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N-doped graphene quantum dots modified with CuO (0D)/ZnO (1D) heterojunction as a new nanocatalyst for environmental being one-pot synthesis of monospiro derivatives

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Experimental Section:

Preparation of CuO (0)/ZnO (1) heterojunction

The CuO/ZnO heterojunction was fabricated by one step hydrothermal method under specific conditions. Copper acetate monohydrate and zinc acetate dihydrate with 1:4 molar ratios were dispersed in 20 mL distilled water about 30 min. Afterward, alkaline pH rang (~ 12) was obtained in the presence of sodium hydroxide (3 M). In the following, obtained solution was transferred to autoclave at 180 °C about 9 h. After that, the dark precipitate was centrifuged and washed twice with distilled water and dry at 70°C for 10 h. At the end, obtained solid was heated from room temperature to 500 °C for 2 h.

$Zn(OAc)2 + Cu(OAc)2 + 4NaOH \rightarrow CuO/ZnO+2H_2O+4\ NaOAc$

Synthesis of CuO/ZnO@N-GQDs nanocomposites

ethylene diamine (0.5 ml) and citric acid (1.2 g) were dissolved in deionized water (50 ml) and stirred (10 min) at 30 ° C, then prepared CuO/ZnO heterojunction (0.20 g) was added to mixture. Reaction solution was placed in 150 ml Teflon Lined stainless steel autoclave for 9 hours at 180°C. final dark brown solid was centrifuged and dried at 60°C for 24 h under vacuum conditions. Schematic of the synthesis steps of nanocomposite is shown in Scheme1.

Typical procedure for the synthesis of spiro[4H-pyran-3,3′-oxindole]

A reaction mixture including isatin derivative (1.0 mmol), activated methylene (1.0 mmol), 1,3 dicarbonyl compounds (1.0 mmol), and the CuO/ZnO@N-GQDs nanocatalyst (10 mol% (0.05 g) was stirred under reflux conditions in water (8 mL). Upon completion of the reactions (monitored by TLC) crude product was recrystallized from EtOH to obtained the pure products. The synthesized spirooxindoles were characterized by ^{1}H and ^{13}C-NMR, IR and elemental analysis.

Characterization data

Physical and spectroscopic data of all products

*7'-Amino-1,1',2,2',3',4'-hexahydro-2,2',4'-trioxospiro[3H-indole-3,5'-[5H]pyrano[2,3-d]pyrimidine]- 6'-carbonitrile (**4a**):* White solid. M.p. 290 – 2928. IR: 3350, 3300, 3195, 2954, 2199, 1720, 1667, 1613, 1522, 1474, 1364, 1224, 1132, 1072, 972, 748. 1 H-NMR: 10.64 (s, NH); 7.95 (d, J ¼ 8.0, 1 arom. H); 7.77 (t, J ¼ 7.6, 1 arom. H); 7.67 (br. s, NH_2); 7.57 (t, J ¼ 7.6, 1 arom. H); 7.50 (d, J ¼ 8.4, 1 arom. H); 7.22 (t, J ¼ 7.6, 2 arom. H); 6.93 (t, J ¼ 7.6, 1 arom. H); 6.85 (d, J ¼ 8.0, 1 arom. H). EI-MS: 357 (Mþ). Anal. calc. for $C_{20}H_{11}N_3O_4$: C 67.23, H 3.10, N 11.76; found: C 67.49, H 3.02, N 11.86.

*Synthesis of 7'-Amino-5-chloro-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro [indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (**4b**)*: Solid, mp 238-240°C. IR ν_{max}(Neat): 3292, 3150, 2818, 2200, 1919, 1688, 1645, 1539, 1475, 1404, 1339, 1166 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.76-6.79 (m, 1H), 7.16-7.21 (m, 3H), 7.30 (brs, 2H), 10.54 (s, 1H), 10.64 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): 47.6, 57.4, 86.3, 111.2, 117.6, 124.0, 126.3, 128.8, 136.3, 141.9, 150.6, 155.0, 159.2, 162.3, 178.2 ppm. Elemental Analysis for $C_{15}H_8ClN_5O_4$ calculated C, 50.37; H, 2.25; N, 19.58; obtained C, 50.36; H, 2.26; N, 19.60.

*7'-Amino-5-bromo-6'-cyano-2,2',4'-trioxo-1,1',2,2',3',4'-hexahydrospiroindole-3,5'-pyrano[2,3 d]pyrimidine (**4c**):* Pale violet, m.p. 220－222 ℃ (from ethanol); ^1H NMR δ: 6.85 (s, 2H, NH2), 6.80 —7.40 (m, 3H, ArH), 10.00 (s, 1H, NH), 11.00 (s, 1H, NH), 11.25 (s, 1H, NH); IR (KBr) ν: 3350—3310 (NH, NH_2), 2210 (CN), 1710—1715 (C＝O) cm^{-1} ; MS m/z (%): 401 (M＋ , 45), 403 (M＋ ＋2, 48). Anal. calcd for $C_{15}H_8BrN_5O_4$ (402.16): C 44.80, H 2.01, N 17.41, Br 19.87; found C 44.39, H 2.11, N 17.52, Br 19.63.

*Amino-5-nitro-2,20,40-trioxo-10,20,30,40tetrahydrospiro[indoline-3,50-pyrano[2,3-d]pyrimidine]60-carbonitrile (**4d**)* ($C_{15}H_8N_6O_6$): White solid; m.p.: 286–288 °C; IR (KBr): v = 3,442, 3,296, 3,173, 2,199, 1,748, 1,687, 1,632, 1,521, 1,477, 1,345, 1,253, 1,230 cm^{-1}; ^1H NMR (400 MHz, DMSOd_6): d = 6.80–7.30 (m, 1H), 7.53 (s, 2H, NH_2), 8.07–8.40 (m, 2H), 11.15–11.30 (m, 2H, 2 9 NH), 12.38 (brs, 1H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): d = 48.5, 57.7, 87.4, 111.0, 118.4, 121.6, 127.5, 136.2, 144.2, 150.2, 150.9, 155.5, 160.3, 163.3, 180.0 ppm.

*Methyl 7'-Amino-1,1',2,2',3',4'-hexahydro-2,2',4'-trioxospiro[3H-indole-3,5'-[5H]pyrano[2,3-d]pyrimidine]-6'-carboxylate (**4f**):* White solid. M.p. 273 – 275 °C. IR: 3380, 3312, 3094, 1712, 1668, 1613, 1530, 1443, 1288, 964, 910, 760, 665 cm^{-1}. ^{1}H-NMR: 10.42 (s, NH); 8.02 (br. s, NH_2); 8.04 (d, J ¼ 8.0, 1 arom. H); 7.74 (t, J ¼ 8.0, 1 arom. H); 7.53 (t, J ¼ 7.6, 1 arom. H); 7.45 (d, J ¼ 8.4, 1 arom. H); 7.11 (t, J ¼ 7.6, 1 arom. H); 7.01 (d, J ¼ 7.2, 1 arom. H); 6.79 (t, J ¼ 7.6, 1 arom. H); 6.75 (d, J ¼ 7.6, 1 arom. H); 3.22 (s, Me). EI-MS: 390 (Mþ). Anal. calc. for $C_{21}H_{14}N_2O_6$: C 64.62, H 3.62, N 7.18; found: C 64.84, H 3.55, N 7.11.

*Methyl-2-amino-5,7-dioxo-spiro[5'-bromo-(30H)-indol30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine](10H)-20-one-3-carboxylate (**4g**):* M.p. 247–250 °C. IR (KBr): 3,345, 3,195, 3,081, 2,946, 2,807, 1,696, 1,666, 1,616, 1,523, 1,433, 1,325, 1,248, 1,109, 999, 822, 665 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 3.31 (3H, s, CH3), 6.63 (1H, d, J = 8.1 Hz, ArH), 7.19 (2H, br s, NH_2), 7.91-7.94 (2H, m, ArH), 10.35 (1H, s, NH), 10.97 (1H, s, NH), 12.21 (1H, s, NH) ppm. Mass m/z (%): 433 (M, 2), 435 (M?2, 2), 306 (9), 285 (79), 226 (53), 192 (100), 173 (32), 128 (43), 91 (49), 65 (36). Anal. calcd for $C_{16}H_{11}BrN_4O_6$: C, 44.16; H, 2.55; N, 12.87. Found: C, 44.20; H, 2.49; N, 12.80

*Ethyl-2-amino-5,7-dioxo-spiro[(3'H)-indol-3',4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine]-(1'H)-2'-one-3-carboxylate (**4i**):* Mp 207–209 °C. IR (KBr) ν_{max}(Neat): 3618, 3495, 3321, 3202, 2980, 1720, 1695, 1682, 1616, 1471, 1327, 1253, 1118, 752 cm^{-1} ; ^{1} H NMR (300 MHz, DMSO-d_6): dH 12.20 (br s, 1H, NH), 11.00 (s, 1H, NH), 10.27 (s, 1H, NH), 7.98 (s, 2H, NH2), 7.09 (t, 1H, J ¼ 7.5 Hz, ArH), 6.97 (d, 1H, J ¼ 7.0 Hz, ArH), 6.80 (t, 1H, J ¼ 7.0 Hz, ArH), 6.70 (d, 1H, J ¼ 7.5 Hz, ArH), 3.37 (q, 2H, J ¼ 7.0 Hz, CH_2), 0.80 (t, 3H, J ¼ 7.0 Hz, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): dC 179.7, 167.9, 161.6, 159.0, 152.6, 149.5, 144.4, 135.7, 127.8, 123.2, 121.1, 108.6, 89.6, 76.6, 59.5, 46.6, 13.4 ppm. Anal. calcd. for $C_{17}H_{14}N_4O_6$: C, 55.14; H, 3.81; N, 15.13%. Found: C, 55.02; H, 3.85; N, 15.25%.

*Ethyl-2-amino-5,7-dioxo-spiro[50-chloro-(30H)-indol30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine](10H)-20-one-3-carboxylate (**4j**):* M.p. [300 °C. IR (KBr): 3,601, 3,496, 3,356, 3,276, 3,207, 2,973, 2,858, 1,686, 1,620, 1,524, 1,441, 1,325, 1,251, 1,116, 985, 773, 687 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 0.80 (3H, t, J = 7.1 Hz, CH_3), 3.50 (2H, q, J = 8.0 Hz, CH_2), 6.48-6.49 (3H, m, ArH, NH_2), 6.67 (1H, d, J = 8.1 Hz, ArH), 7.10 (1H, t, J = 5.6 Hz, ArH), 10.28 (1H, s, NH), 10.32 (1H, s, NH), 10.54 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 13.0, 49.1,

54.5, 83.6, 109.5, 123.0, 126.2, 131.1, 141.1, 151.3, 164.0, 165.3, 170.1, 172.4, 176.5, 179.1, 180.4 ppm. Anal. calcd for $C_{17}H_{13}ClN_4O_6$: C, 50.45; H, 3.24; N, 13.84. Found: C, 50.52; H, 3.31; N, 13.80.

*Ethyl-7'-amino-5-bromo-6'-cyano-2,2',4'-trioxo-1,1',2,2',3',4'-hexahydrospiroindole-3,5'-pyrano[2,3- d]pyrimidine-6'-carboxylate (**4k**):* Pale brown powder, m.p. 230—232 ℃ (from methanol); ^{1} H NMR δ: 1.38 (t, J＝6.0 Hz, 3H, CH3), 3.70 (q, J＝8.0 Hz, 2H, CH2), 6.85 (s, 2H, NH_2), 6.85—7.35 (m, 3H, ArH), 9.75 (s, 1H, NH), 10.35 (s, 1H, NH), 10.65 (s, 1H, NH); IR (KBr) ν: 3353—3305 (NH, NH_2), 1697, 1700 —1725 (C＝O's) cm^{-1} ; MS m/z (%): 448 (M＋ , 100), 450 (M ＋ ＋2, 97.9). Anal. calcd for $C_{17}H_{13}BrN_4O_6$ (449.21): C 45.55, H 2.92, N 12.47, Br 17.79; found C 45.33, H 2.75, N 12.27, Br 17.68

*6'-Amino-1',3'-dimethyl-2,2',4'-trioxo-1',3',4',5'-tetrahydro-2'H-spiro[indoline-3,8' pyrido[3,2d]pyrimidine]-7'-carbonitrile (**6a**):* White solid; m.p. > 300 ºC; ^{1}H NMR (250 MHz, CDCl3) δ: 2.66 (s, 6H, CH_3), 6.81-7.66 (m, 7H. ArH, NH and NH_2), 8.56 (brs, 1H, NH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 28.9, 29.6, 54.1, 57.1, 103.1, 114.8, 117.2, 121.8, 124.8, 127.8, 129.8, 141.0, 152.1, 158.0, 162.5, 164.5, 168.8; IR (KBr, cm^{-1}): 3621, 3152, 3068, 2113 (CN Stretching), 1173, 1651, 1484, 692, 581; Anal. Calcd for $C_{17}H_{14}N_6O_3$: C, 58.28; H, 4.03; N, 23.99; Found: C, 58.24; H, 4.08; N, 24.07.

*2-Amino-6,8-dimethyl-5,7-dioxo-spiro[50-chloro-(30H)indol-30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3d)pyrimidine]-(10H)-20-one-3-carbonitrile (**6b**):* M.p.[300 °C. IR (KBr): 3,477, 3,380, 3,345, 3,180, 2,961, 2,196, 1,693, 1,646, 1,481, 1,387, 1,193, 978, 772, 557 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 3.03 (3H, s, CH_3), 3.33 (3H, s, CH_3), 6.80 (1H, d, J = 8.2 Hz, ArH), 7.19–7.21 (1H, m, ArH), 7.27 (1H, d, J = 7.1 Hz, ArH), 7.62 (2H, s, NH_2), 10.61 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 27.6, 29.3, 40.3, 56.9, 63.3, 86.4, 110.6, 116.6, 125.7, 128.3, 129.5, 135.6, 141.0, 152.1, 158.0, 159.4, 177.2 ppm. Mass m/z (%): 385 (M+2), 387 (M+2, 1), 359 (4), 320 (35), 229 (100), 202 (78), 174 (27), 156 (96), 139 (84), 112 (37), 99 (37), 87 (37), 71 (32), 58 (42). Anal. calcd for $C_{17}H_{12}ClN_5O_4$: C, 52.93; H, 3.14; N, 18.15. Found: C, 52.88; H, 3.17; N, 18.10.

Spiro[2-amino-4H-pyran-oxindole] (**6c**): White powder; mp 259–260 °C. IR (KBr) (ν_{max}, cm^{-1}): 3375, 3310, 3248, 3202, 2197, 1730, 1707, 1653, 1475, 1371, 1195, 977, 816 771, 685, 544, 422.

^{1} H NMR (400 MHz, DMSO-d_6) (ppm): 3.04 (s, 3H, CH_3), 3.11 (s, 3H, CH_3), 6.78 (d, J = 8.0 Hz, 1H, Ar), 7.35 (d, J = 8.4 Hz, 1H, Ar), 7.40. Anal. calcd. for $C_{17}H_{12}BrN_5O_4$: C 47.46, H 2.81, N 16.28%; found: C 47.29, H 2.92, N 16.13%.

*Methyl-2-amino-6,8-dimethyl-5,7-dioxo-spiro[(30H)-indol30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine](10H)-20-one-3-carboxylate (**6e**):* M.p. 246–249 °C. IR (KBr): 3,505, 3,344, 3,250, 3,192, 3,135, 2,965, 1,695, 1,644, 1,533, 1,475, 1,385, 1,285, 1,118, 976, 770, 684 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 2.49 (3H, s, CH_3), 3.35 (3H, s, CH_3), 3.94 (3H, s, CH_3), 6.86 (1H, d, J = 7.7 Hz, ArH), 7.00 (1H, t, J = 7.7 Hz, ArH), 7.44 (1H, d, J = 7.6 Hz, ArH), 7.88 (2H, s, NH_2), 8.11 (1H, d, J = 8.0 Hz, ArH), 11.07 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 27.8, 29.7, 40.0, 53.8, 79.4, 83.8, 104.1, 110.8, 114.1, 118.6, 122.1, 129.3, 131.1, 136.0, 145.5, 145.8, 161.8, 165.1 ppm. Mass m/z (%): 384 (M+, 2), 368 (4), 286 (6), 228 (93), 197 (46), 169 (63), 141 (96), 114 (100), 88 (42), 59 (48). Anal. calcd for $C_{18}H_{16}N_4O_6$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.28; H, 4.14; N, 14.62.

*Methyl-2-amino-6,8-dimethyl-5,7-dioxo-spiro[50-bromo(30H)-indol-30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3d)pyrimidine]-(10H)-20-one-3-carboxylate (**6f**):* M.p. 266–268 °C. IR (KBr): 3,342, 3,191, 3,122, 2,927, 2,809, 1,735, 1,695, 1,662, 1,470, 1,387, 1,245, 1,101, 926, 744, 664 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 3.25 (3H, s, CH_3), 3.59 (3H, s, CH_3), 3.94 (3H, s, CH_3), 6.64 (1H, d, J = 8.0 Hz, ArH), 6.84 (1H, m, ArH), 7.37 (1H, d, J = 8.2 Hz, ArH), 7.77 (2H, s, NH_2), 10.74 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 28.5, 30.4, 38.9, 39.9, 40.0, 50.4, 51.6, 56.8, 111.4, 112.6, 129.3, 131.5, 131.9, 141.9, 150.6, 161.6, 165.7, 169.3 ppm. Mass m/z (%): 462 (M+, 1), 464 (M+2, 1), 364 (11), 320 (14), 308 (100), 249 (46), 221 (36), 156 (43), 140 (95), 114 (57), 99 (38), 87 (53), 71 (32), 59 (60). Anal. calcd for $C_{18}H_{15}BrN_4O_6$: C, 46.67; H, 3.26; N, 12.09. Found: C, 46.71; H, 3.29; N, 13.04.

*Ethyl-2-amino-6,8-dimethyl-5,7-dioxo-spiro[50-chloro(30H)-indol-30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3d)pyrimidine]-(10H)-20-one-3-carboxylate (**6g**):* M.p. 229–231°C. IR (KBr): 3,256, 3,170, 2,917, 2,828, 1,726, 1,693, 1,650, 1,616, 1,470, 1,341, 1,162, 997, 779, 572 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): d 1.04 (3H, t, J = 7.0 Hz, CH_3), 2.85 (3H, s, CH_3), 3.24 (3H, s, CH_3), 3.44 (2H, q, J = 7.0 Hz, CH_2), 6.80 (1H, d, J = 7.9 Hz, ArH), 7.26 (1H, m, ArH), 7.42 (1H, d, J = 8.2 Hz, ArH), 7.74 (2H, s, NH_2), 10.94 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 13.7, 28.5, 51.5, 63.2, 110.8, 112.2, 125.7, 126.7, 128.5, 128.9, 135.2, 141.5, 144.6,

150.5, 161.1, 165.6, 168.8, 169.4, 174.0 ppm. Mass m/z (%): 432 (M+, 8), 434 (M+2, 3), 359 (9), 320 (100), 276 (91), 231 (35), 204 (80), 176 (52), 156 (89), 114 (44), 99 (35), 71 (51), 58 (83). Anal. calcd for $C_{19}H_{17}ClN_4O_6$: C, 52.73; H, 3.96; N, 12.94. Found: C, 52.70; H, 3.99; N, 12.90.

*Ethyl-2-amino-6,8-dimethyl-5,7-dioxo-spiro[50-bromo(30H)-indol-30,4,4(H)-5,6,7,8-tetrahydropyrano(2,3d)pyrimidine]-(10H)-20-one-3-carboxylate (**6h**):* M.p. 242–244 °C. IR (KBr): 3,371, 3,316, 3,144, 2,932, 1,699, 1,652, 1,474, 1,388, 1,220, 1,194, 972, 759,669 cm^{-1}. 1HNMR(DMSO-d_6,500 MHz): d0.84(3H, t, J = 6.8 Hz, CH_3), 3.10 (3H, s, CH_3), 3.42 (3H, s, CH_3), 3.75 (2H, q, J = 6.6 Hz, CH_2), 6.63 (1H, d, J = 8.0 Hz, ArH), 7.22 (1H, t, J = 8.2 Hz, ArH), 7.55 (1H, d, J = 8.0 Hz, ArH),8.08(2H,s,NH_2),10.37(1H,s,NH)ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): d 13.0, 27.5, 29.3, 45.0, 59.1, 64.0, 75.4, 88.8, 104.3, 109.4, 112.2, 123.1, 125.8, 126.0, 135.1,149.5, 166.9,178.9,184.0 ppm. Mass m/z(%): 476 (M+, 12), 478 (M+2, 11), 403 (39), 320 (100), 250 (40), 222 (29), 156 (90), 140 (41), 114 (48), 99 (31), 71 (42), 58 (43). Anal. calcd for $C_{19}H_{17}BrN_4O_6$: C, 47.81; H, 3.59; N, 11.74. Found: C, 47.77; H, 3.57; N, 11.80.

*Ethyl-6'-amino-1',3'-dimethyl-2,2',4'-trioxo-1',3',4',5'-tetrahydro-2'H-spiro[indoline-3,8'pyrido[3,2-d]pyrimidine]-7'-carboxylate (**6i**):* White solid; m.p. > 300 ºC; ^1H NMR (250 MHz, CDCl3) δ: 1.22 (t, J= 7.5 Hz, 3H, CH_3), 2.66 (s, 6H, CH_3), 4.20 (q, J= 5.0 Hz, 2H, CH_2), 6.817.66 (m, 7H, ArH, NH and NH_2), 8.16 (brs, 1H, NH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 14.3, 29.6, 32.7, 45.0, 57.4, 86.5, 114.8, 123.6, 127.0, 129.1, 132.0, 134.3, 141.0, 162.1, 164.5, 168.9, 169.9, 173.4; IR (KBr, cm^{-1}): 3627, 3189, 3118, 1173, 1652, 1485, 681, 579; Anal. Calcd for $C_{19}H_{19}N_5O_5$: C, 57.43; H, 4.82; N, 17.62; Found: C, 57.53; H, 4.75; N, 17.68.

*2'-Amino-6'-(Hydroxymethyl)-2,8'-Dioxo8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'-Carbonitrile (**8a**):* White crystal; mp 327 °C (dec); ^{1} H-NMR (300 MHz, DMSO- d_6) δ 4.04 (d(AB-q), 2 J = 15.7 Hz, 3 J = 5.7 Hz, 2H, CH_2OH), 5.66 (t, 3 J = 7.6 Hz, 1H, OH), 6.37 (s, 1H, CH vinyl), 6.92-7.35 (m, 4H, CH arom), 7.55 ((s, 2H, NH_2), 10.87 (s, 1H, NH amide) ppm; ^{13}C-NMR (75 MHz, DMSO- d_6) δ 51.74, 55.49, 59.46, 110.80, 112.14, 117.69, 123.34, 125.58, 130.49, 130.82, 138.29, 142.21, 146.27, 160.36, 168.89, 169.89, 175.98 ppm. FT-IR (KBr) ν: 3432, 3297, 3172, 2201, 1717, 1633, 1597, 1226 cm^{-1}; MS (EI, 70 eV) m/z (%): 337 (M+, 5), 319 (18), 309 (22), 294 (15), 220 (42), 57 (100); Anal. calc. for $C_{17}H_{11}N_3O_5$: C 60.54, H 3.29, N 12.46; Found: C 60.39, H 3.30, N 12.42.

*2'-Amino-5-Chloro-6'-(Hydroxymethyl)-2,8'-Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'- Carbonitrile (**8b**):* White crystals; mp 300 °C (dec); ^{1} H-NMR (300 MHz, DMSO-d_6) δ 4.05 (m, 2H, CH_2OH), 5.67 (t, 3 J = 5.7 Hz, 1H, OH), 6.38 (s, 1H, CH vinyl), 6.94-7.57 (m, 3H, CH arom), 7.61 ((s, 2H, NH_2), 11.0 (s, 1H, NH amide) ppm; ^{13}CNMR (75 MHz, DMSO-d6) δ 51.98, 54.97, 59.47, 112.19, 112.25, 117.66, 126.01, 127.29, 130.49, 132.64, 138.44, 141.17, 145.42, 160.42, 168.86, 169.92, 175.86 ppm; FT-IR (KBr) ν: 3309, 3184, 2204, 1736, 1638, 1592, 1476, 1442, 1216 cm^{-1}; MS (EI, 70 eV): m/z (%): 373 (M+ +2, 4), 371 (M+ , 13), 124 (43), 111 (58), 83 (100); Anal. calc. for $C_{17}H_{10}Cl\ N_3O_5$: C 54.93, H 2.71, N 11.30; Found: C 55.04, H 2.69, N 11.33.

*2'-Amino-6'-(Hydroxymethyl)-5-Nitro-2,8'- Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'- Carbonitrile (**8d**):* White crystals; mp>300; ^{1} H-NMR (400 MHz, DMSO-d_6) δ 4.07 (d(AB-q), 2 J = 15.8 Hz, 3 J = 6.0 Hz, 2H, CH_2OH), 5.64 (t, 3 J = 6.0 Hz, 1H, OH), 6.38 (s, 1H, CH vinyl), 7.17 (d, 3J = 8.8 Hz, 1H, CH arom), 7.71 (s, 2H, NH_2), 8.29 (dd, 3 J = 8.8 Hz, 4 J = 2.4 Hz, CH arom), 8.47 (d, 4J = 2.4 Hz, 1H, CH arom), 11.58 (s, 1H, NH amide) ppm; ^{13}C-NMR (100 MHz, DMSO- d_6) δ: 51.38, 53.84, 58.93, 110.67, 111.70, 117.08, 121.59, 127.19, 131.08, 138.16, 143.15, 144.14, 148.08, 160.13, 168.35, 169.42, 176.20 ppm; FT-IR (KBr) ν: 3495, 3418, 3278, 3157, 2189, 1742, 1671, 1633, 1589, 1433, 1339, 1212 cm-1; MS (EI, 70 eV): m/z (%): 382 (M+ +2, 11), 253 (5), 179 (10), 137 (20), 125 (40), 57 (100); Anal. calc. for $C_{17}H_{10}N_4O_7$: C 53.41, H 2.64, N 14.66; Found: C 53.20, H 2.66, N 14.69.

*Methyl 2'-Amino-6'-(Hydroxymethyl)-2,8'- Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'- Carboxylate (**8e**):* White cristals; mp 269 °C (dec); ^{1} H NMR (400 MHz, DMSO-d_6) δ 3.29 (s, 3H, CH_3), 4.03 (d(AB-q), 2 J = 15.6 Hz, 3 J = 5.6 Hz, 2H, CH_2OH), 5.65 (s, 1H, OH), 6.33 (s, 1H, CH vinyl), 6.85-7.22 (m, 4H, CH arom), 8.06 (s, 2H, NH_2), 10.64 (s, 1H, NH amide) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 50.51, 51.12, 55.99, 58.96, 73.71, 109.34, 111.38, 121.92, 123.39, 128.83, 133.45, 136.34, 142.30, 147.88, 159.75, 167.09, 168.29, 169.36, 177.07 ppm; FT-IR (KBr) ν: 3411, 3369, 3296, 2945, 1730, 1691, 1673, 1645, 1623, 1520, 1471, 1441, 1298, 1222 cm^{-1}; MS (EI, 70 eV) m/z (%): 370 (M+ , 11), 342 (11) 339 (47), 329 (18), 251 (22), 77 (100); Anal. calc. for $C_{18}H_{14}N_2O_7$: C 58.38, H 3.81, N 7.56; Found: C 58.49, H 3.84, N 7.50.

*Methyl 2'-Amino-5-Chloro-6'-(Hydroxymethyl)-2,8'-Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'-Carboxylate (**8f**):* White crystals, mp 263 °C (dec); ^{1} H NMR (400 MHz, DMSO-d_6)

δ 3.32 (s, 3H, CH_3), 4.03 (d(AB-q), 2 J = 16.0 Hz, 3 J = 6.0 Hz, 2H, CH_2OH), 5.65 (t, 3 J = 6.0 Hz, 1H, OH), 6.34 (s, 1H, CH vinyl), 6.71(d, 3 J = 8 Hz, 1H CH arom), 7.25 (dd, 3 J = 8 Hz, 4 J = 2 Hz, CH arom), 7.30 (d, 4 J = 1.6 Hz, 1H, CH arom), 8.10 (s, 2H, NH_2), 10.78 (s, 1H, NH amide) ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ 50.58, 51.39, 55.99, 58.97, 73.32, 110.71, 111.47, 123.81, 125.77, 128.75, 135.35, 136.52, 141.32, 146.98, 159.80, 166.94, 168.26, 169.39, 176.96 ppm; FT-IR (KBr) ν: 3561, 3382, 3276, 2949, 1725, 1693, 1672, 1644, 1529, 1477, 1441, 1303, 1223 cm^{-1}. MS (EI, 70 eV) m/z (%): 406 (M+ +2, 3), 404 (M+ , 10), 388 (14), 386 (22), 378 (14), 376 (10), 375 (28), 373 (20), 363 (15), 361 (10), 281 (30), 115 (10), 57 (100); Anal. Calcd for $C_{19}H_{11}ClN_2O_7$: C 53.41, H 3.24, N 6.92; Found: C 53.27, H 3.26, N 6.98.

*Ethyl 2'-Amino-6'-(Hydroxymethyl)-2,8'- Dioxo-8'H-spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'-Carboxylate (**8g**):* White crystals; mp 208 °C (dec); ^{1} H-NMR (400 MHz, DMSO-d_6) δ 0.75 (t, 3 J = 7.2 Hz, 3H, CH_3), 3.73 (m, 2H, CH_2O), 4.03 (d(AB-q), 2 J = 15.6 Hz, 3 J = 6.0 Hz, 2H, CH_2OH), 5.63 (t, 3 J = 6.0 Hz, 1H, OH), 6.33 (s, 1H, CH vinyl), 6.83-7.23 (m, 4H, CH arom), 8.10 (s, 2H, NH2), 10.60 (s, 1H, NH amide) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6) δ 13.09, 30.67, 50.50, 58.97, 73.57, 109.33, 111.38, 121.88, 123.41, 128.73, 133.68, 136.40, 142.55, 147.88, 159.85, 166.95, 168.30, 169.38, 177.21 ppm; FT-IR (KBr) ν: 3386, 3288, 2914, 1711, 1656, 1619, 1522, 1296, 1211 cm^{-1}; MS (EI, 20 eV) m/z (%): 312 (M+ -72, 16), 311 (62), 283 (22), 69 (100); Anal. calc. for $C_{19}H_{16}N_2O_7$: C 59.38, H 4.20, N 7.29; Found: C 59.59, H 4.23, N 7.23.

*Ethyl 2'-Amino-5-Bromo-6'-(Hydroxymethyl)-2,8'-Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]-3'-Carboxylate (**8h**):* White crystals; mp 280 °C (dec); ^{1} H-NMR (400 MHz, DMSO-d_6) δ 0.78 (brs, 3H, CH_3), 3.76 (brs, 2H, CH_2O), 4.06 (brs, 2H, CH_2OH), 5.69 (brs, 1H, OH), 6.34 (s, 1H, CH vinyl), 6.84 (s, 1H, CH arom), 7.39 (s, 2H, CH arom), 8.12 (s, 2H, NH_2), 10.78 (s, 1H, NH amide) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6) δ 13.11, 51.26, 58.98, 59.19, 73.15, 111.32, 111.49, 113.48, 126.45, 131.55, 135.87, 136.57, 141.91, 147.03, 159.91, 166.80, 168.27, 169.48, 177.01 ppm; FT-IR (KBr) ν: 3401, 3327, 2984, 2854, 1732, 1693, 1674, 1642, 1526, 1434, 1297, 1215 cm^{-1}; MS (EI, 70 eV) m/z (%): 464 (M+ +2, 8), 462 (M+ , 7), 419 (22), 417 (22), 97 (100); Anal. calc. for C19H15BrN2O7: C 49.26, H 3.26, N 6.05; Found: C 49.40, H 3.25, N 6.02.

*Ethyl 2'-Amino-5-Chloro-6'-(Hydroxymethyl)-2,8'-Dioxo-8'H-Spiro[Indoline-3,4'-Pyrano[3,2-b]Pyran]- 3'-Carboxylate (**8j**):* White crystals; mp 272 °C (dec); ^{1} H-NMR (400 MHz, DMSO-d_6) δ 0.78 (t, 3 J = 7.2 Hz, 3H, CH_3), 3.76 (m, 2H, CH_2O), 4.06 (d(AB-q), 2 J = 16.0 Hz, 3 J = 6.0 Hz,

2H, CH_2OH), 5.63 (t, 3 J = 6.0 Hz, 1H, OH), 6.34 (s, 1H, CH vinyl), 6.85-7.30 (m, 3H, CH arom), 8.15 (s, 2H, NH2), 10.74 (s, 1H, NH amide) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6) δ 13.14, 51.33, 58.99, 59.11, 73.13, 110.70, 111.48, 123.85, 125.77, 128.64, 135.57, 136.58, 141.55, 147.01, 159.95, 166.80, 168.27, 169.40, 177.07 ppm. FT-IR (KBr) ν: 3404, 3323, 2901, 1736, 1694, 1672, 1643, 1526, 1477, 1298, 1217 cm^{-1}; MS (EI, 70 eV) m/z (%): 420 (M+ +2, 4), 418 (M+ , 10), 3751 (25), 373 (14), 71 (100); Anal. calc. for $C_{19}H_{15}ClN_2O_7$: C 54.49, H 3.61, N 6.69; Found: C 54.58, H 3.59, N 6.75.

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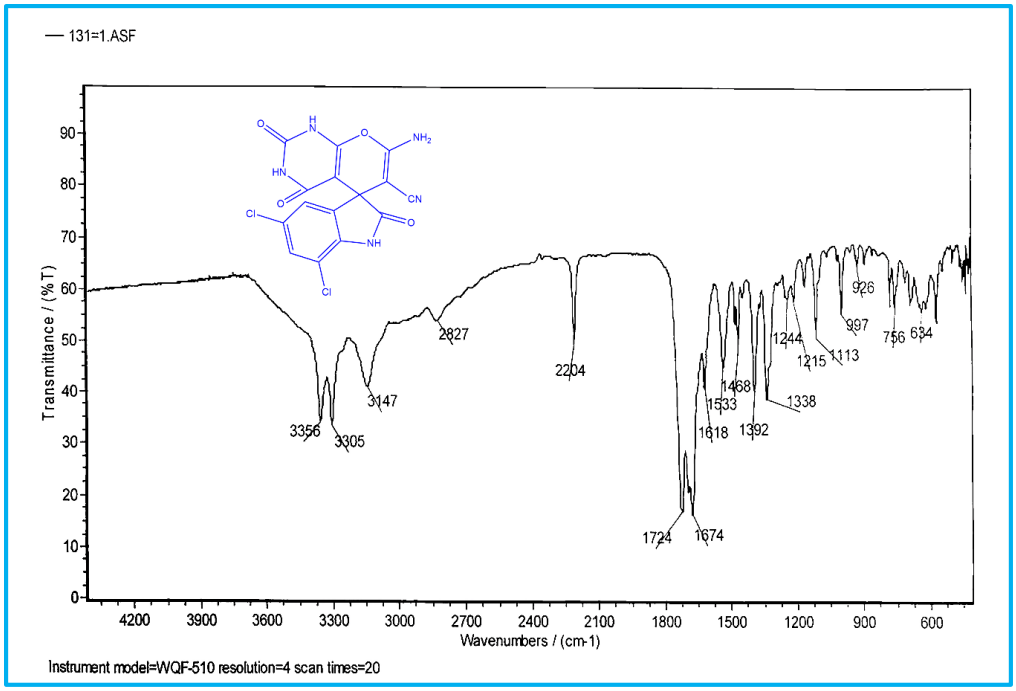
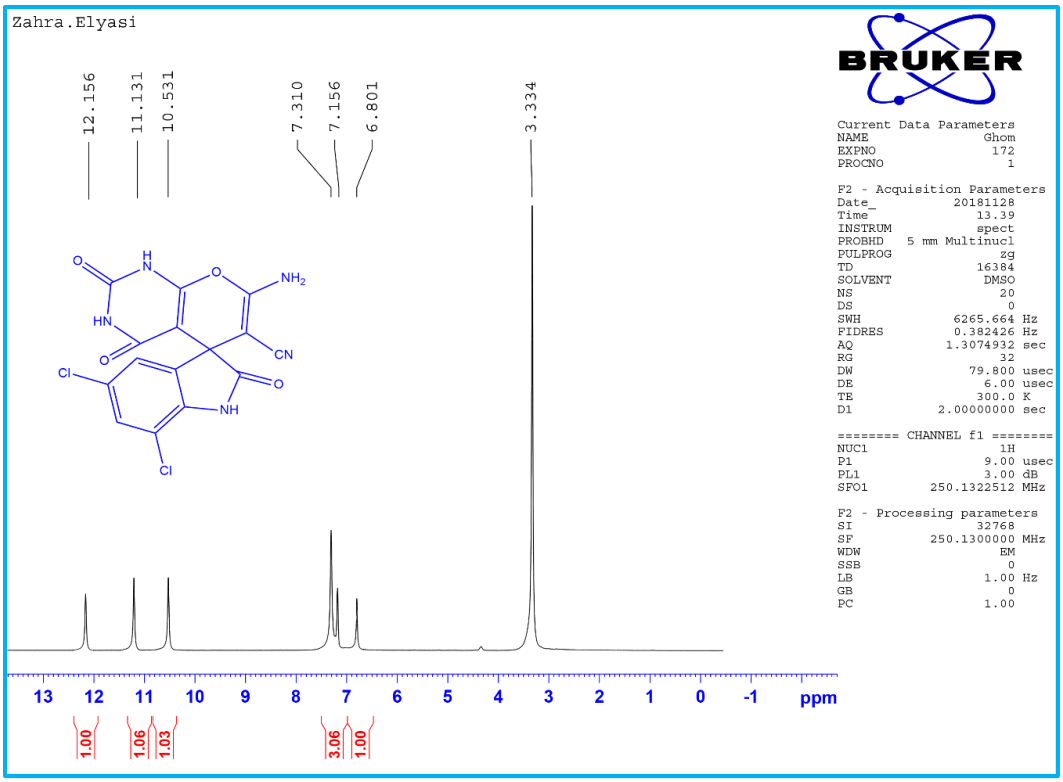
Spectral data of the new compounds

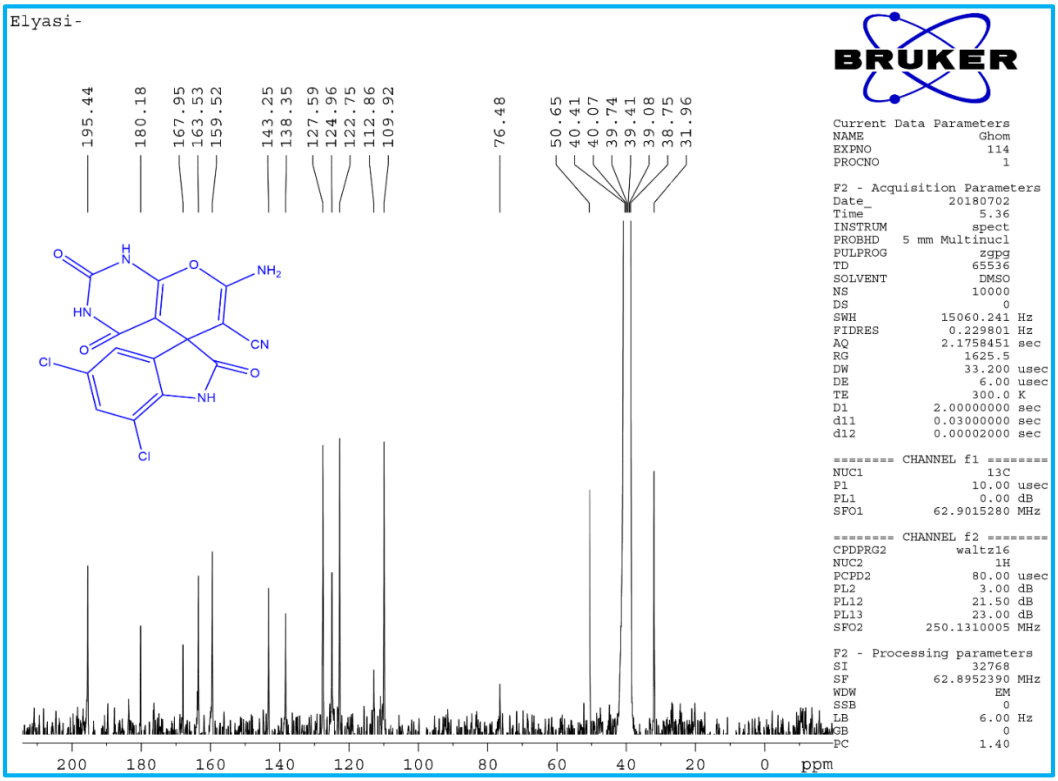
*7'-Amino-5,7-dichloro-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro [indoline-3,5'- pyrano[2,3-d]pyrimidine]-6'-carbonitrile (**4e**)*: Yield 98%. White Solid, mp 300°C. IR ν_{max}(Neat): 3356, 3305, 3147, 2827, 2204, 1724, 1674, 1618, 1539, 1468, 1392, 1338, 1113, 997, 756 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.801 (s,1H), 7.156 (s, 1H), 7.31 (s, 2H), 10.53 (s, 1H), 11.13 (s, 1H), 12.15 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 31.96, 50.65, 76.48, 109.92, 112.86, 122.75, 124.96, 127.59, 138.35, 143.25, 159.52, 163.53, 167.95, 180.18, 195.44 ppm. Elemental Analysis for $C_{15}H_7Cl_2N_5O_4$ calculated C, 45.71; H, 2.30; N, 17.77; obtained C, 45.72; H, 2.28; N, 17.76.



FT-IR of **4e**

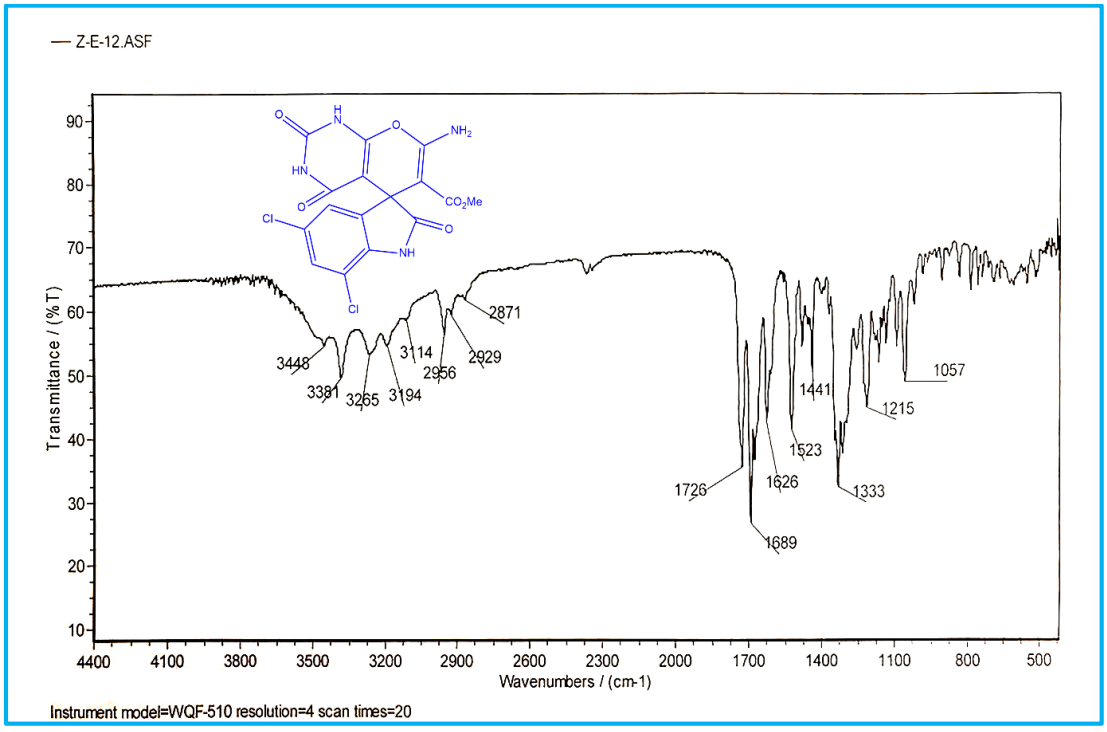


^{1}H NMR of **4e**

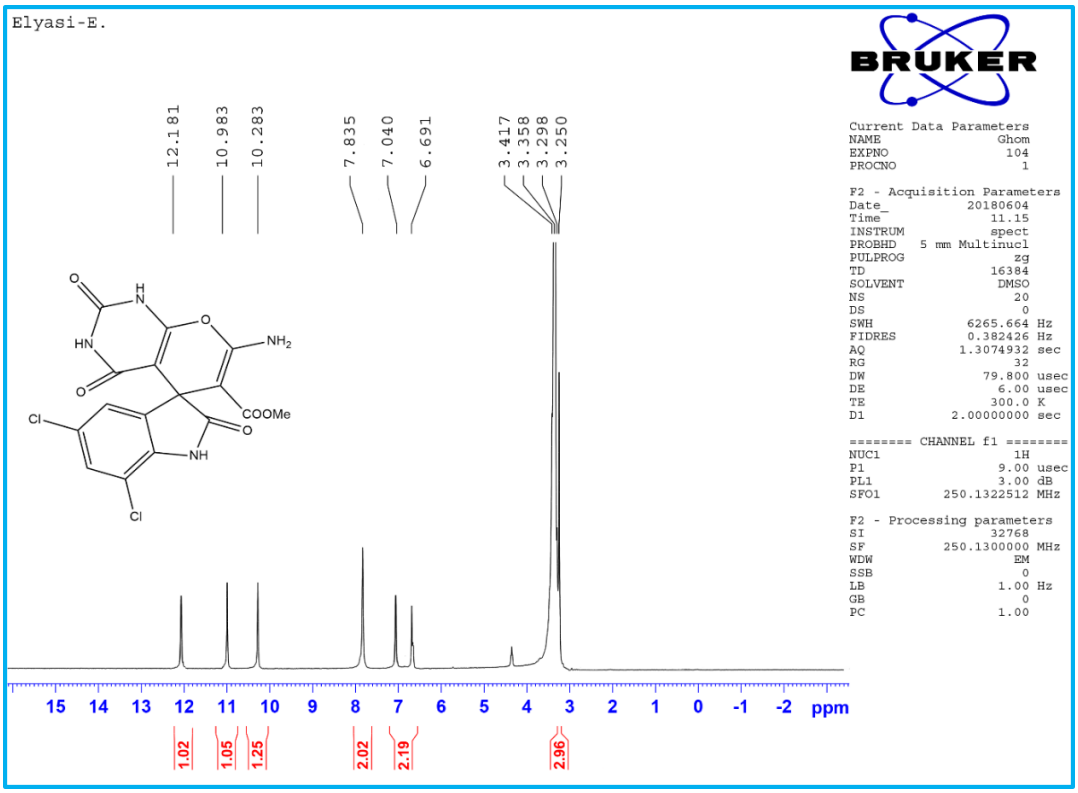


^{13}C NMR of **4e**

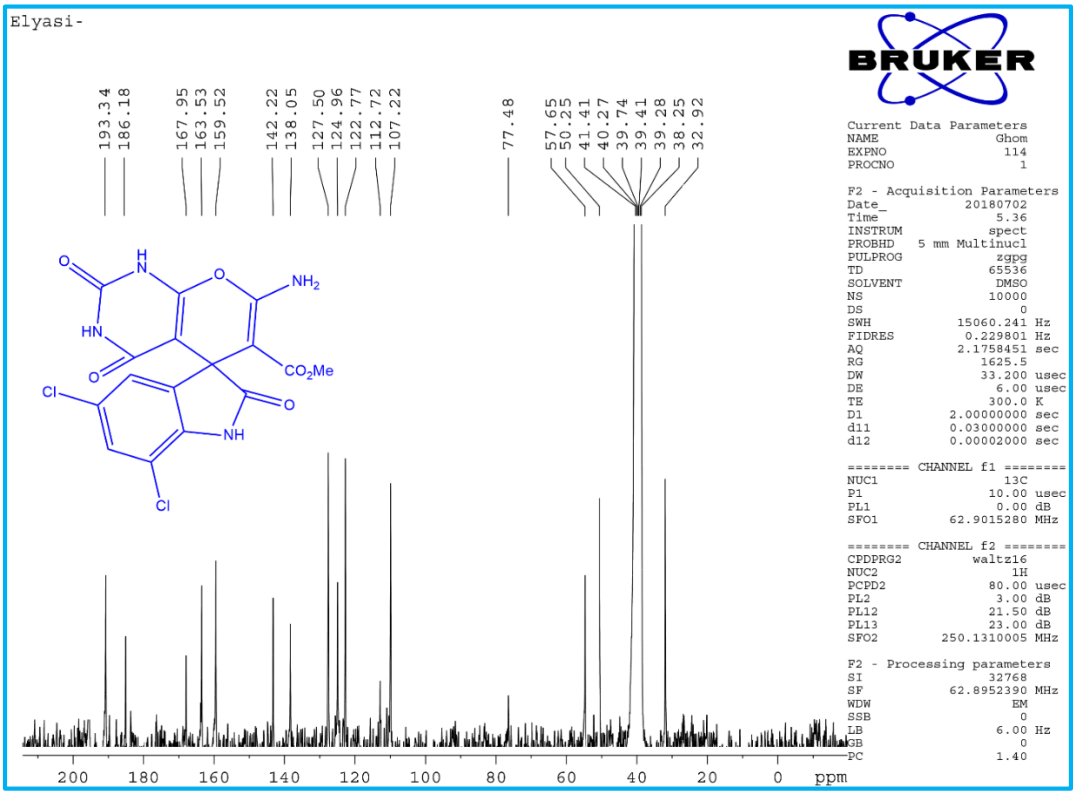
*Methyl-2-amino-5,7-dioxo-spiro[5,7-dichloro-(3'H)-indol3,4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine](10H)-20-one-3-carboxylate (**4h**)*: Yield: 95 %. M.p. 300°C>. IR ν_{max}(Neat): 3448, 3381, 3265, 3194, 3114, 2956, 2929, 1726, 1674, 1689, 1626, 1523, 1441, 1333, 1215, 1057, 856 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz): 3.35 (3H, s, CH_3), 6.63 (1H, ArH), 7.04 (1H, s, ArH), 7.83 (2H, s, NH_2), 10.28 (1H, s, NH), 10.98 (1H, s, NH), 12.18 (1H, s, NH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 32.92, 50.25, 57.65, 77.48, 107.22, 112.72, 122.77, 124.96, 127.50, 138.05, 142.22, 159.52, 163.53, 167.95, 186.18, 193.34 ppm Anal. calcd for $C_{16}H_{10}Cl_2N_4O_6$: C, 44.98; H, 2.83; N, 13.12. Found: C, 44.96; H, 2.80; N, 13.10.



FT-IR of **4h**



^{1}H NMR of **4h**



^{13}C NMR of **4h**