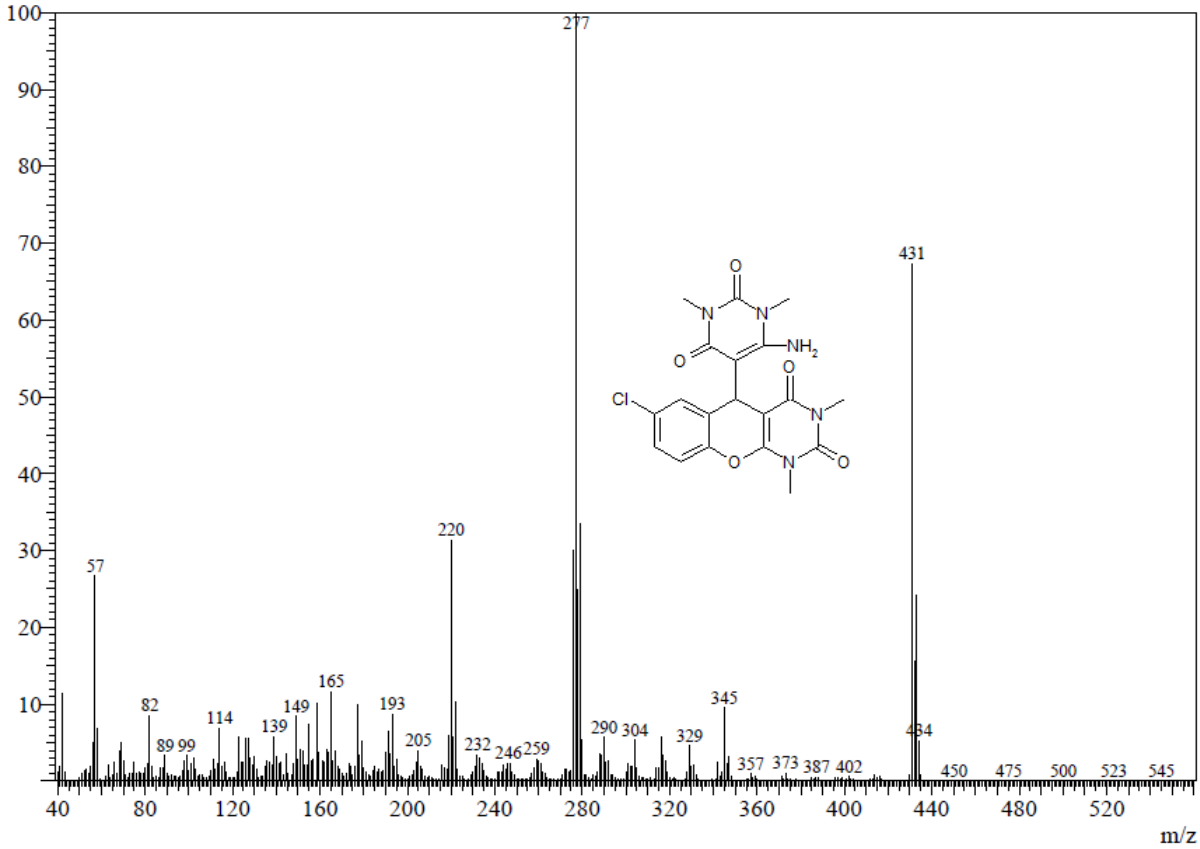
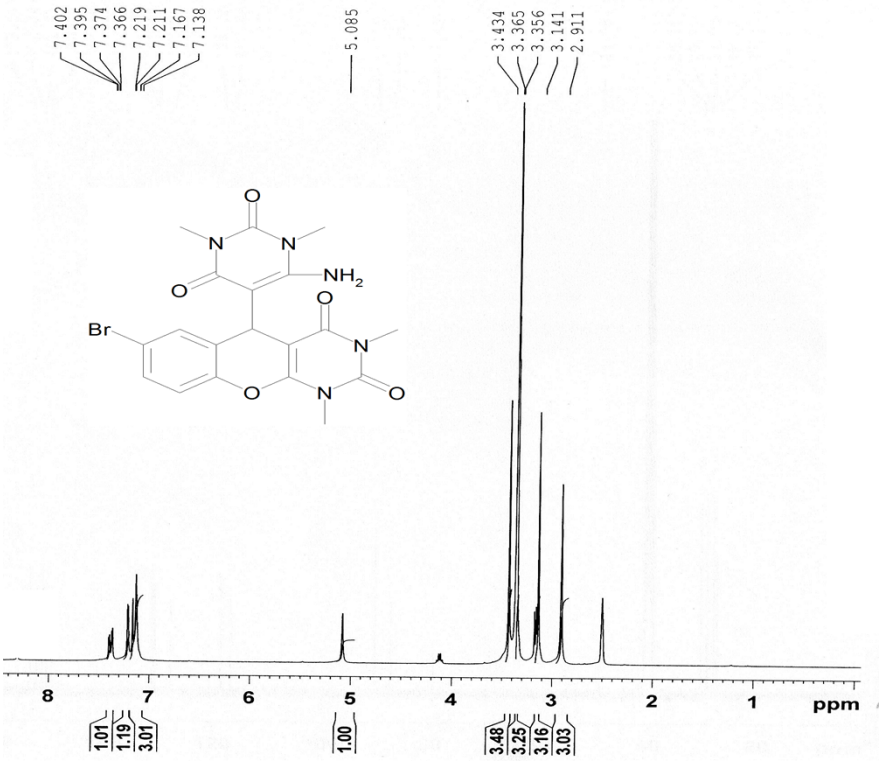
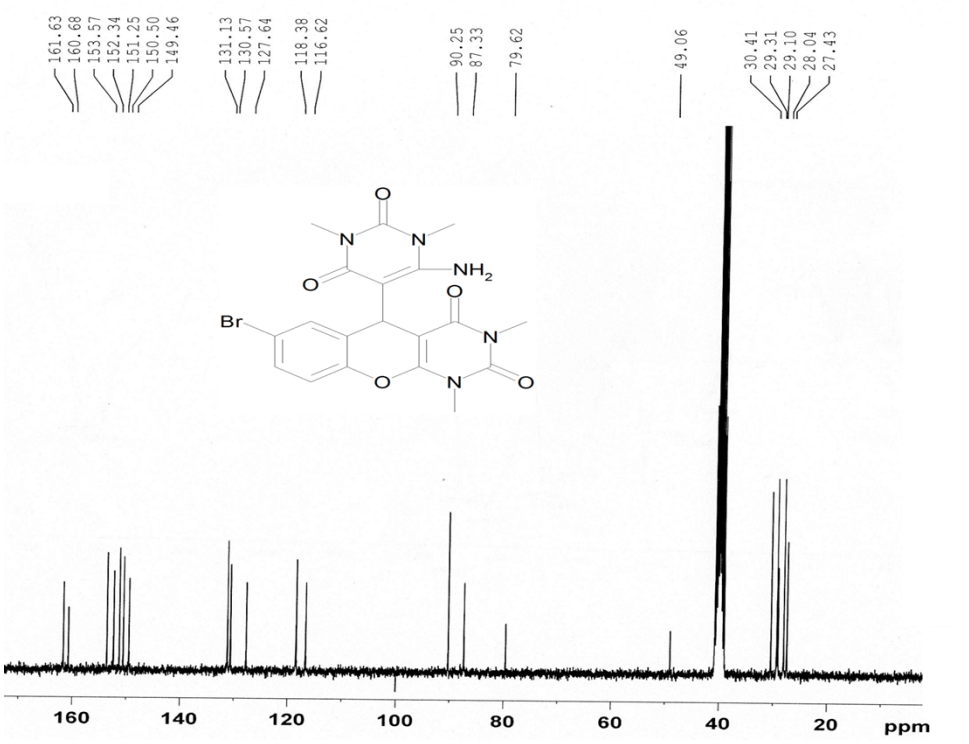
160.70
153.62
152.36
151.26
150.51
148.97
128.65
128.22
127.72
127.19
118.00
90.25
87.26
30.41
29.32
29.20
28.05
27.44
O
N
N
NH2
O
O
Cl
N
O
N
O
160
140
120
100
80
60
40
20
ppm


29.0
25
20
15
10
5
0
-5.0
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
O
N
N
NH2
O
O
Cl
N
O
N
O



Entry i, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7-bromo-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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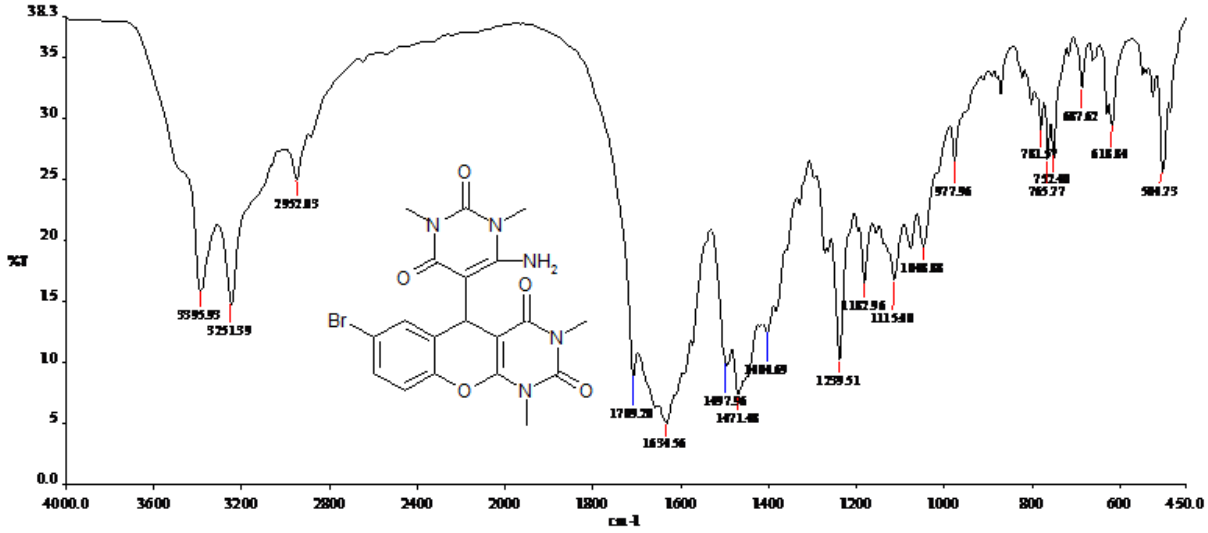
160.68
153.57
152.34
151.25
150.50
149.46
131.13
130.57
127.64
118.38
116.62
90.25
87.33
79.62
49.06
30.41
29.31
29.10
28.04
27.43
NH2
Br
160
140
120
100
80
60
40
20
ppm


%T
4000.0
3600
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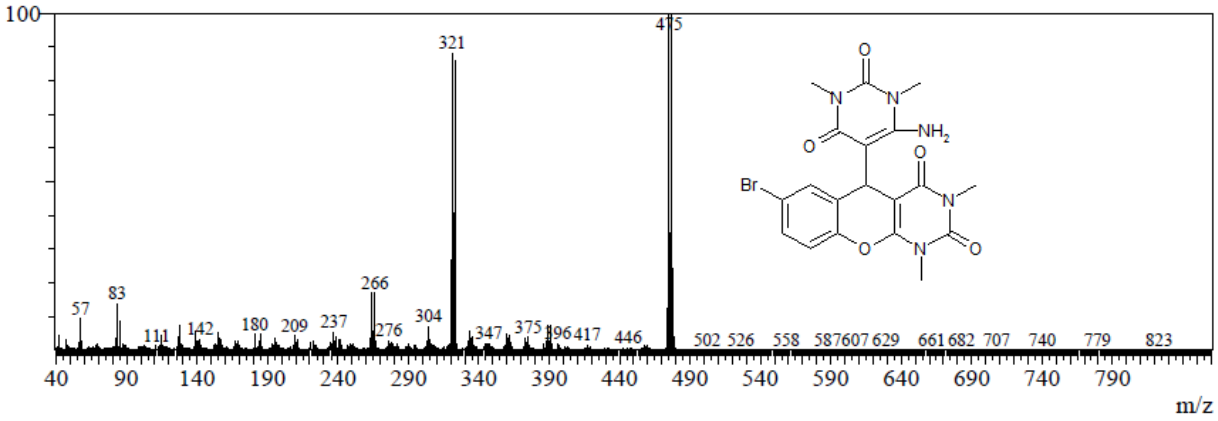
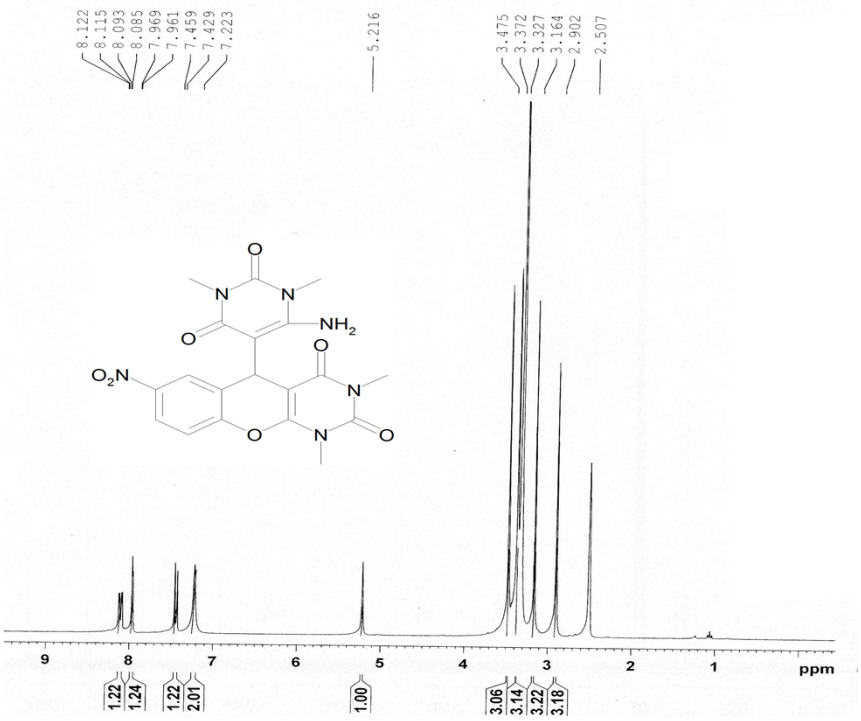
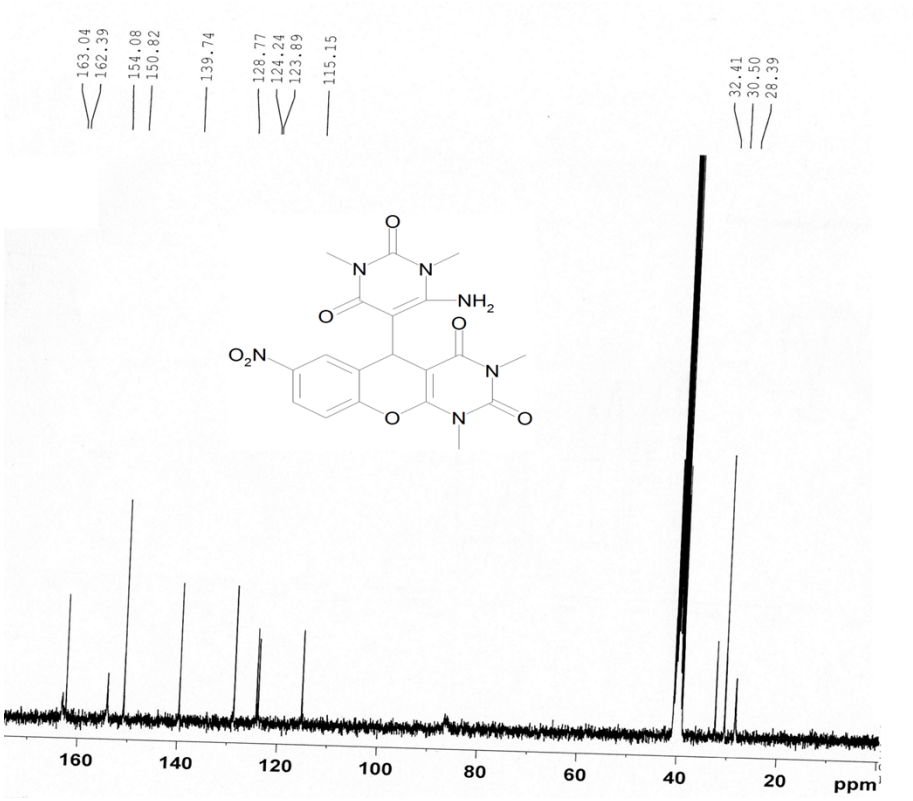
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
NH2
Br



Entry j, Table 3: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-7-nitro-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

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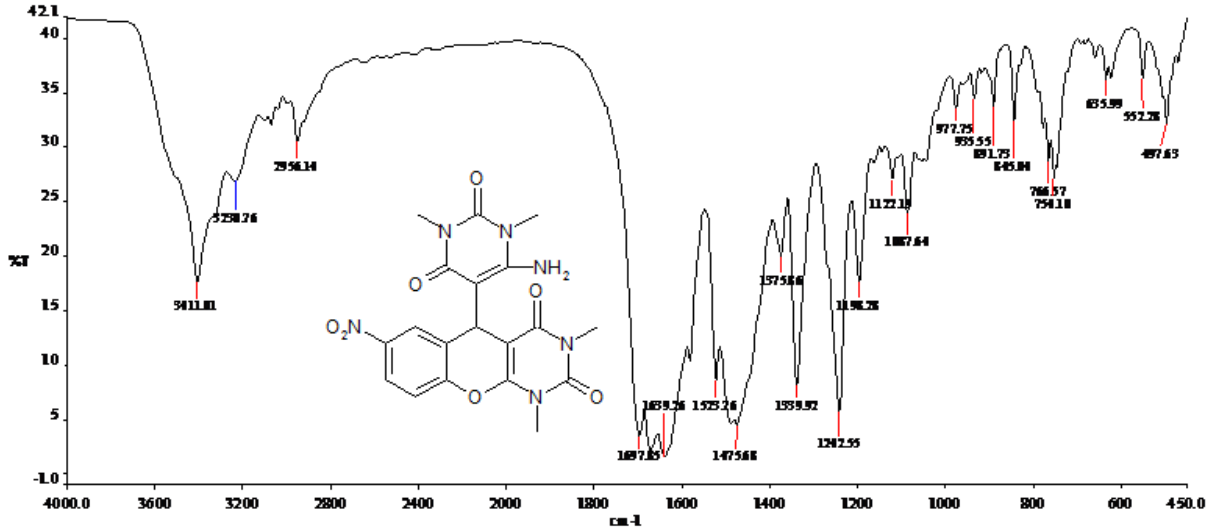
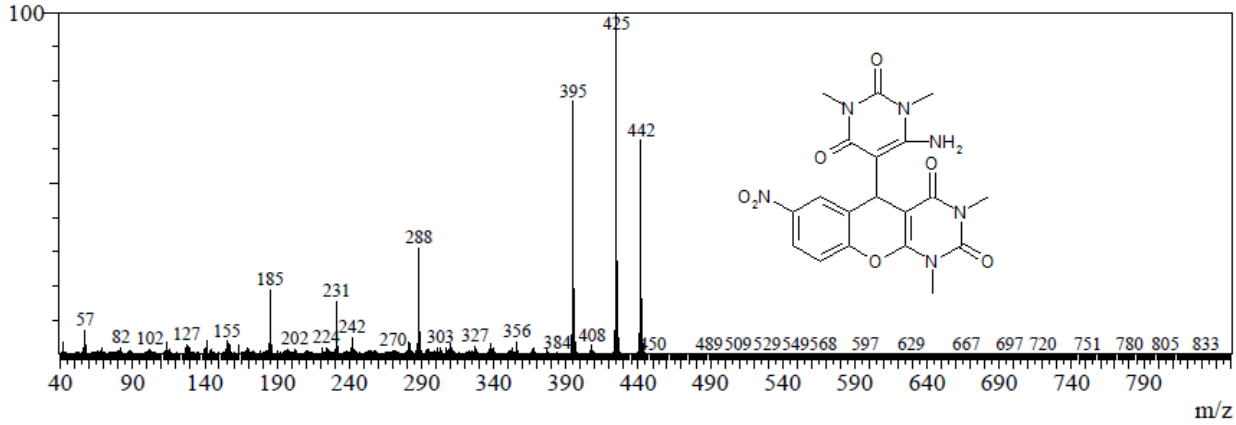
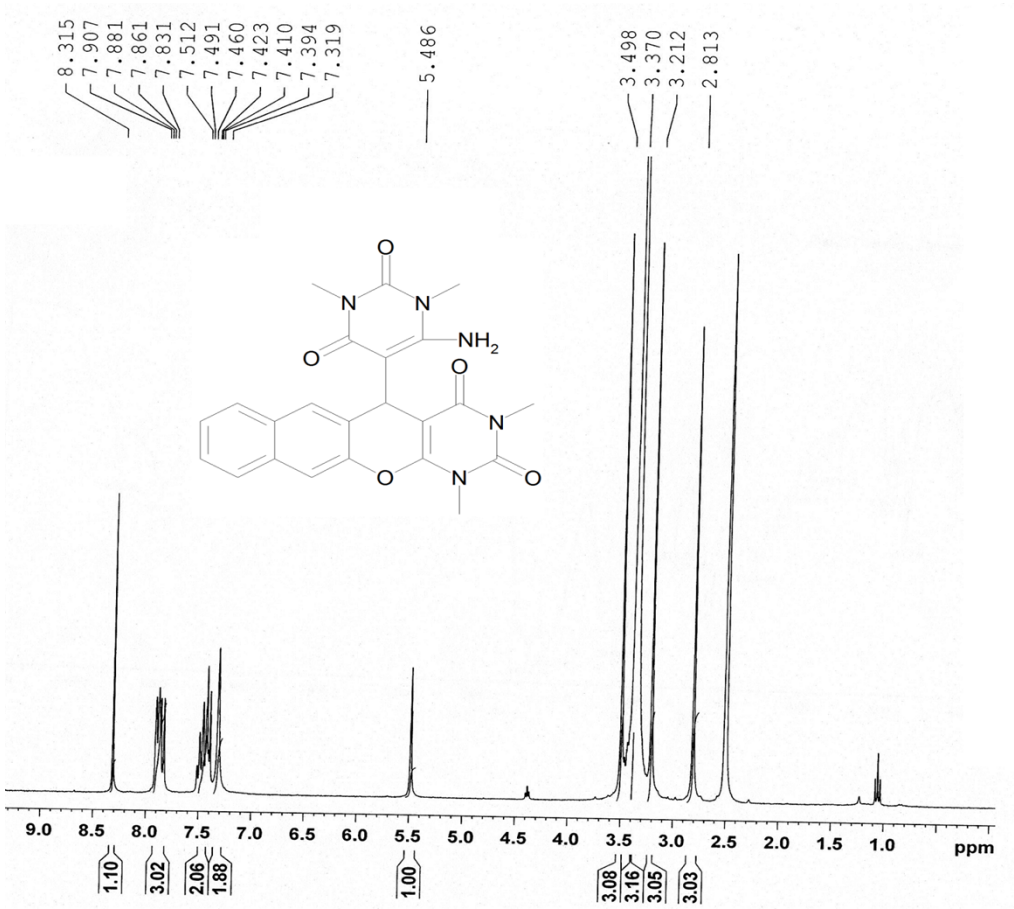
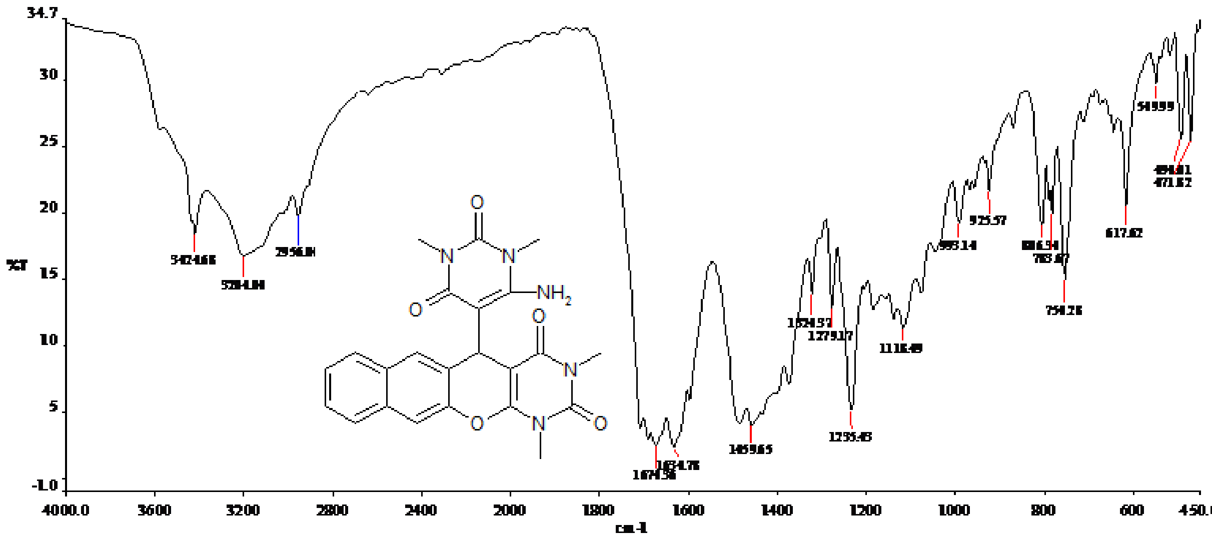
162.39
154.08
150.82
139.74
128.77
124.24
123.89
115.15
32.41
30.50
28.39
O
N
N
O
NH2
O2N
O
N
O
N
O
160
140
120
100
80
60
40
20
ppm


%T
42.1
40
35
30
25
20
15
10
5
-1.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
O
N
N
O
NH2
O2N
O
N
O
N
O

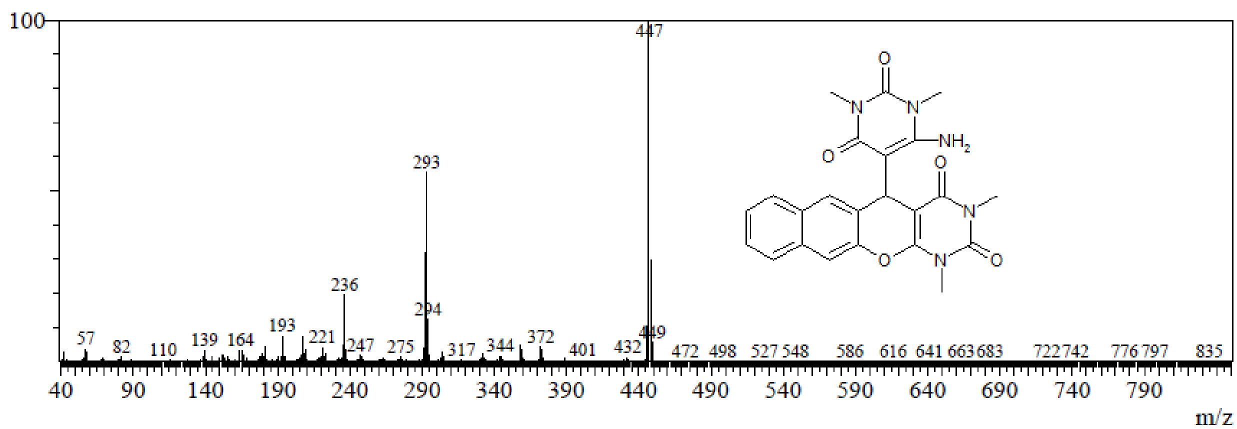


Entry k, Table 3:





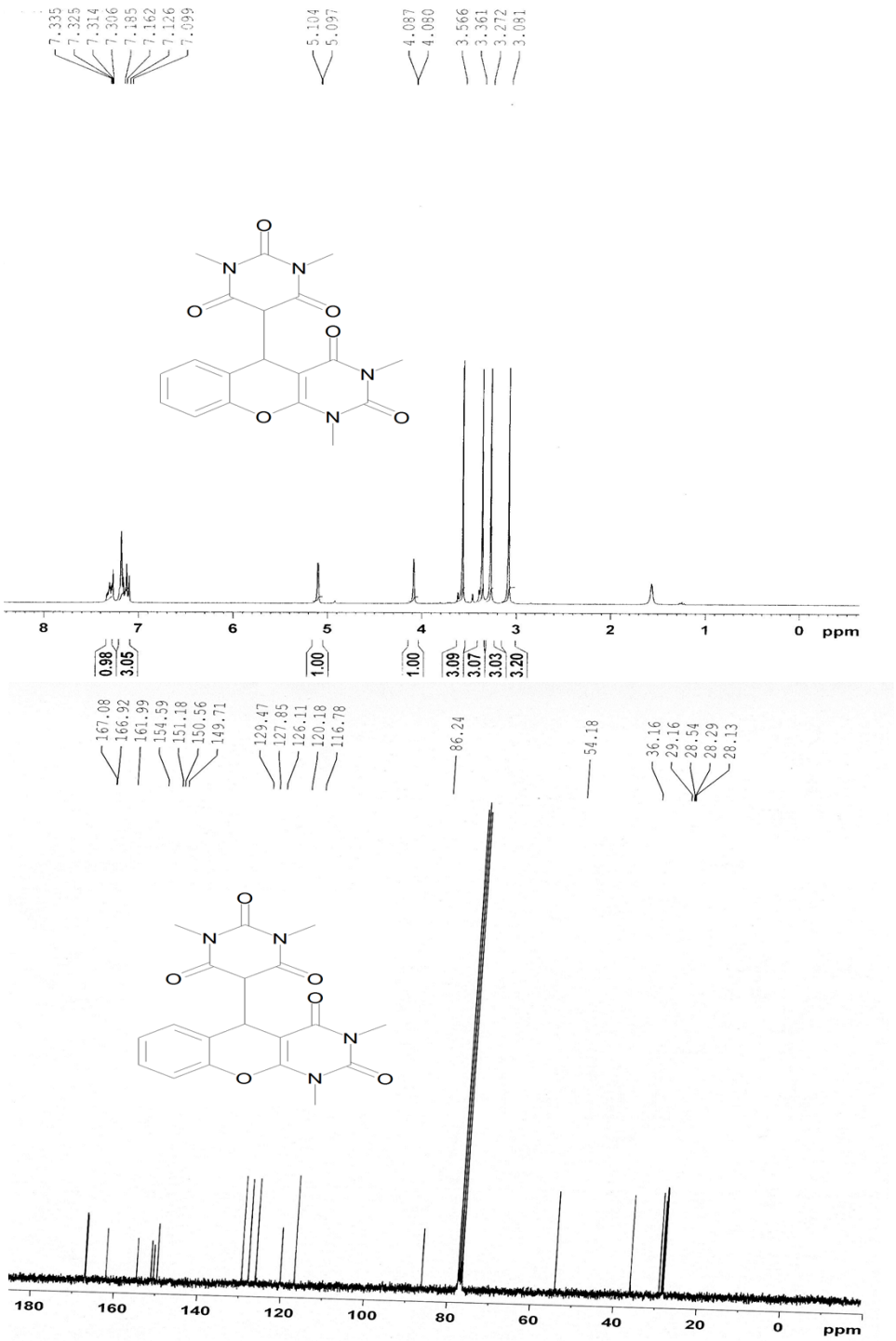
34.7
30
25
20
15
10
5
-1.0
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
1459.65
1235.43
1118.49
925.57
750.28
617.02
O
N
N
NH2
O
O
N
O
N
O
O

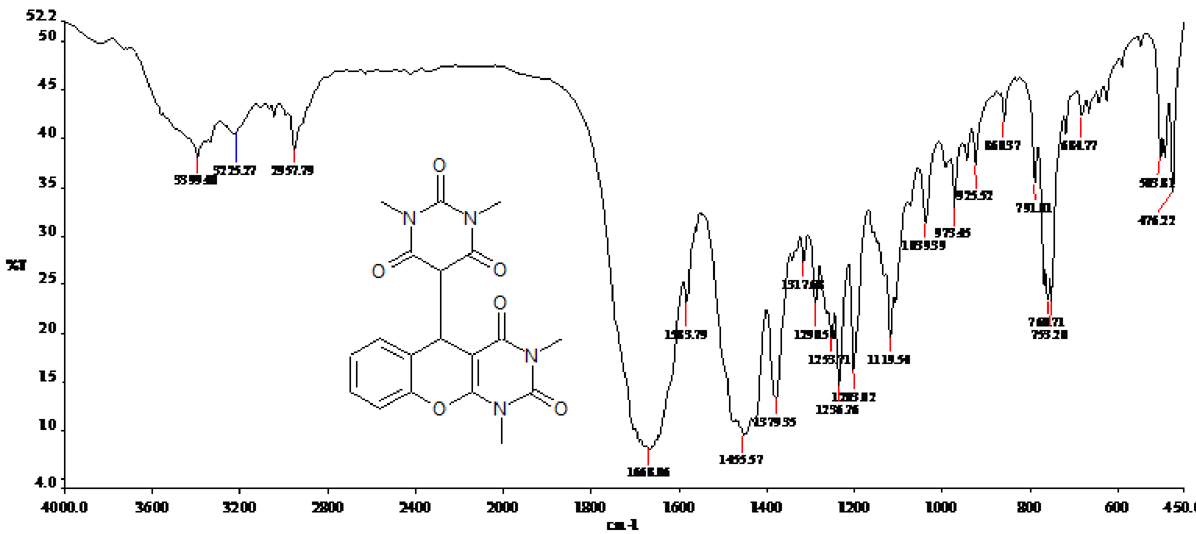


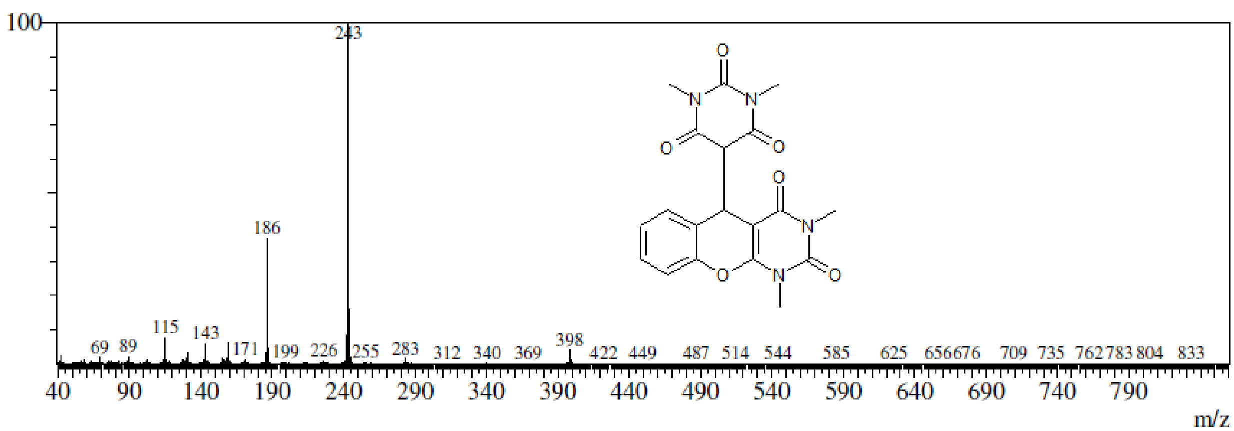
100
447
293
236
294
193
57
82
110
139
164
221
247
275
317
344
372
401
432
449
472
498
527
548
586
616
641
663
683
722
742
776
797
835
40
90
140
190
240
290
340
390
440
490
540
590
640
690
740
790
m/z
O
N
N
NH2
O
O
N
O
N
O
O

^{1}H NMR, ^{13}C NMR, IR and MS (EI) spectra of Synthesized Pyranopyrimidinetrione products

Entry a, Table 4: 5-(1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3 *d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione

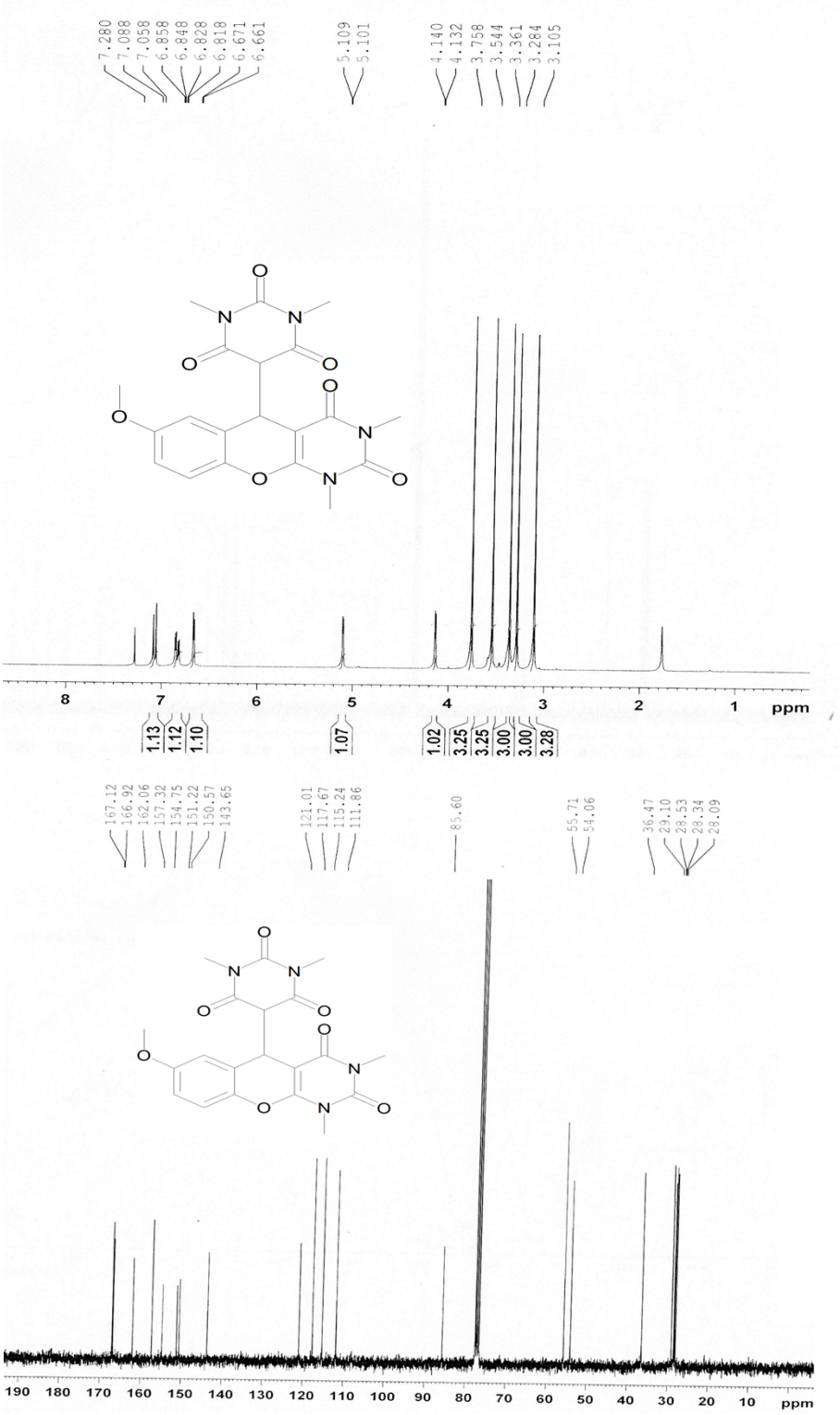


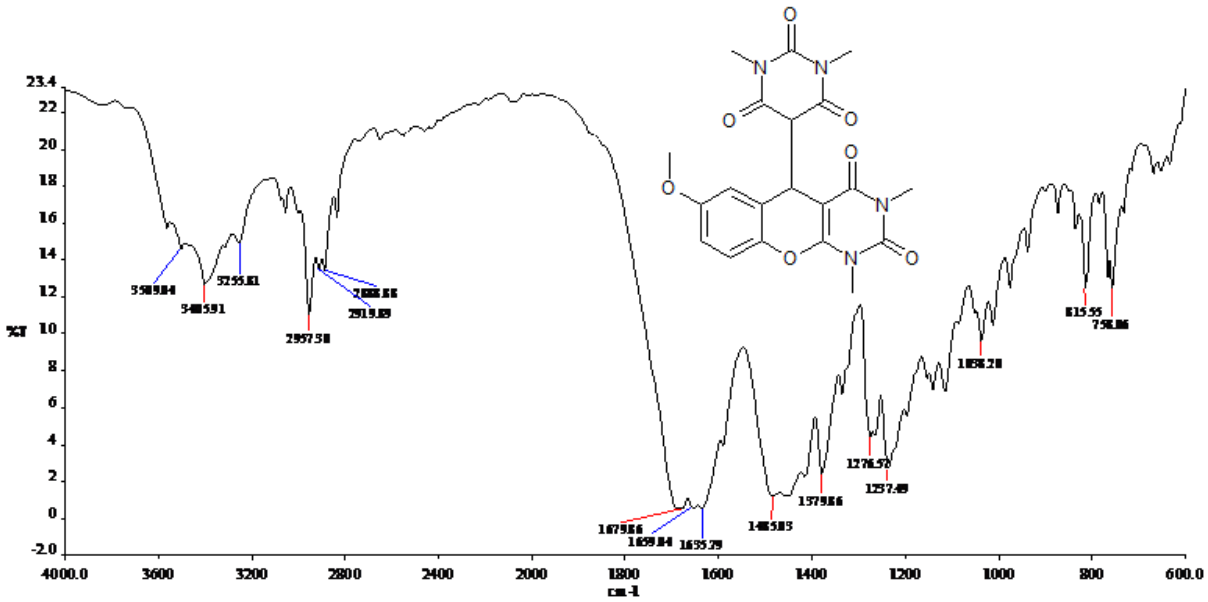




100
243
186
115
143
171
69
89
199
226
255
283
312
340
369
398
422
449
487
514
544
585
625
656676
709
735
762783
804
833
40
90
140
190
240
290
340
390
440
490
540
590
640
690
740
790
m/z

Entry b, Table 4: 5-(7-methoxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione

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cm-1
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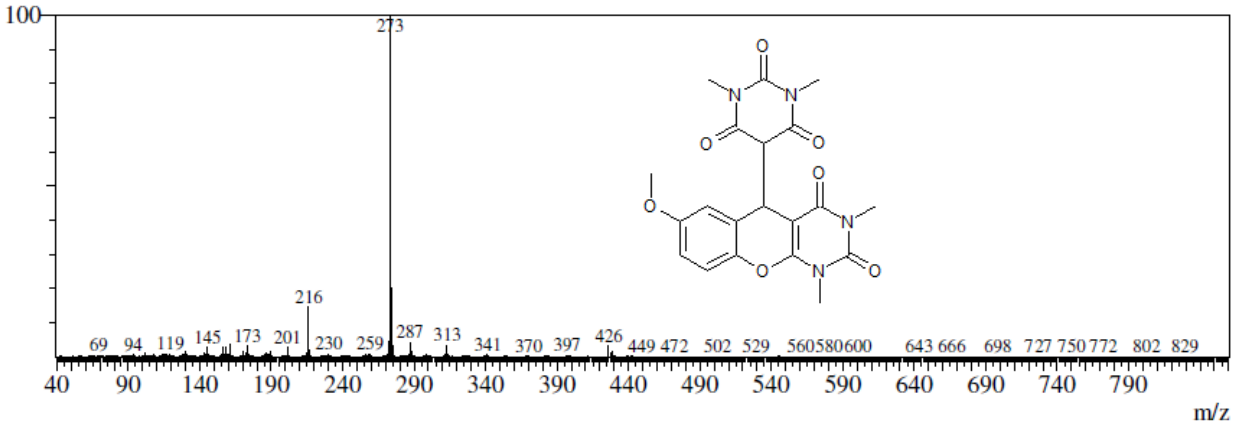
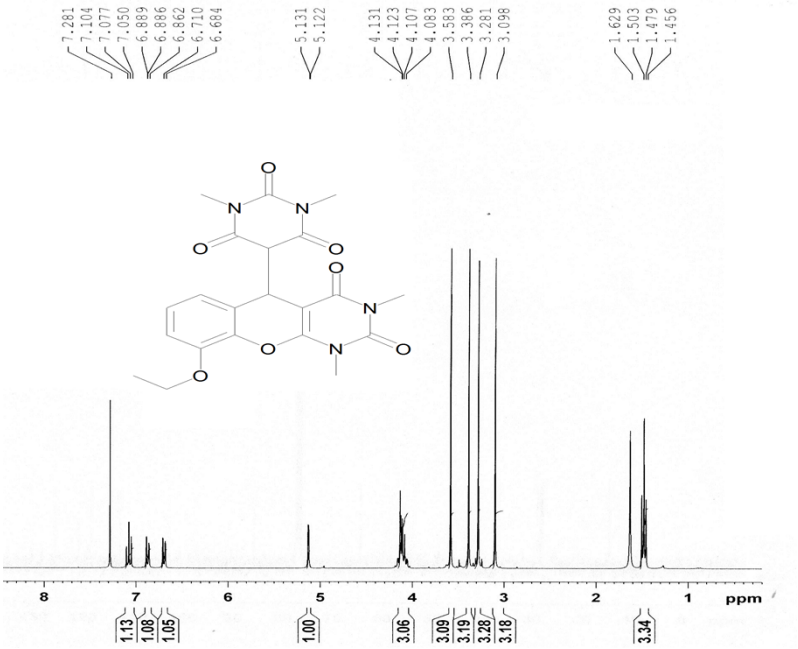
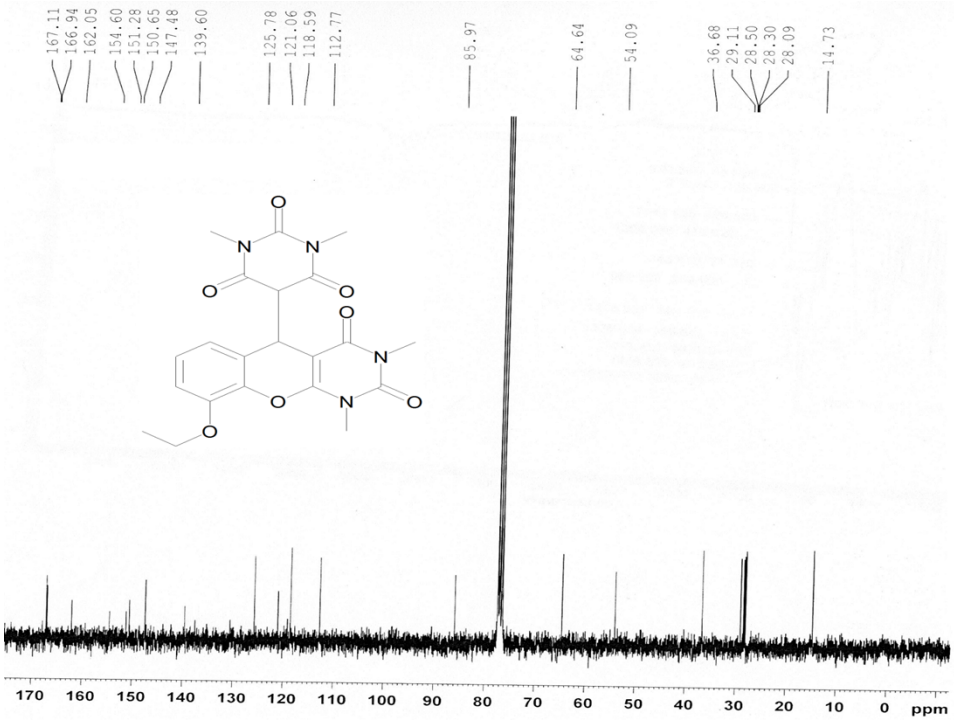
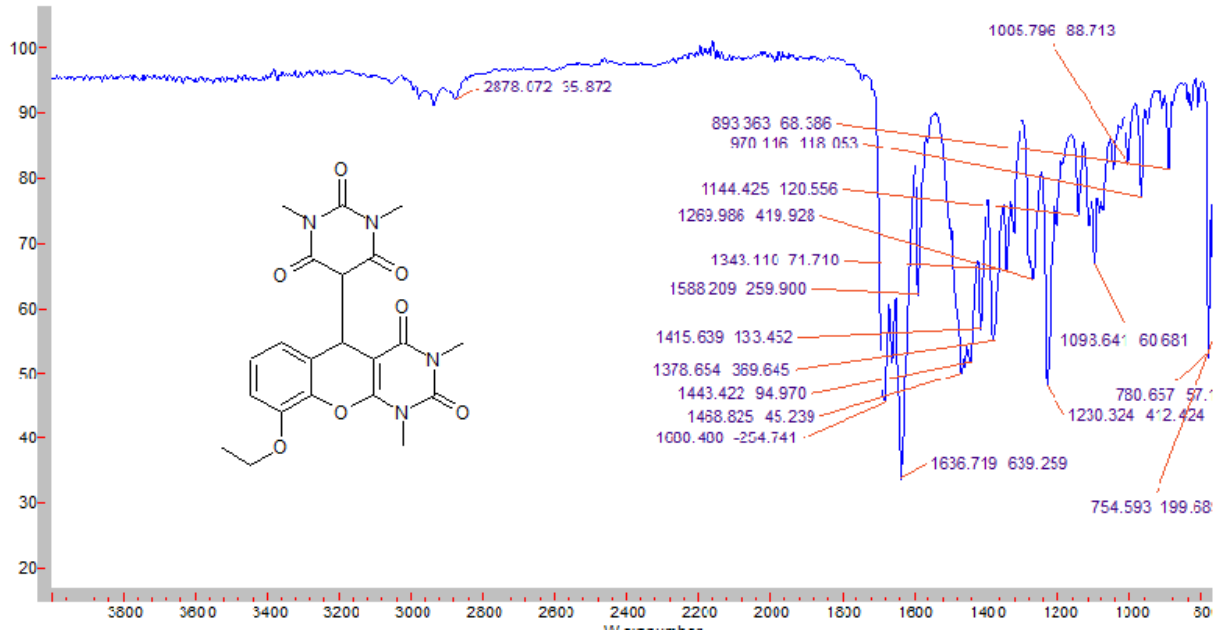
2000
1800
1600
1400
1200
1000
800
600.0


100
273
216
69 94 119 145 173 201 230 259 287 313 341 370 397 426 449 472 502 529 560580600 643 666 698 727 750 772 802 829
40 90 140 190 240 290 340 390 440 490 540 590 640 690 740 790
m/z

Entry c, Table 4: 5-(7-ethoxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



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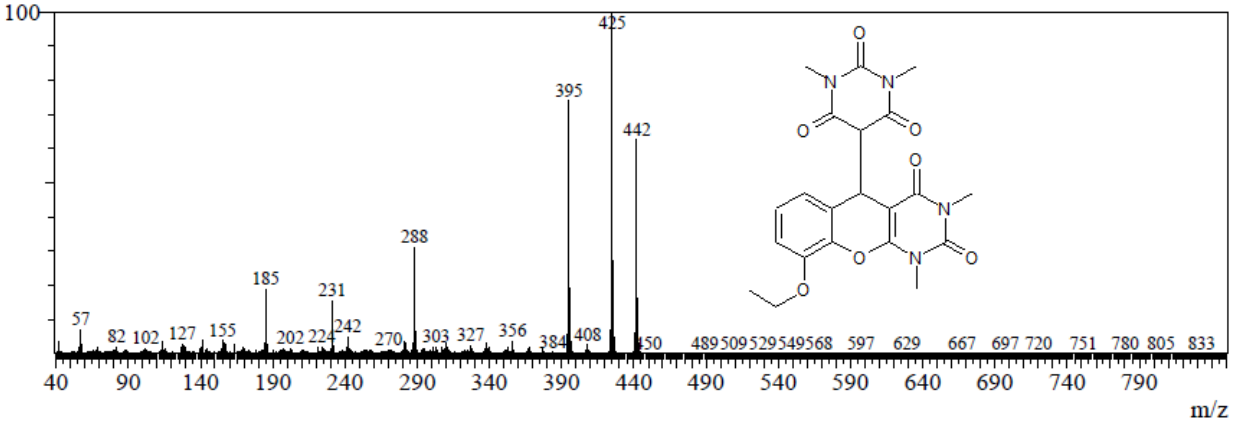
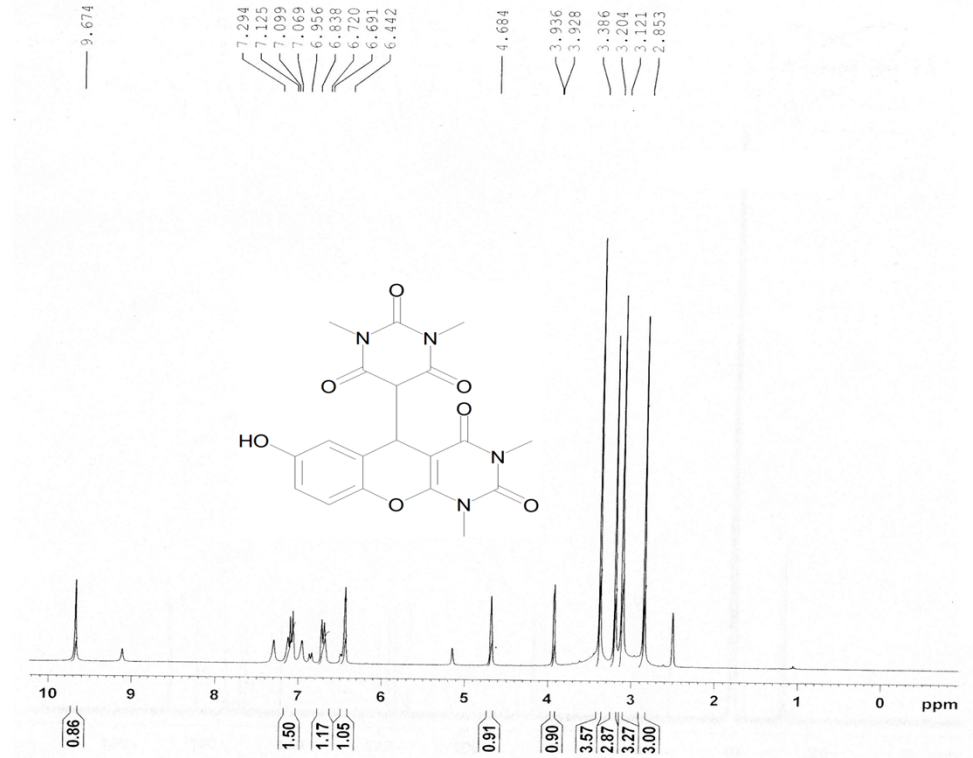
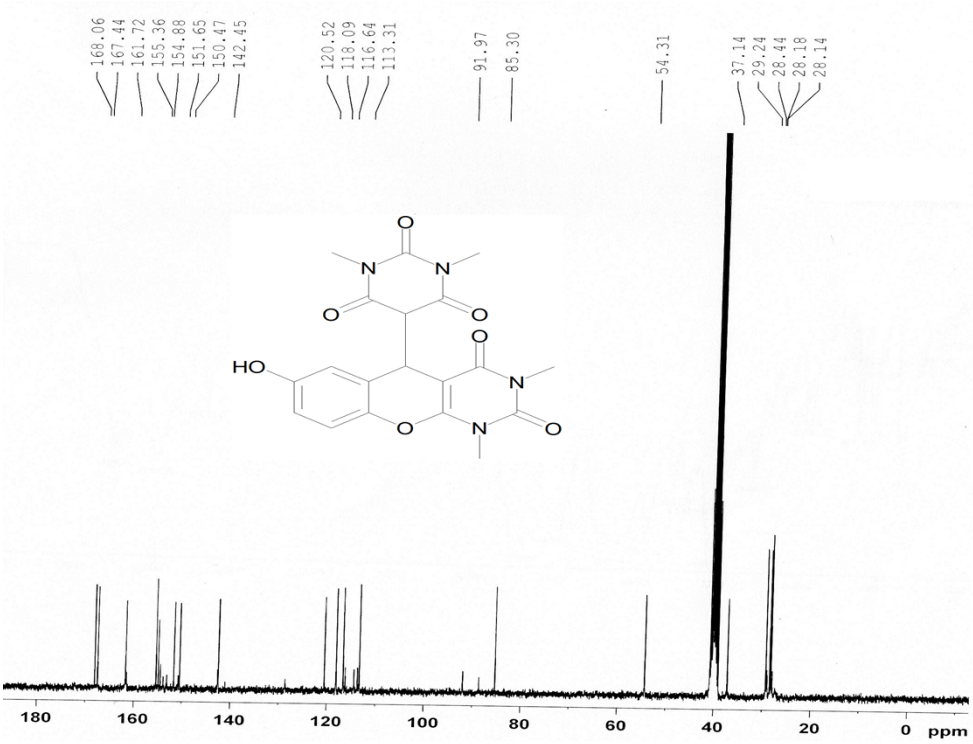
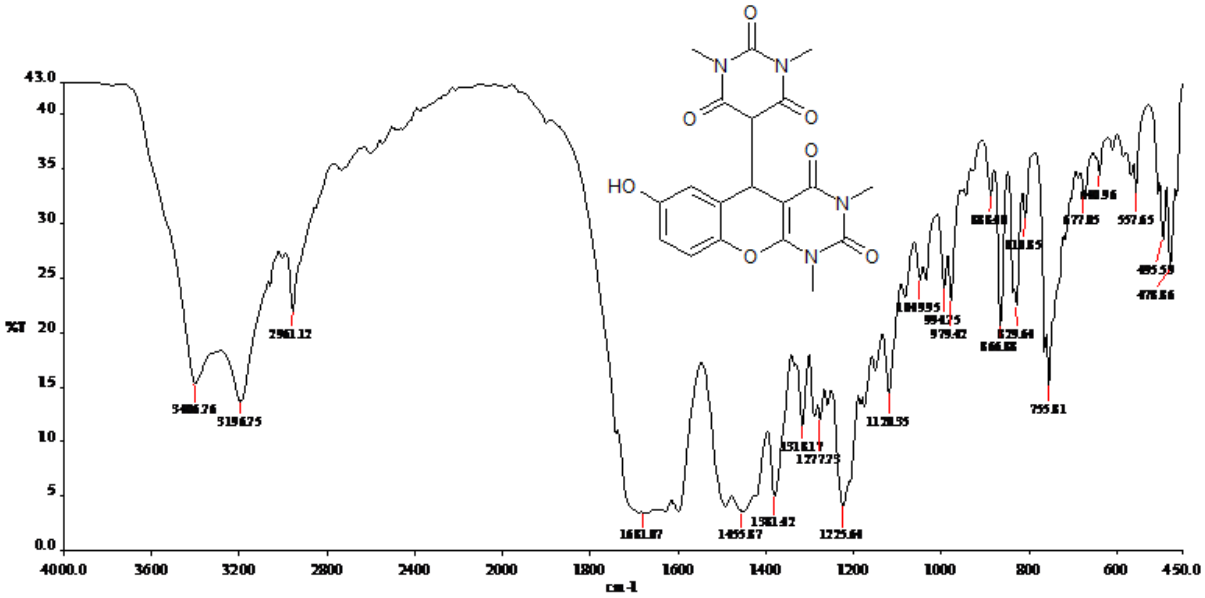
2878.072 35.872
893.363 68.386
970.116 118.053
1144.425 120.556
1269.986 419.928
1343.110 71.710
1588.209 259.900
1415.639 133.452
1378.654 389.645
1443.422 94.970
1458.825 45.239
1600.400 -254.741
1636.719 639.259
1093.64 60.681
1230.324 42.424
780.657
754.593 199.68
100
90
80
70
60
50
40
30
20
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 80


100
425
395
442
288
185
231
57
82 102 127 155 202 224 242 270 303 327 356 384 408 450 489 509 529 549 568 597 629 667 697 720 751 780 805 833
40 90 140 190 240 290 340 390 440 490 540 590 640 690 740 790
m/z

Entry d, Table 4: 5-(7-hydroxy-1,3-dimethyl-2,4-dioxo-1,3,4,5-tetrahydro-2*H*-chromeno[2,3-*d*]pyrimidin-5-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione



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800
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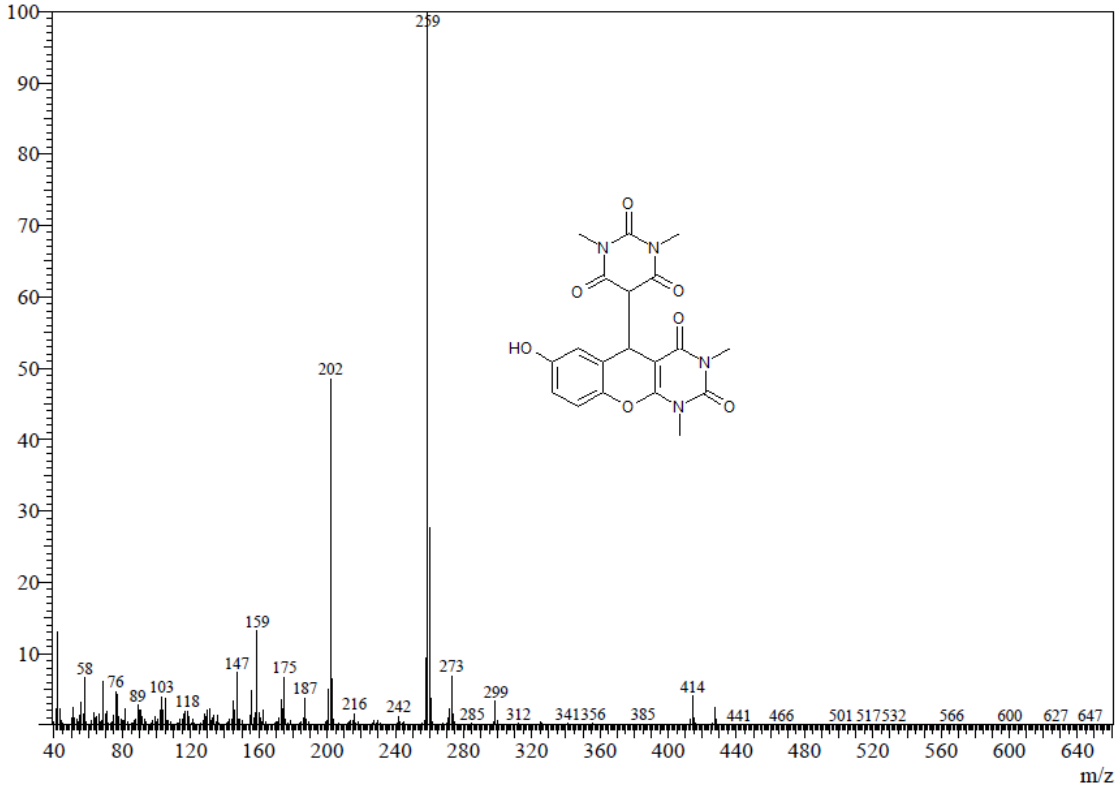
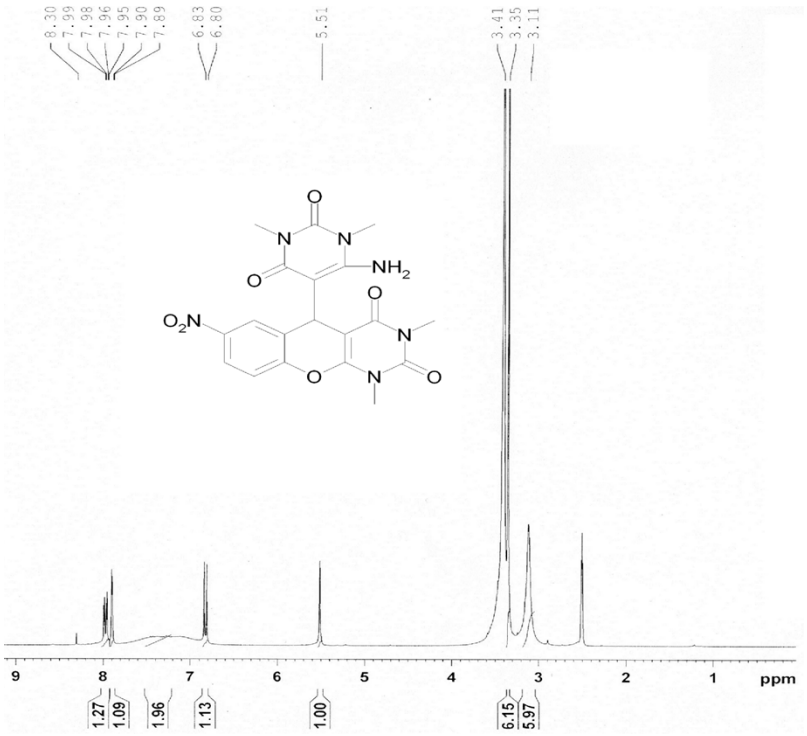
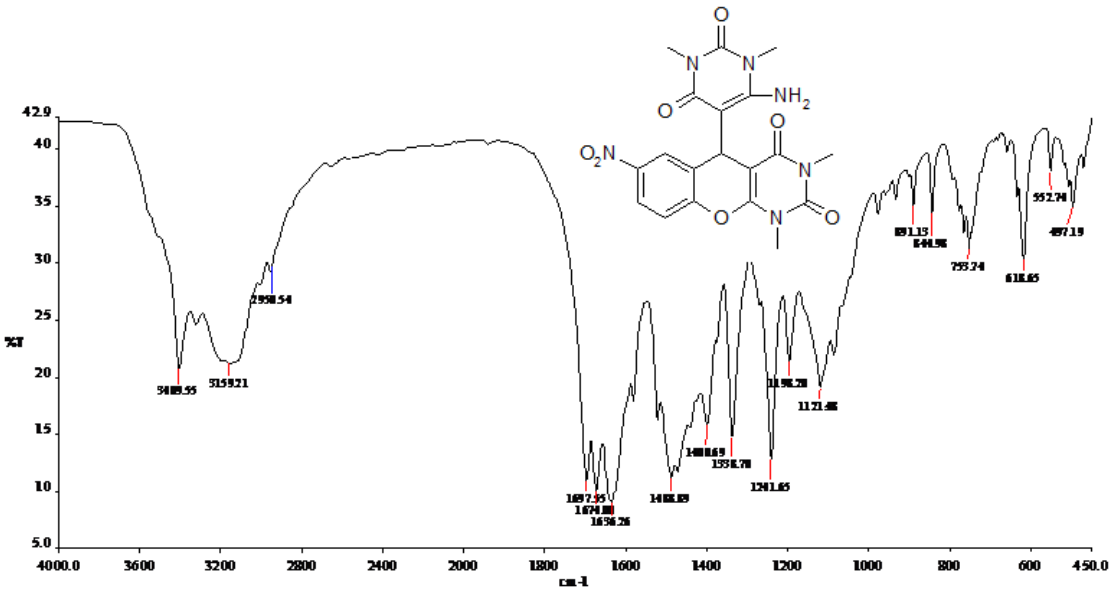
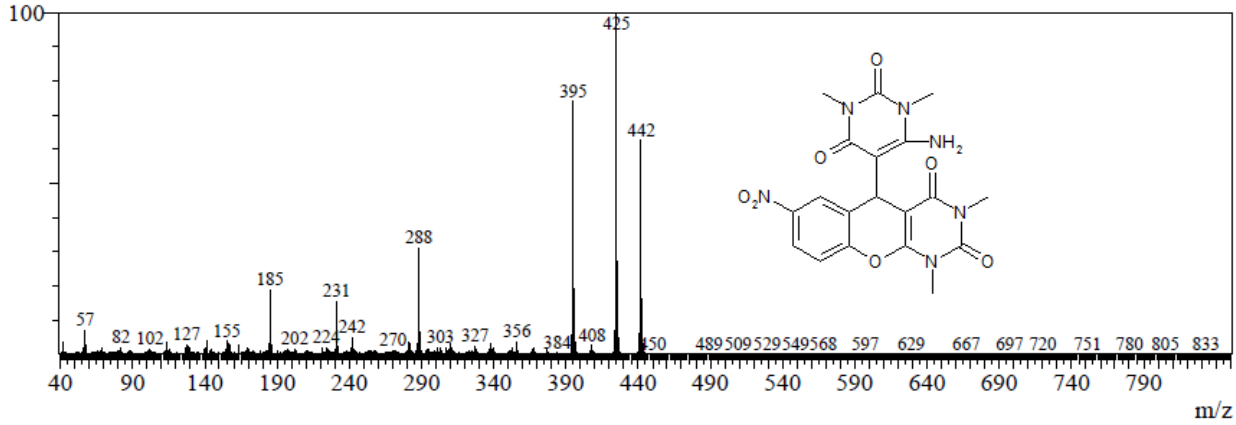
1681.87
1455.87
1225.64
755.81
HO


m/z
259
202
159
147
58
76
89
103
118
175
187
216
242
273
299
285
312
341
356
385
414
441
466
501
517
532
566
600
627
647
HO

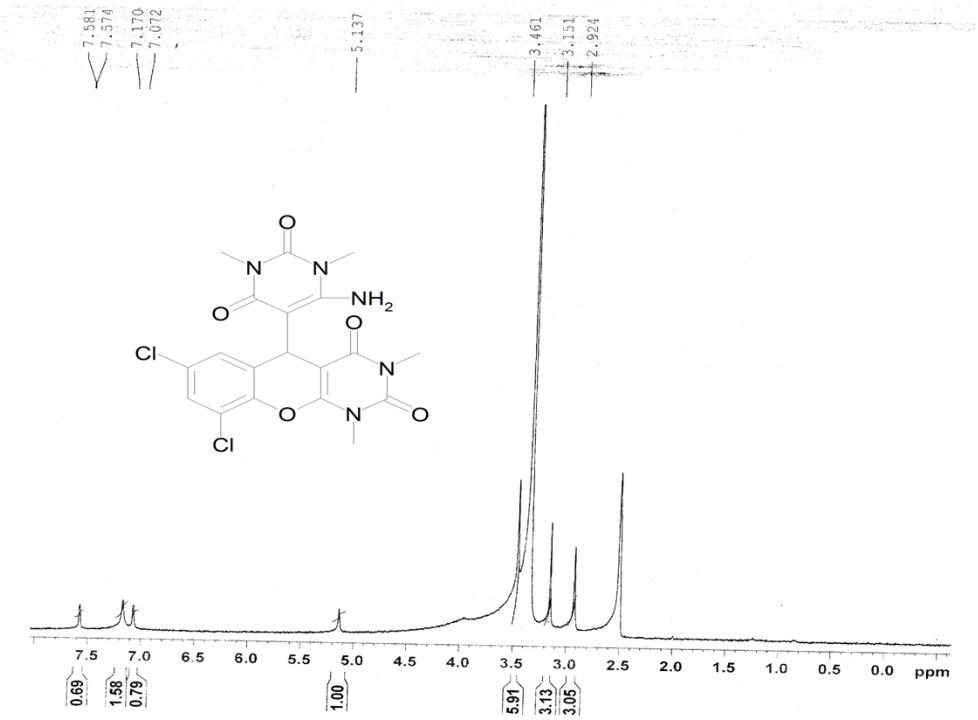
Entry e, Table 4: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-1,3-dimethyl-7-nitro-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione

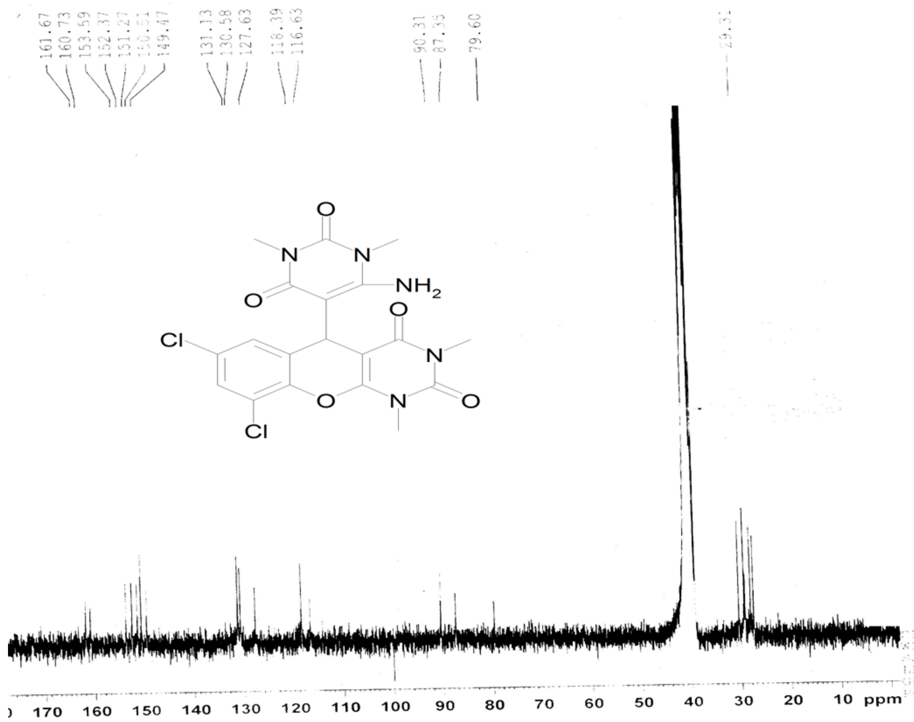


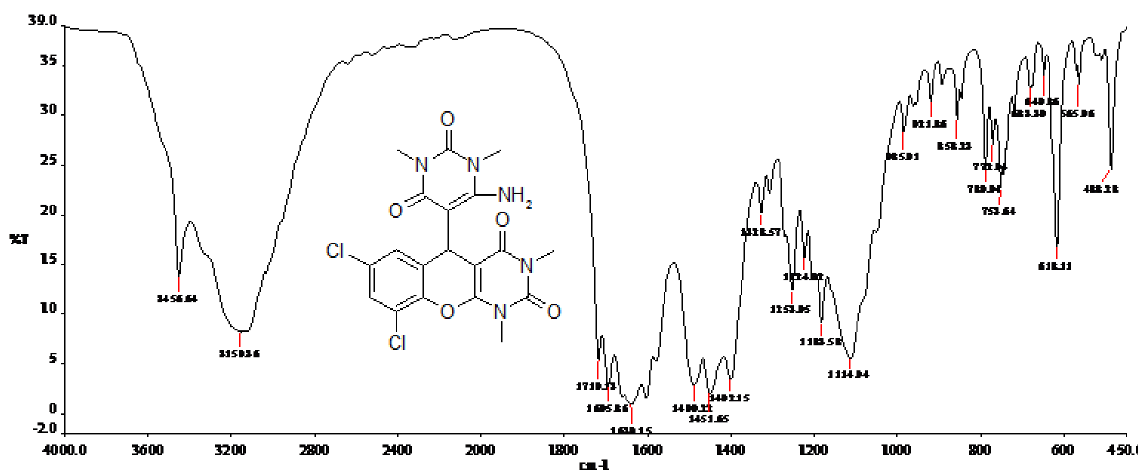




Entry f, Table 4: 5-(6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-7,9-dichloro-1,3-dimethyl-1,5-dihydro-2*H*-chromeno[2,3-*d*]pyrimidine-2,4(3*H*)-dione




161.67
160.73
153.59
152.37
151.27
150.51
149.47
131.13
130.58
127.63
118.39
116.63
90.31
87.35
79.60
O
N
N
NH2
O
O
Cl
N
O
O
N
O
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


39.0
35
30
25
20
%T
15
10
5
0
-2.0
O
N
N
NH2
O
O
Cl
N
O
O
N
O
Cl
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 450.0
cm-1