Supplementary Materials: Computational and Experimental Study on Molecular Structure of benzo[*g*]pyrimido[4,5-*b*]quinoline Derivatives: Preference of Linear over the Angular Isomer

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General Information

All reagents used in this work were purchased commercially without further purification. Identifications of compounds and measurements of properties were carried out by general procedures employing the following equipment: Microwave irradiation was carried out with microwave oven CEM Discover with controlled power and temperature. Melting points were determined in a Büchi Melting Point Apparatus and are reported uncorrected. The ^{1}H and ^{13}C NMR spectra were measured at RT on a Bruker Avance 400 spectrometer operating at 400 and 100 MHz, respectively, and using DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. The mass-spectra were scanned on a Hewlett Packard HP Engine-5989 spectrometer (equipped with a direct inlet probe) which was operating at 70 eV. Elemental analyses were obtained using a LECO CHNS-900 elemental analyzer.

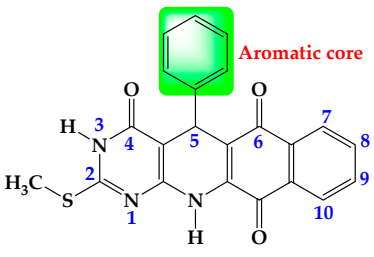
The compound **4c** was optimized based on the crystal structure. The geometry have been fully optimized using DFT with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation density functional (B3LYP) and the Pople's split-valence 6-31G(d,p) extended basis set. The optimum structures so obtained were further certified as true minima by constructing and diagonalizing the corresponding Cartesian Hessian matrix, this procedure providing also the harmonic vibrational frequencies which, after properly scaled by the recommended scaling factor 0.964, allow reliable calculations of the thermal corrections to the molecular energy. The conformational studies, natural bond orbital (NBO) and nonlinear optical (NLO) analysis NBO and NLO analysis on the title compound were performed; the NBO analyses have been done on B3LYP/6-31+G(d,p) wave functions obtained with the B3LYP/6-31G(d,p) optimum geometries. All calculations were performed by using Gaussian 09W program package [42].

General Procedure for the MCR's of compounds 4a-q.

The mixture of 6-aminopyrimidin-4-one **1** (1 mmol), naphthalene-1,2,4(3*H*)-trione **2** (1 mmol) and aldehyde **3** (1 mmol), were irradiated for 5-9 minutes and 200 °C under solvent-free conditions. Upon completion, monitored by TLC, the reaction mixture was cooled to room temperature. The solid was further purified by recrystallization from EtOH (95%).

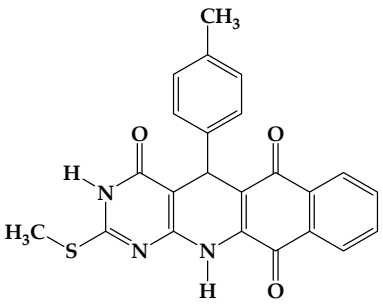
Spectroscopic Data of 4a- q

2-methylthio-5-phenyl-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4a**).



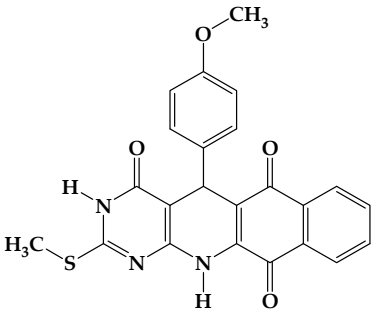
80%. M.p. >300 °C. IR (KBr, υ cm^{-1}), 3398 (N-H st), 2689 (CH_3 st), 1652, 1630 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.55 (s, 3H, SCH_3), 5.25 (s, 1H, CH), 7.11 (t, *J* = 6.78 Hz, 1H, H*p*), 7.21 (t, *J* = 7.28 Hz, 2H, H*m*), 7.30 (d, *J* = 7.78 Hz, 2H, H*o*), 7.76 – 7.84 (m, 2H, H8, H9), 7.90 (d, *J* = 7.28 Hz, 1H, H7), 8.03 (d, *J* = 7.03 Hz, 1H, H10), 9.60 (s, 1H, NH), 12.49 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.7 (SCH_3), 54.3 (C5), 117.4 (C4a), 124.5 (C*p*), 125.3 (C*o*), 125.6 (C10), 127.3 (C*m*), 127.9 (C7), 130.3, 131.8 (C10a), 133.2 (C8), 134.6 (C9), 139.3 (C5a), 145.0 (C*i*), 179.1 (C=O), 181.6 (C=O). MS: (70 eV) *m*/*z* = 401 (16, M^+), 325 (19), 324 (100), 276 (13). Anal. Calcd. for $C_{22}H_{15}N_3O_3S$ C, 65.82; H, 3.77; N, 10.47; found C, 65.85; H, 3.80; N, 10.45.

2-methylthio-5-(4-methylphenyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4b**).



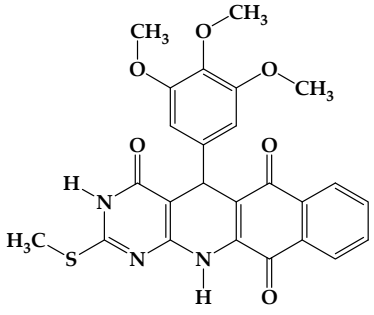
80%. M.p. >300 °C (dec). IR (KBr, υ cm^{-1}), 3395 (N-H st), 2929 (CH_3 st), 1651 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.18 (s, 3H, CH_3), 2.55 (s, 3H, SCH_3), 5.21 (s, 1H, CH), 7.00 (d, *J* = 8.03 Hz, 2H, Hm), 7.16 (d, *J* = 8.03 Hz, 2H, H*o*), 7.77 – 7.84 (m, 2H, H8, H9), 7.90 (d, *J* = 7.53 Hz, 1H, H7), 8.02 (d, *J* = 7.03 Hz, 1H, H10), 9.58 (s, 1H, NH), 12.51 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.7 (*p*-CH_3), 20.5 (SCH_3), 34.1 (C5), 117.7 (C4a), 125.6 (C10), 125.9 (C7), 127.7 (C*o*), 128.7 (C*m*), 130.3 (C6a), 131.9 (C10a), 133.3 (C8), 134.8 (C9), 135.6 (C2), 139.2 (C5a), 142.2 (C*i*), 179.2 (C=O), 181.7 (C=O). MS: (70 eV) *m*/*z* (%) = 415 (30, M^+), 324 (100), 276 (14). Anal. Calcd. for $C_{23}H_{17}N_3O_3S$ C, 66.49; H, 4.12; N, 10.11; found C, 66.48; H, 4.13; N, 10.14.

5-(4-methoxyphenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4c**).



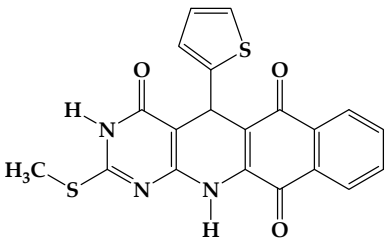
Yellow crystalline solid, 80%. M.p. >300°C (dec). IR (KBr, υ cm^{-1}), 3272 (N-H st), 2841 (CH_3 st), 1674, 1650 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.55 (s, 3H, SCH_3), 3.65 (s, 3H, OCH_3), 5.18 (s, 1H, H5), 6.76 (d, *J* = 8.79 Hz, 2H, H*o*), 7.18 (d, *J* = 8.79 Hz, 2H, H*m*), 7.77-7.85 (m, 2H, H8, H9), 7.90 (d, *J* = 7.53 Hz,1H, H7), 8.02 (d, *J* =7.03 Hz, 1H, H10), 9.60 (s, 1H, H12), 12.52 (s, 1H, H3). ^{13}C NMR δ (ppm): 12.7 (SCH_3), 34.0 (OCH_3), 55.0 (C5), 114.0 (C*o*), 129.0 (C*p*), 158.0 (C=O). MS: (70 eV) *m*/*z* = 431 (61, M^+), 325 (19), 324 (100), 276 (18), 248 (12). Anal. Calcd. for $C_{23}H_{17}N_3O_4S$ C, 64.03; H, 3.97; N, 9.74; found C, 64.02; H, 4.01; N, 9.78.

2-methylthio-5-(3,4,5-trimethoxyphenyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4d**).



80%. M.p. 265 °C. IR (KBr, υ cm^{-1}), 3264 (N-H st), 2933 (CH3 st), 1656 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.55 (s, 3H, SCH_3), 3.58 (s, 3H, OCH_3), 3.67 (s, 6H, OCH_3), 5.22 (s, 1H, CH), 6.57 (s, 2H), 7.77 – 7.85 (m, 2H, H9, H8), 7.93 (d, *J* = 8.53 Hz, 1H, H7), 8.03 (d, *J* = 8.78 Hz, 1H, H10), 9.49 (s, 1H, NH), 12.48 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.5 (SCH_3), 34.5 (C5), 55.7 (OCH_3), 59.6 (OCH_3), 105.2 (C*o*), 125.4 (C7), 125.7 (C10), 133.0 (C8), 134.5 (C9), 135.6, 136.3 (C5a), 139.2, 140.3 (C*i*), 152.4 (C11a), 178.9 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 491 (48, M^+), 460 (17), 325 (19), 324 (100), 276 (18). Anal. Calcd. for $C_{25}H_{21}N_3O_6S$ C, 61.09; H, 4.31; N, 8.55; found C, 61.12; H, 4.30; N, 8.58.

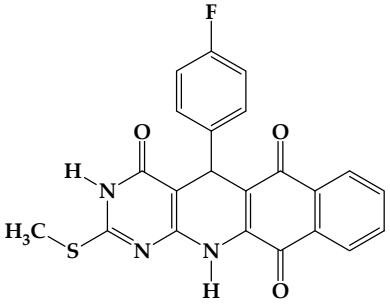
2-methylthio-5-(2-thienyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4e**).



70%. M.p. 315 °C. IR (KBr, υ cm^{-1}), 3384 (N-H st), 2969 (CH_3 st), 1655 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.55 (s, 3H, SCH_3), 5.53 (s, 1H, CH), 6.81 – 6.85 (m, 2H, Hetaryl), 7.25 (d, *J* = 6.28 Hz, 1H, Hetaryl) 7.77 – 7.86 (m, 2H, H9, H8), 7.97 (d, *J* = 8.53 Hz, 1H, H7), 8.04 (d, *J* = 8.53 Hz, 1H, H10), 9.86 (s, 1H, NH), 12.64 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.7 (SCH_3), 29.1 (CH), 116.6 (C4a), 124.3 (CH, Hetaryl), 124.5 (CH, Hetaryl), 125.7 (C10), 126.0 (CH, Hetaryl),

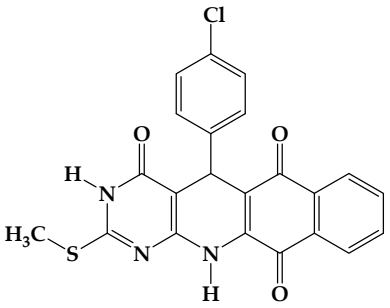
126.7 (C7), 130.3 (C6a), 131.7 (C10a), 133.3 (C8), 134.8 (C9), 138.9 (C5a), 148.0 (C2), 179.1 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 407 (100, M^+), 392 (11), 346 (18), 324 (59), 276 (18). Anal. Calcd. for $C_{20}H_{13}N_3O_3S_2$ C, 58.95; H, 3.22; N, 10.31; found C, 58.99; H, 3.25; N, 10.34.

5-(4-fluorophenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4f**).



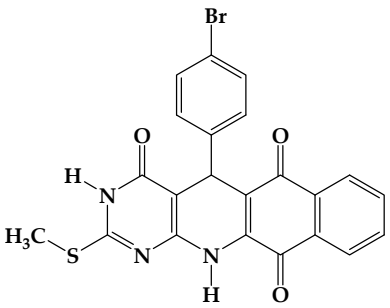
70%. M.p. >300 °C. IR (KBr, υ cm^{-1}), 3337 (NH st), 1656 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.56 (s, 3H, SCH_3), 5.25 (s, 1H, H5), 7.03 (t, *J* = 8.79 Hz, 2H, H*o*), 7.34 (d, *J* = 7.03 Hz, 2H, H*m*), 7.79 – 7.83 (m, 2H, H8, H9), 7.90 (d, *J* = 6.78 Hz, 1H, H7), 8.03 (d, *J* = 7.28 Hz, 1H, H10), 9.64 (s, 1H, NH), 12.53 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.8 (SCH_3), 35.7 (C5), 114.8 (C4a), 124.8 (C10), 128.6 (C7), 129.4 (C*o*), 129.5 (C*m*), 131.1 (C8), 134.6 (C9), 141.2 (C*i*), 145.5, 162.3, 178.6 (C=O). MS: (70 eV) *m*/*z* (%) = 419 (84, M^+), 417, (25), 474 (50), 324 (100). Anal. Calcd. for $C_{22}H_{14}FN_3O_3S$ C, 63.00; H, 3.36; N, 10.02; found C, 63.04; H, 3.34; N, 10.05.

5-(4-chlorophenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4g**).



80%. M.p. >300 °C. IR (KBr, υ cm^{-1}), 3367 (NH st), 2684 (CH_3 st), 1652, 1626 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.55 (s, 3H, SCH_3), 5.23 (s, 1H, H5), 7.26 (d, *J* = 8.54 Hz, 2H, H*o*), 7.32 (d, *J* = 8.54 Hz, 2H, H*m*), 7.79 – 7.82 (m, 2H, H8, H9), 7.90 (d, *J* = 7.03 Hz, 1H, H7), 8.03 (d, *J* = 7.03 Hz, 1H, H10), 9.66 (s, 1H, NH), 12.53 (s, 1H, NH). ^{13}C NMR δ (ppm): 12.7 (SCH_3), 34.3 (C5), 125.6 (C10), 125.9 (C7), 128.1 (C*o*), 129.7 (C*m*), 130.4 (C6a), 131.8 (C10a), 133.3, 134.7 (C9), 139.4 (C5a), 143.9 (C*i*), 178.5 (C4), 179.2 (C=O), 181.6 (C=O). MS: (70 eV) *m*/*z* (%) = 437 (6, M^{+2}), 436 (5.7, M^{+1}), 435 (15, M^+), 326 (6), 325 (18), 324 (100), 276 (13). Anal. Calcd. for $C_{22}H_{14}ClN_3O_3S$ C, 60.62; H, 3.24; N, 9.64; found C, 60.64; H, 3.22; N, 9.68.

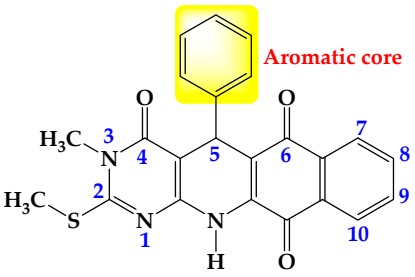
5-(4-bromophenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4h**).



80%. M.p. >300 °C. IR (KBr, υ cm^{-1}), 3369 (NH st), 1658 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.56 (s, 3H, SCH_3), 5.33 (s, 1H, H5), 7.54 (d, *J* = 8.28 Hz, 2H, H*o*), 7.58 (d, *J* = 8.28 Hz, 2H, H*m*), 7.77 – 7.82 (m, 2H, H8, H9), 7.89 (d, 1H, *J* = 7.27 Hz, H7), 8.03 (d, 1H, *J* = 7.03 Hz, H10), 9.72 (s, 1H, NH), 12.55 (s, 1H, NH).^{13}C NMR δ (ppm): 12.7 (SCH_3), 35.0 (C5), 116.5 (C5a), 125.0, 125.6 (C10), 125.9 (C7), 127.8 (C*o*), 129.5 (C*m*), 131.7 (C10a), 133.2 (C8), 134.7 (C9), 139.7 (C*i*), 149.3 (C2), 162.2, 178.9 (C4), 179.0 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 469 (17), 467 (8), 325 (19), 324 (100), 276 (14). Anal. Calcd. for $C_{22}H_{14}BrN_3O_3S$ C, 55.01; H, 2.94; N, 8.75; found C, 55.04; H, 2.98 N, 8.72.

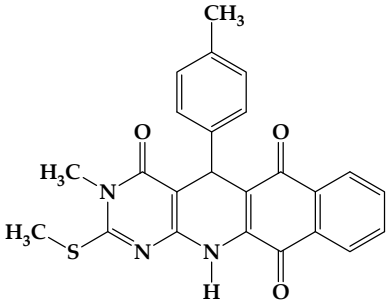
3-methyl-2-(methylthio)-5-phenyl-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4i**).

Red solid. 81%. M.p. 277 °C. IR (KBr, υ cm^{-1}), 3227 (N-H st), 1647 (C=O, st), 1522 (C=C, st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.62 (s, 3H, SCH_3), 3.31 (s, 3H, NCH_3), 5.24 (s, 1H. CH) 7.10 (t, *J* = 7.03 Hz, 1H, H*p*), 7.20 (t, *J* = 7.53 Hz, 2H, H*m*), 7.29 (d, *J* = 7.28 Hz, 2H, H*o*), 7.70 – 7.81 (m, 2H, H9, H8), 7.87 (d, *J* = 7.53 Hz, 1H, H7), 8.01 (d, *J* = 7.28 Hz, 1H, H10), 9.68 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 30.0 (NCH_3), 35.3 (C5), 117.4 (C4a), 125.6 (C10), 125.8 (C7), 126.4 (C*p*), 128.0 (C*o*), 128.6 (C*m*), 130.3 (C6a), 131.8 (C10a), 133.2 (C8), 134.7 (C9), 139.2 (C5a), 145.0 (C*i*), 149.7 (C2), 160.2 (C4, C=O), 161.6 (C12a), 179.1 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 414 (11, M^+), 337 (100). Anal. Calcd. for $C_{23}H_{17}N_3O_3S$ C, 66.49; H, 4.12; N, 10.11; found C, 66.47; H, 4.15; N, 10.12.



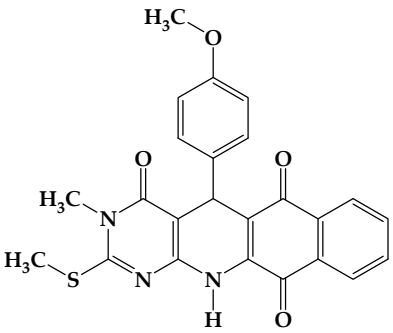
3-methyl-2-(methylthio)-5-(4-methylphenyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4j**).

Red solid. 75 %. M.p. 280 °C. IR (KBr, υ cm^{-1}), 3234 (NH st), 1650 (C=0 st), (1521 C=C st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.18 (s, 3H, *p*-CH_3), 2.63 (s, 3H, SCH_3), 2.75 (s, 3H, NCH_3), 5.22 (s, 1H, H5), 7.02 (d, *J* = 8.03 Hz, 2H, H*m*), 7.17 (d, *J* = 8.03, 2H, H*o*), 7.79-7.83 (m, 2H, H8, H9), 7.90 (d, *J* = 7.28 Hz, 1H, H7), 8.03 (d, *J* = 7.28 Hz, 1H, H-10), 9.72 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (*p*-CH_3), 20.5 (SCH_3), 29.8 (NCH_3), 34.9 (C5), 117.6 (C4a), 125.6 (C10), 125.8 (C7), 127.8 (C*o*), 128.6 (C*m*), 130.3 (C6a), 131.8 (C10a), 133.2 (C8), 134.7 (C9), 135.5 (C11a), 139.1 (C5a), 142.1 (C*i*), 149.7 (C2), 160.2 (C=O), 161.4 (C12a), 179.2 (C=O), 181.6 (C=O). MS: (70 eV) *m*/*z* (%) = 429 (22, M^+), 337 (100). Anal. Calcd. for $C_{24}H_{19}N_3O_3S$ C, 67.12; H, 4.46; N, 9.78; found C, 67.15; H, 4.45; N, 9.76.



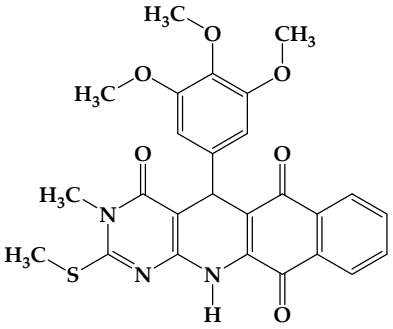
3-methyl-5-(4-methoxyphenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4k**).

Red solid. 70%. M.p. 282 °C. IR (KBr, υ cm^{-1}), 3222 (NH st), 1647 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.63 (s, 3H, SCH_3), 3.32 (s, 3H, NCH_3), 3.84 (s, 3H, OCH_3), 5.21 (s, 1H, H5), 6.77 (d, *J* = 8.79 Hz, 2H, H*o*), 7.21 (d, *J* = 8.53 Hz, 2H, H*m*), 7.78 – 7.82 (m, 2H, H8, H9), 7.89 (d, *J* = 8.54 Hz, 1H, H7), 8.03 (d, *J* = 8.53 Hz, 1H, H10), 9.66 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 29.9 (NCH_3), 34.4 (C5), 54.9 (OCH_3), 113.5 (C*o*), 117.7 (C4a), 125.6 (C10), 128.8 (C*m*), 130.3 (C6a), 131.8 (C*i*), 133.1 (C7), 134.7 (C9), 137.3 (C10a), 138.9 (C5a), 149.6 (C2), 157.8 (C2), 160.2 (C=O), 161.4 (C12a). MS: (70 eV) *m*/*z* (%) = 445 (45, M^+), 337 (100). Anal. Calcd. for $C_{24}H_{19}N_3O_4S$ C, 64.71; H, 4.30; N, 9.43; found C, 64.75; H, 4.27; N, 9.45.



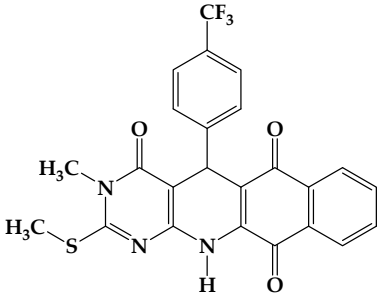
3-methyl-2-(methylthio)-5-(3,4,5-trimethoxyphenyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4l**).

Brown solid. 80%. M.p. 263 °C. IR (KBr, υ cm^{-1}), 3243 (NH st), 1648 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.62 (s, 3H, SCH_3), 3.33 (s, 3H, NCH_3), 3.56 (s, 3H, OCH_3), 3.67 (s, 6H, OCH_3), 5.21 (s, 1H, H5), 6.57 (s, 2H, H*o*) 7.78 – 7.82 (m, 2H, H8, H9), 7.91 (d, *J* = 7.28 Hz, 1H, H7), 8.03 (d, *J* = 7.28 Hz, 1H, H10), 9.60 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 29.9 (NCH_3), 35.6 (C5), 55.8 (OCH_3), 59.7 (OCH_3), 105.6 (C*o*), 117.1 (C4a), 125.6 (C7), 125.8 (C10), 130.4 (C6a), 131.8 (C10a), 133.1 (C8), 134.6 (C9), 136.5 (C5a), 140.6 (C*i*), 149.7 (C2,), 152.5 (C11a), 161.5 (C12a), 179.1 (C=O), 181.6 (C=O). MS: (70 eV) *m*/*z* (%) = 505 (76, M^+), 474 (15), 337 (100). Anal. Calcd. for $C_{26}H_{23}N_3O_6S$ C, 61.77; H, 4.59; N, 8.31; found C, 61.79; H, 4.62; N, 8.34.



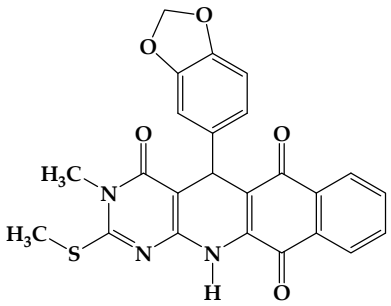
3-methyl-2-(methylthio)-5-(4-trifluoromethylphenyl)-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4m**).

Red solid. 75%. M.p. >300 °C. IR (KBr, υ cm^{-1}), 3447 (NH st), 1687 (C=O st), 1519 (C=C st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.74 (s, 3H, SCH_3), 2.88 (s, 3H, NCH_3), 5.33 (s, 1H, H5), 7.39 (d, *J* = 7.03 Hz, 1H, H7), 7.56 (d, *J* = 7.06 Hz, 2H, H*o*), 7.72 – 7.74 (d, *J* = 7.03 Hz, 2H, H*m*), 7.80 (t, 1H, H8), 7.89 (t, 1H, H9), 8.03 (d, *J* = 7.03 Hz, 1H, H10), 9.88 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.5 (SCH_3), 29.9 (NCH_3), 35.7 (C5), 99.5 (C4a), 111.6 (C5a), 127.0 (C10), 127.3 (C*o*), 128.0 (C7), 128.9 (C*m*), 133.2 (C8), 135.4 (C9), 139.7 (C*i*), 149.8 (C2), 157.3, 159.2 (C6a), 160.2 (C=O), 166.1 (C12a), 178.3 (C=O), 198.50 (C6). MS: (70 eV) *m*/*z* (%) = 480 (18, M^+), 337 (100), 437 (40). Anal. Calcd. for $C_{24}H_{16}F_3N_3O_3S$ C, 59.62; H, 3.34; N, 8.69; found C, 59.65; H, 3.30; N, 8.73.



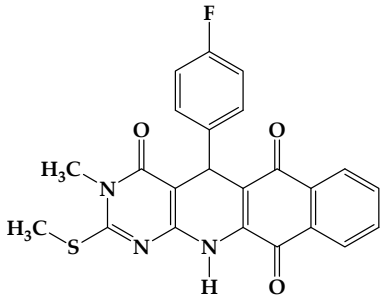
5-(benzo[*d*][1,3]dioxol-6-yl)-3-methyl-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4n**).

Red solid. 75%. M.p. 254 °C. IR (KBr, υ cm^{-1}), 3225 (NH st), 1647 (C=O st), 1519 (C=C st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.63 (s, 3H, SCH_3), 3.34 (s, 3H, NCH_3), 5.19 (s, 1H, H5), 5.91 (s, 2H, CH_2), 6.74 (d, *J* = 6.79 Hz, 2H, aryl), 6.86 (s, 1H, aryl), 7.78–7.84 (m, 2H, H8, H9), 7.91 (d, *J* = 7.89 Hz, 1H, H7), 8.03 (d, *J* = 8.02 Hz, 1H, H10), 9.72 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.45 (SCH_3), 29.9 (NCH_3), 35.0 (C5), 100.7 (CH_2), 107.8, 108.6 (C2′-C6′), 117.3 (C4a), 121.0 (C5′), 125.6 (C10), 125.9 (C7), 130.4 (C6a), 131.8 (C10a), 133.2 (C8), 134.7 (C9), 139.1 (C5a), 145.8 (C*i*), 146.9 (C11a), 149.6 (C2), 160.3 (C=O), 161.6 (C12a), 179.2 (C=O), 181.6 (C6). MS: (70 eV) *m*/*z* (%) = 458 (38, M^+), 337 (100). Anal. Calcd for $C_{24}H_{17}N_3O_5S$ C, 62.74; H, 3.73; N, 9.15; found C, 62.71; H, 3.71; N, 9.18.



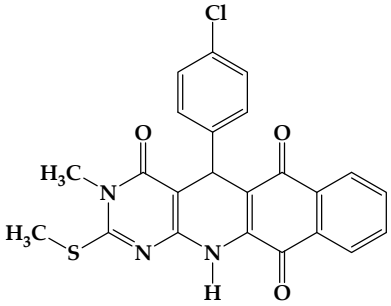
5-(4-fluorophenyl)-3-methyl-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4o**).

Red solid. 74%. M.p. 276 °C. IR (KBr, υ cm^{-1}), 3237 (NH st), 1646 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.61 (s, 3H, SCH_3), 3.30 (s, 3H, NCH_3), 5.22 (s, 1H, H5), 7.01 (d, *J* = 7.30 Hz, 2H, H*o*), 7.32 (t, *J* = 7.30 Hz, 2H, H*m*), 7.77-7.82 (m, 2H, H8, H9), 7.87 (d, *J* = 7.98 Hz, 1H, H7), 8.01 (d, *J* = 7.03 Hz, 1H, H10), 9.73 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 29.9 (NCH_3), 34.8 (C5), 114.6 (C4a), 114.8 (C6a), 117.1 (C10a), 125.6 (C10), 125.9 (C7), 129.8 (C*o*), 130.3 (C*m*), 131.7 (C11a), 133.2 (C8), 134.7 (C9), 139.3 (C*i*), 149.8 (C2), 179.1 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 441 (7, M^+), 432 (22), 430 (42), 387 (75), 337 (100). Anal. Calcd. for $C_{23}H_{16}FN_3O_3S$ C, 63.73; H, 3.72; N, 9.69; found C, 63.77; H, 3.76; N, 9.70.



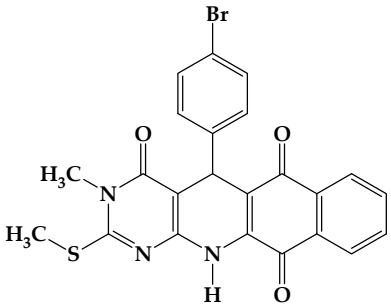
5-(4-chlorophenyl)-3-methyl-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4p**).

Red solid. 71%. M.p. 283 °C. IR (KBr, υ cm^{-1}), 3233 (NH st), 1648 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.62 (s, 3H, SCH_3), 3.31 (s, 3H, NCH_3), 5.24 (s, 1H, H5), 7.24 (d, *J* =8.28 Hz, 2H, H*o*), 7.32 (d, *J* = 8.28 Hz, 2H, H*m*), 7.78– 7.82 (m, 2H, H8, H9), 7.88 (d, *J* = 7.28 Hz, 1H, H7), 8.02 (d, *J* = 7.28 Hz, 1H, H10), 9.75 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 29.8 (NCH_3), 35.1 (C5), 116.8 (C4a), 125.6 (C10), 125.9 (C7) 127.9 (C*o*), 129.8 (C*m*), 133.2 (C8), 134.7 (C9), 139.5 (C5a), 143.9 (C*i*), 149.7 (C2), 160.2 (C4), 161.8 (C12a), 179.1 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) 448 (12, M^+), 337 (100). Anal. Calcd. for $C_{23}H_{16}ClN_3O_3S$ C, 61.40; H, 3.58; N, 9.34; found C, 61.37; H, 3.57; N, 9.33.



5-(4-bromophenyl)-3-methyl-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione (**4q**).

Red solid. 76%. M.p. 264 °C. IR (KBr, υ cm^{-1}), 3228 (NH st), 1650 (C=O st). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.62 (s, 3H, SCH_3), 3.30 (s, 3H, NCH_3), 5.20 (s, 1H, H5), 7.25 (d, *J* = 8.29 Hz, 2H, H*o*), 7.37 (d, *J* = 8.53 Hz, 2H, H*m*), 7.77 – 7.81 (m, 2H, H8, H9), 7.88 (d, *J* = 7.27 Hz, 1H, H7), 8.01 (d, *J* = 8.03 Hz, 1H, H10), 9.73 (s, 1H, NH). ^{13}C NMR δ (ppm): 14.4 (SCH_3), 29.8 (NCH_3), 35.2 (C5), 99.4 (C4a), 116.7 (C5a), 119.5 (C*p*) 125.5 (C10), 125.8 (C7), 130.2 (C*o*), 130.3 (C6a), 130.9 (C*m*), 131.7 (C10a), 133.2 (C8), 134.7 (C9), 139.4 (C*i*), 144.3 (C11a), 149.7 (C2), 160.1 (C4), 161.8 (C12a), 179.0 (C=O), 181.5 (C=O). MS: (70 eV) *m*/*z* (%) = 492 (9, M^+), 337 (100). Anal. Calcd. for $C_{23}H_{16}BrN_3O_3S$ C, 55.88; H, 3.26; N, 8.50; found C, 55.91; H, 3.29; N, 8.49.



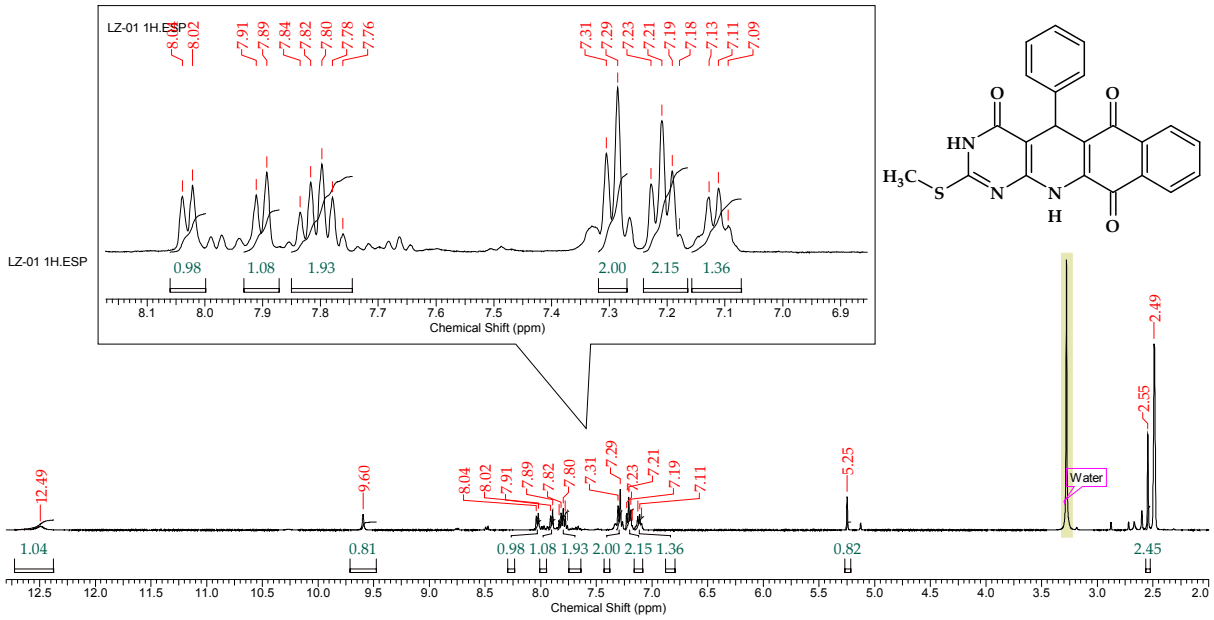


Figure S1. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4a**.

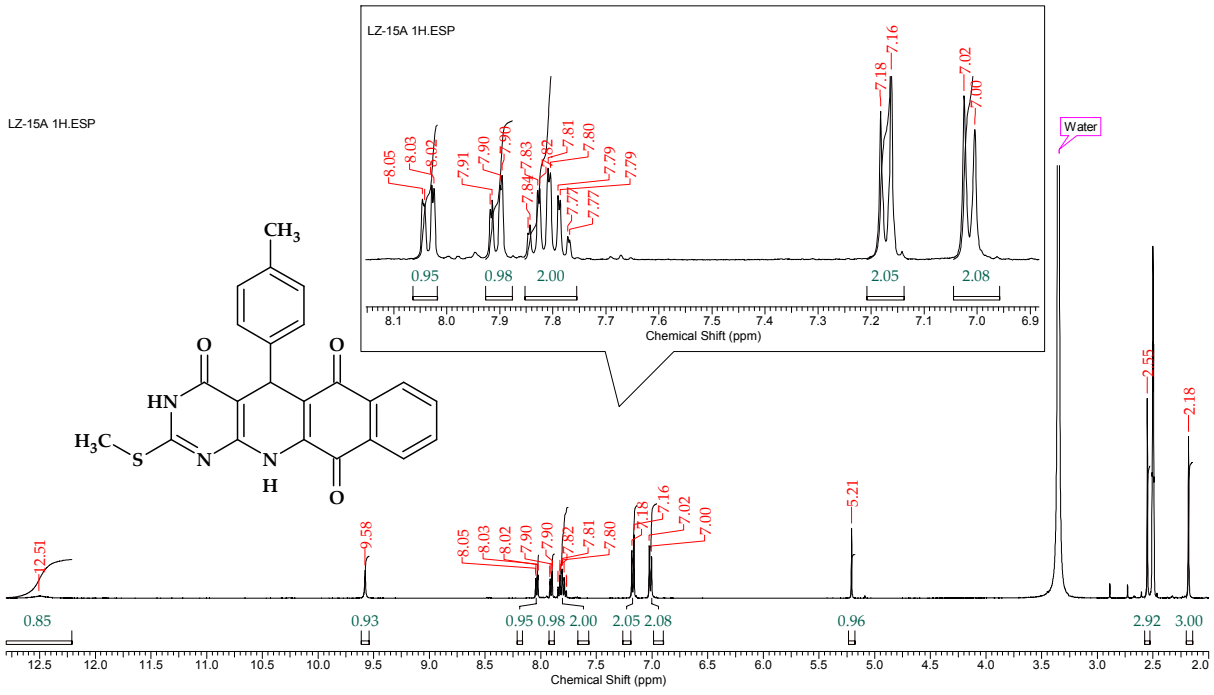


Figure S2. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4b**.

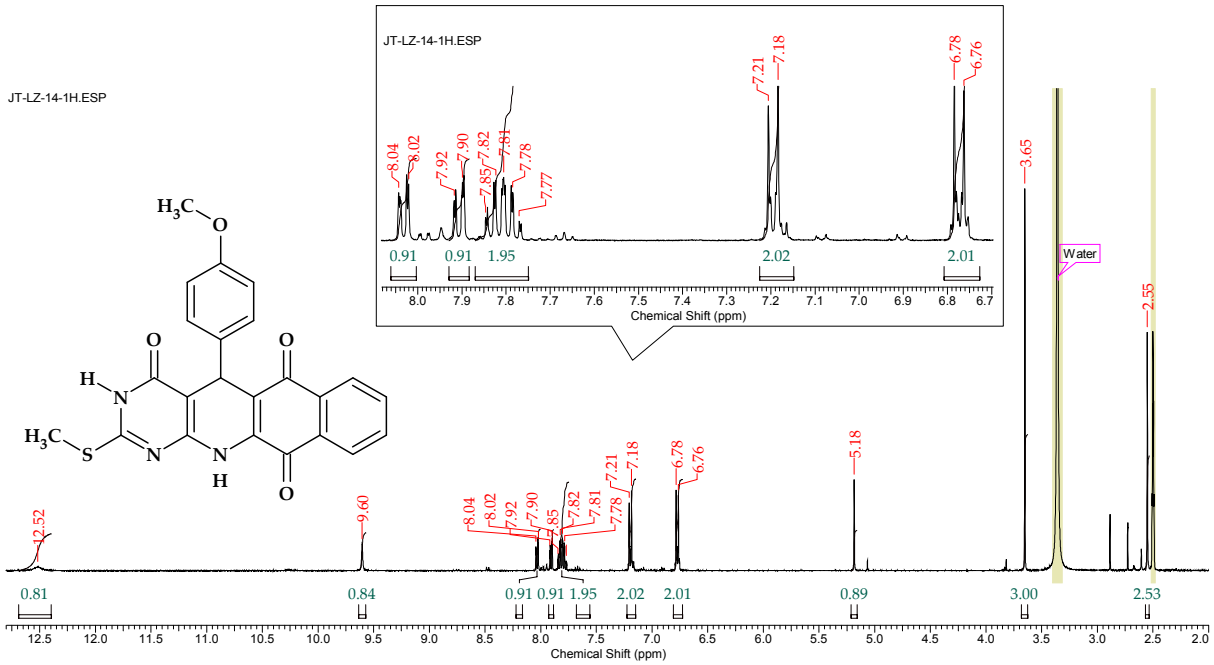


Figure S3. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4c**.

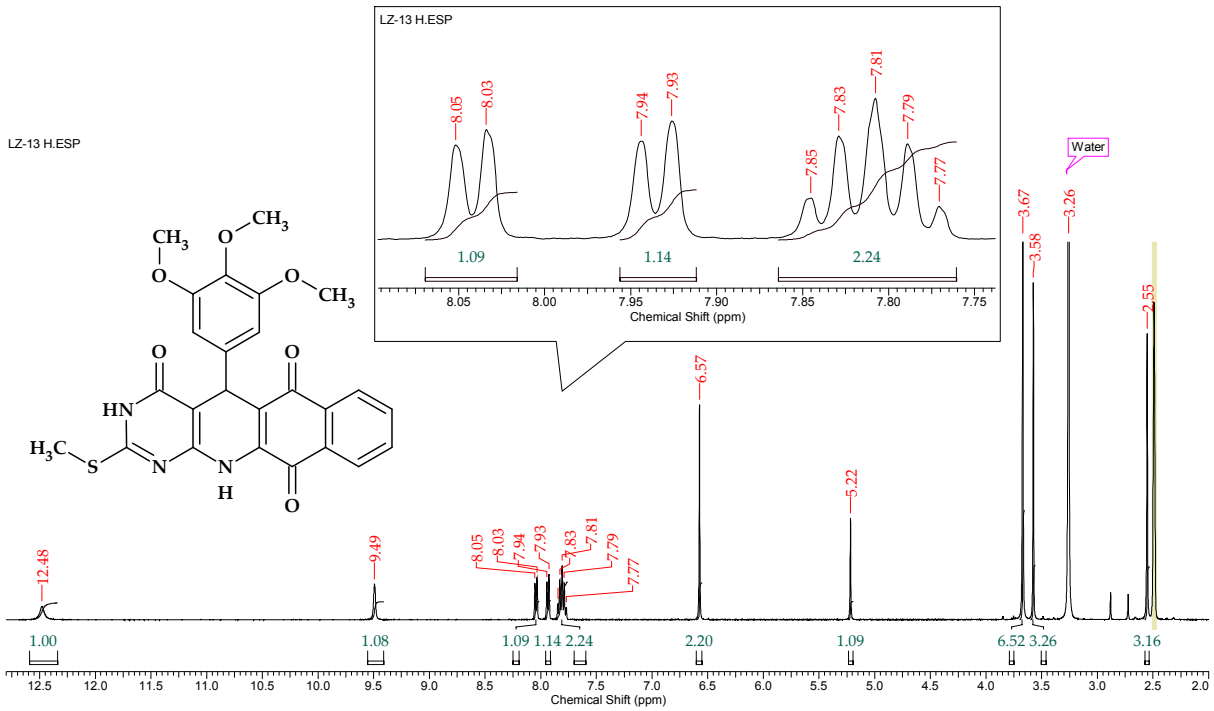


Figure S4. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4d**.

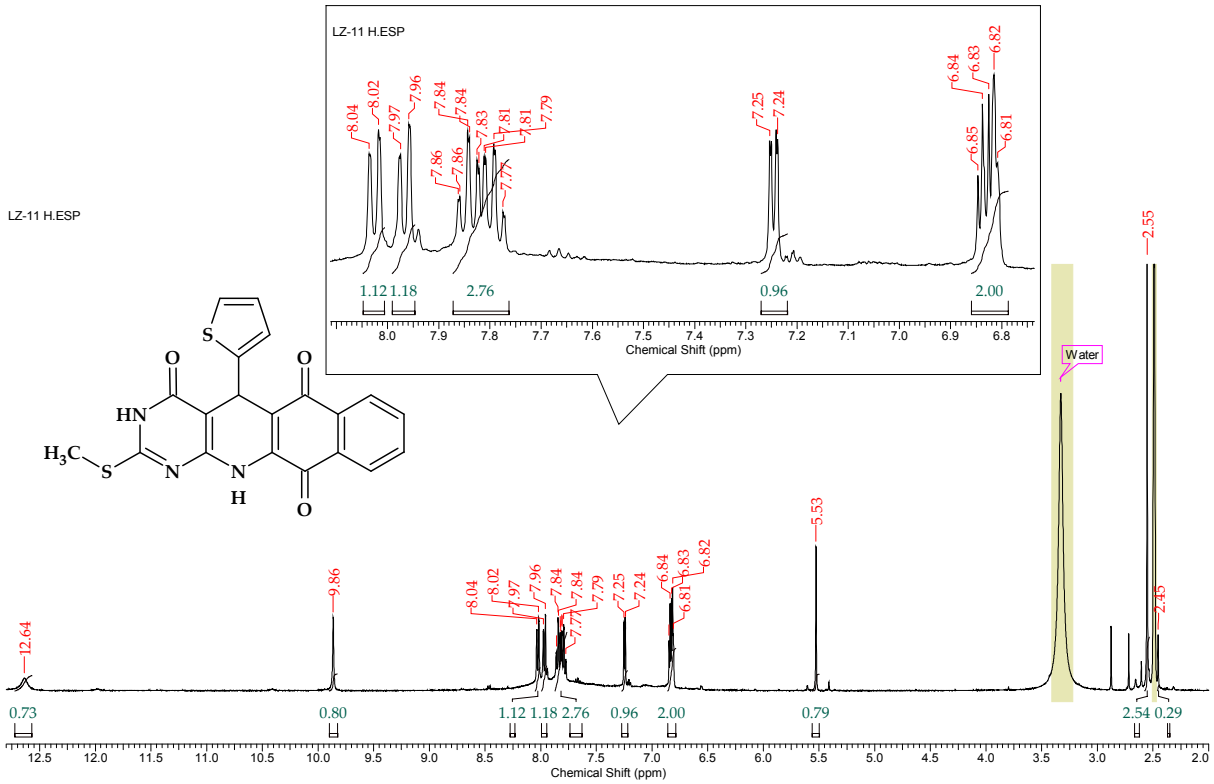


Figure S5. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4e**.

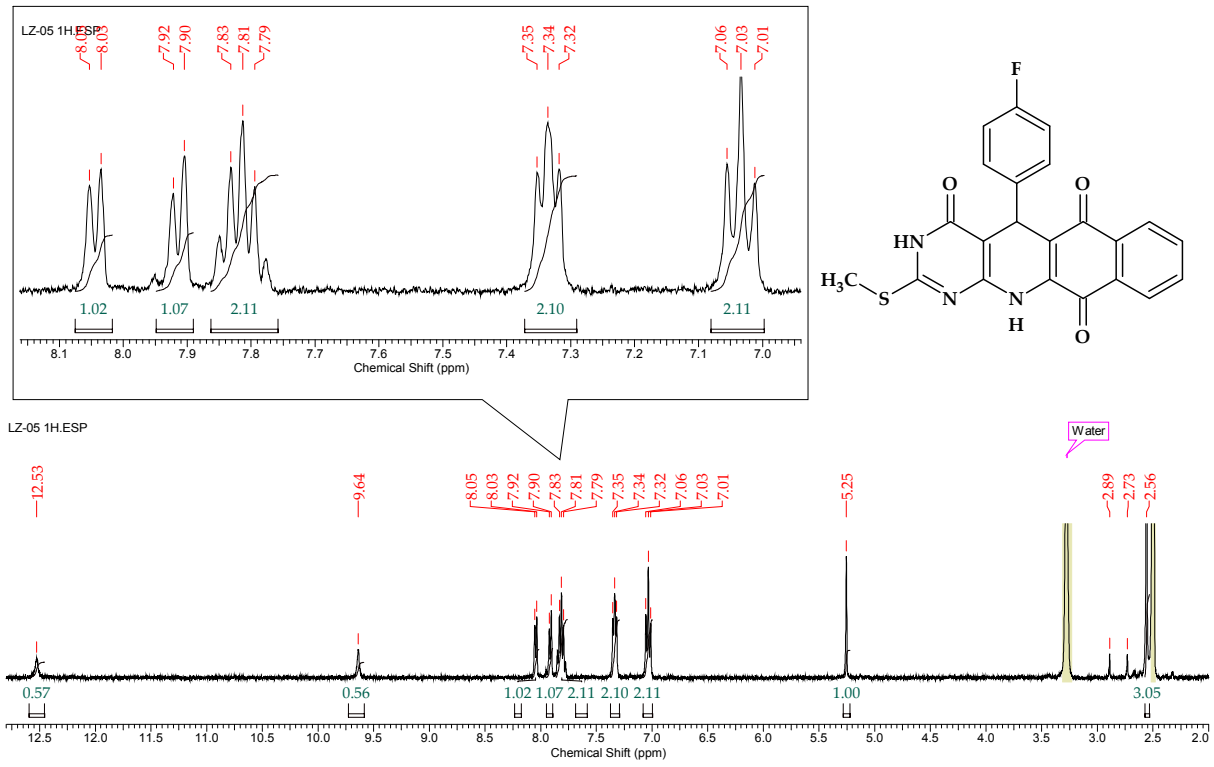


Figure S6. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4f**.

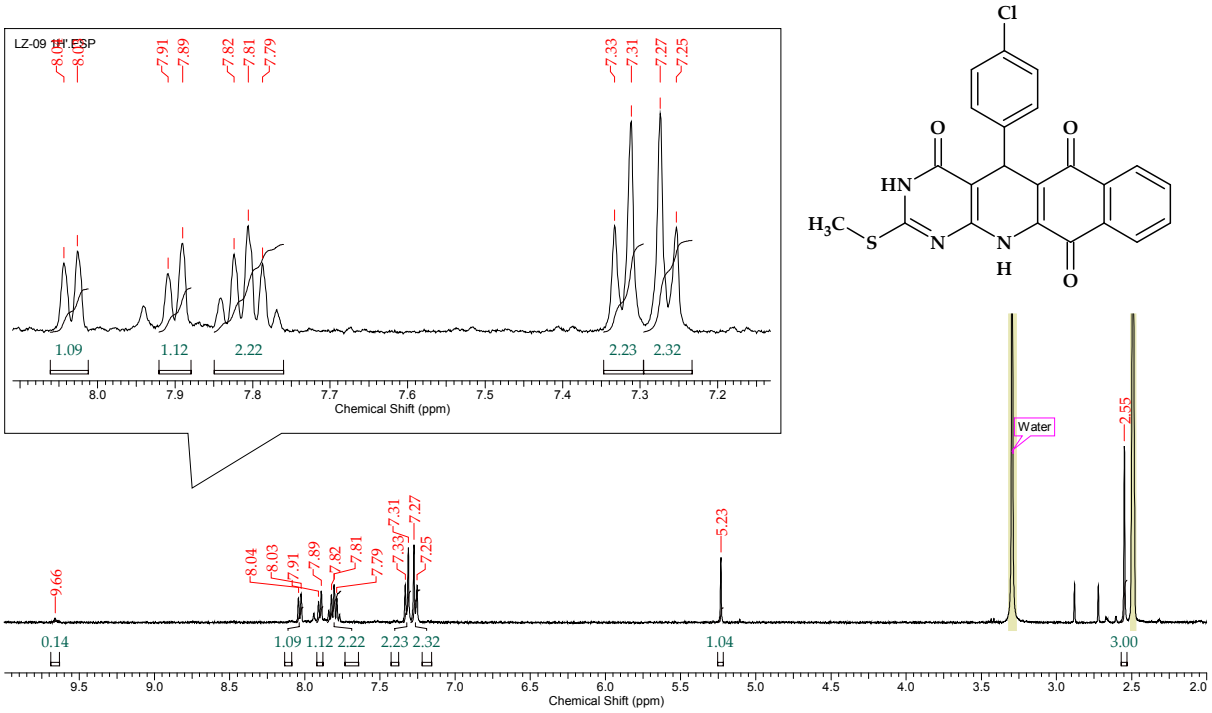


Figure S7. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4g**.

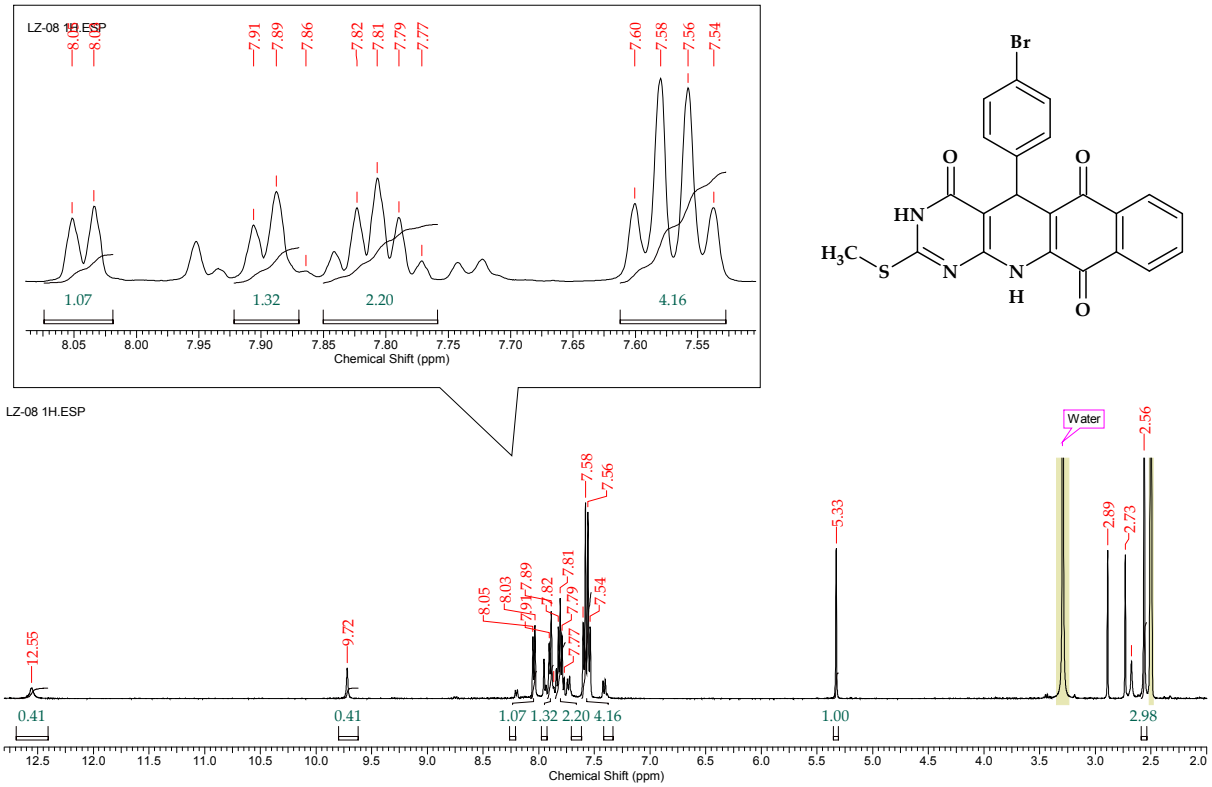


Figure S8. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4h**.

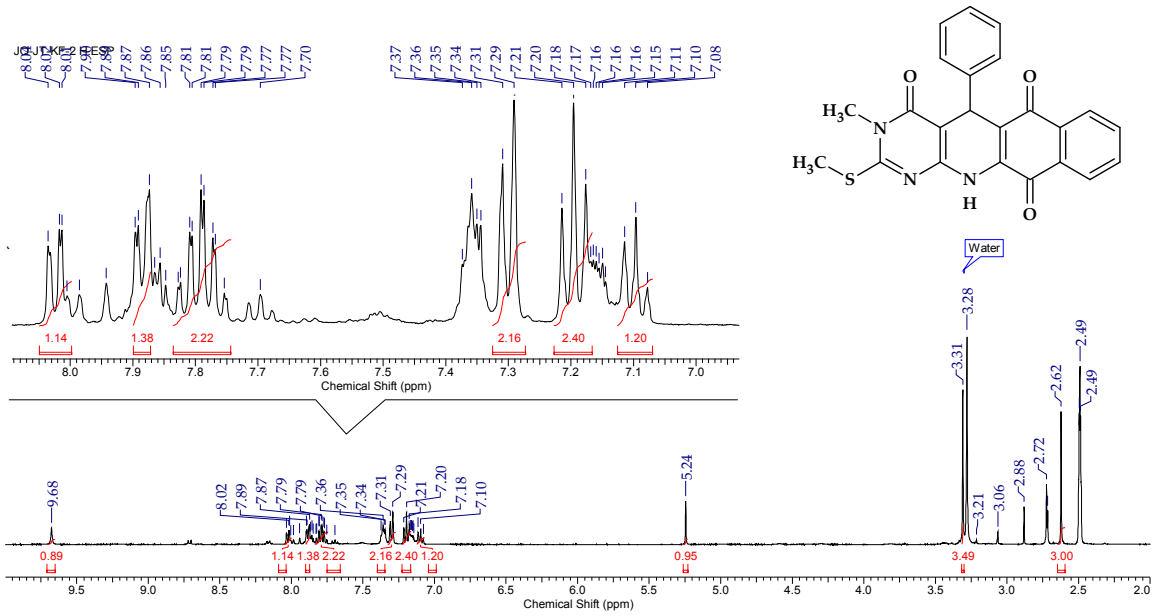


Figure S9. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4i**.

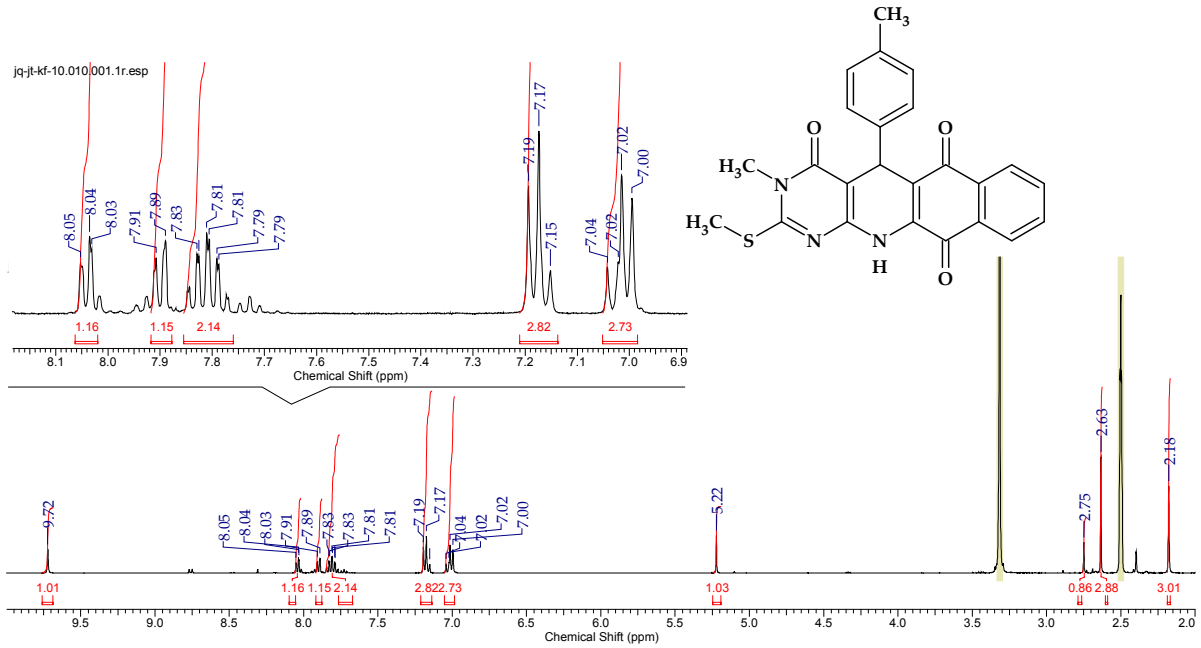


Figure S10. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4j**.

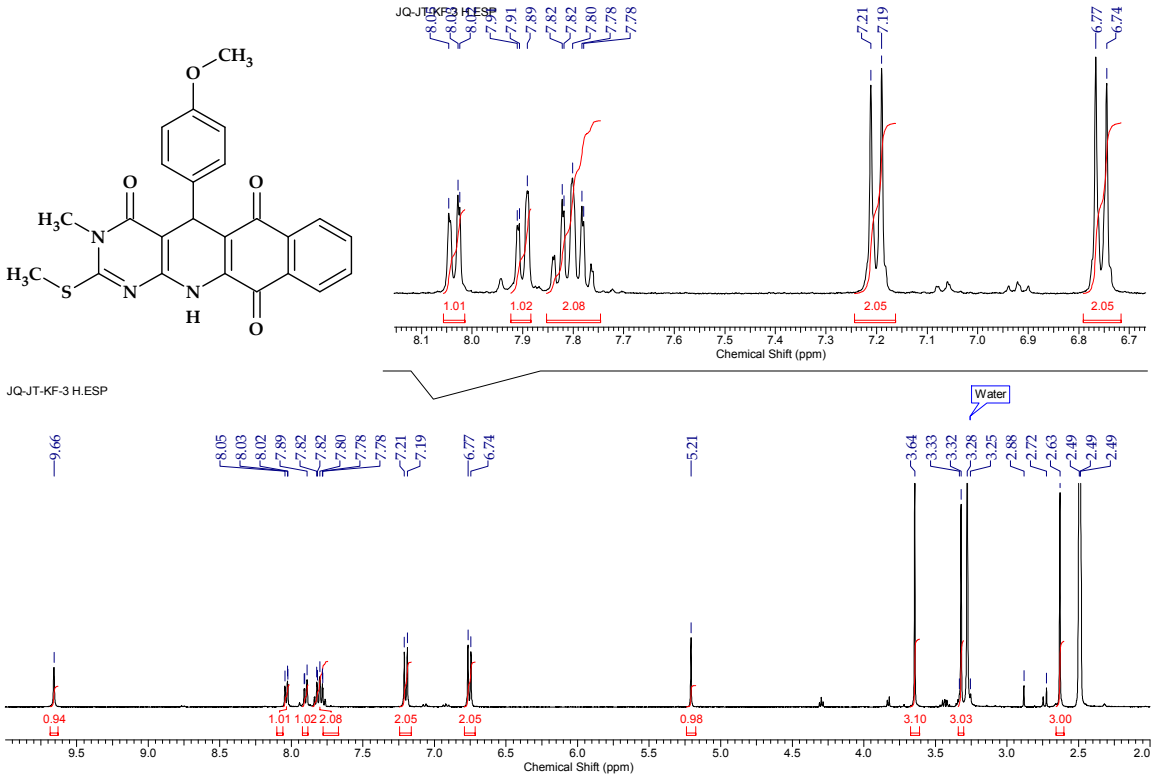


Figure S11. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4k**.

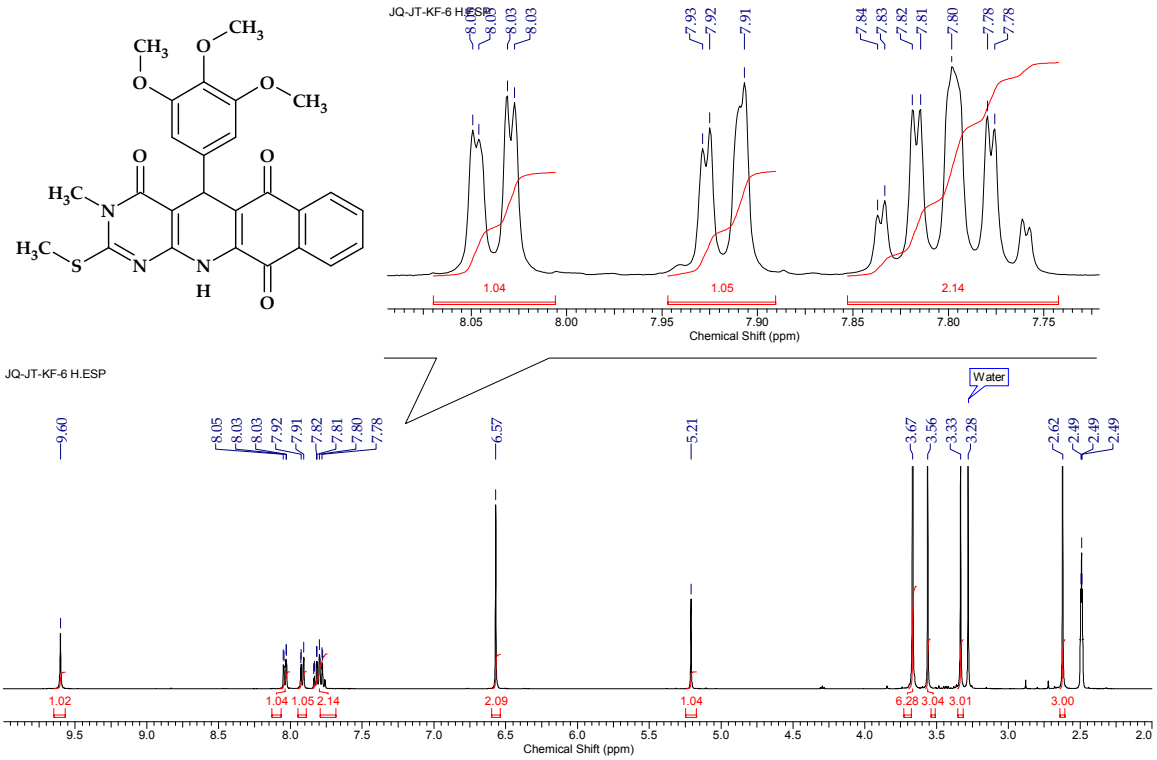


Figure S12. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4l**.

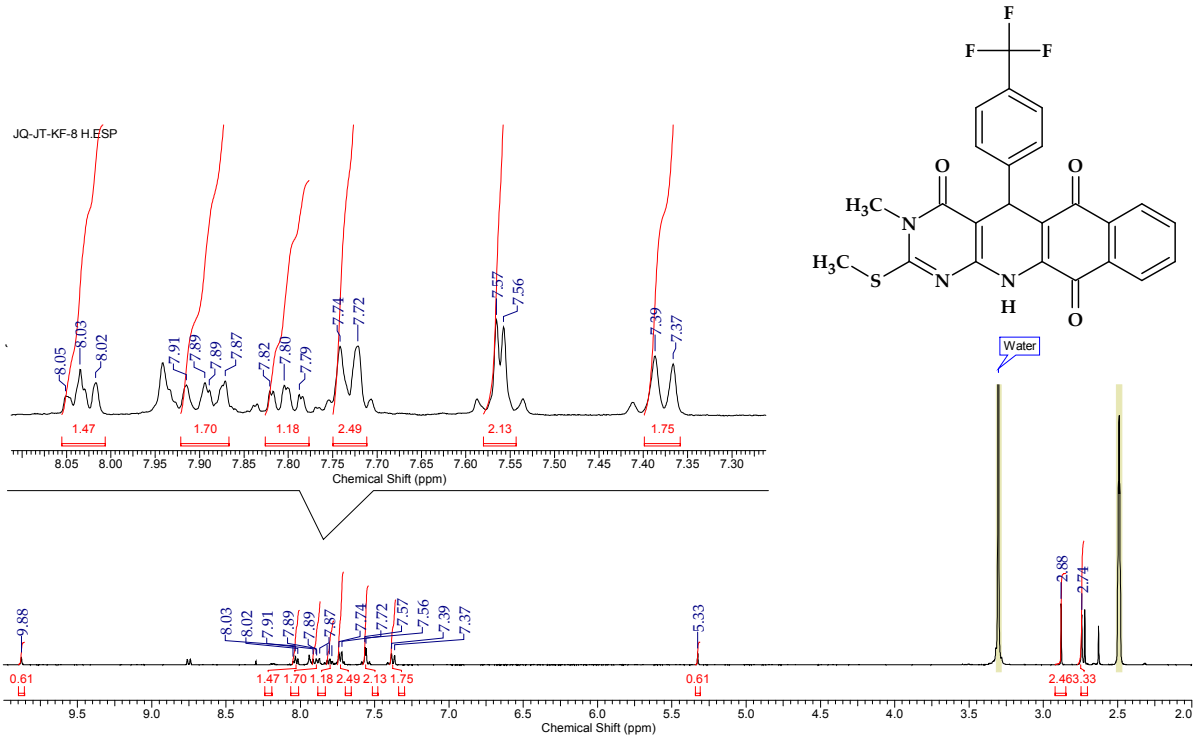


Figure S13. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4m**.

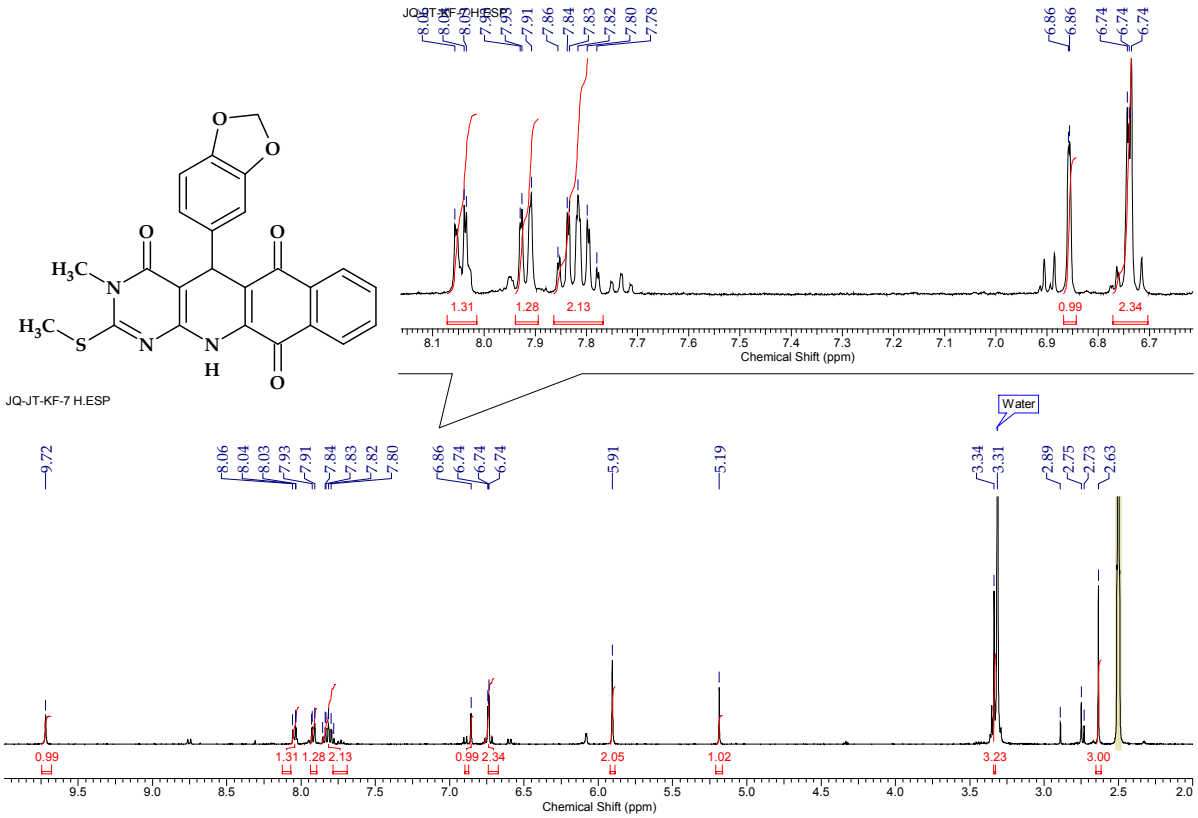


Figure S14. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4n**.

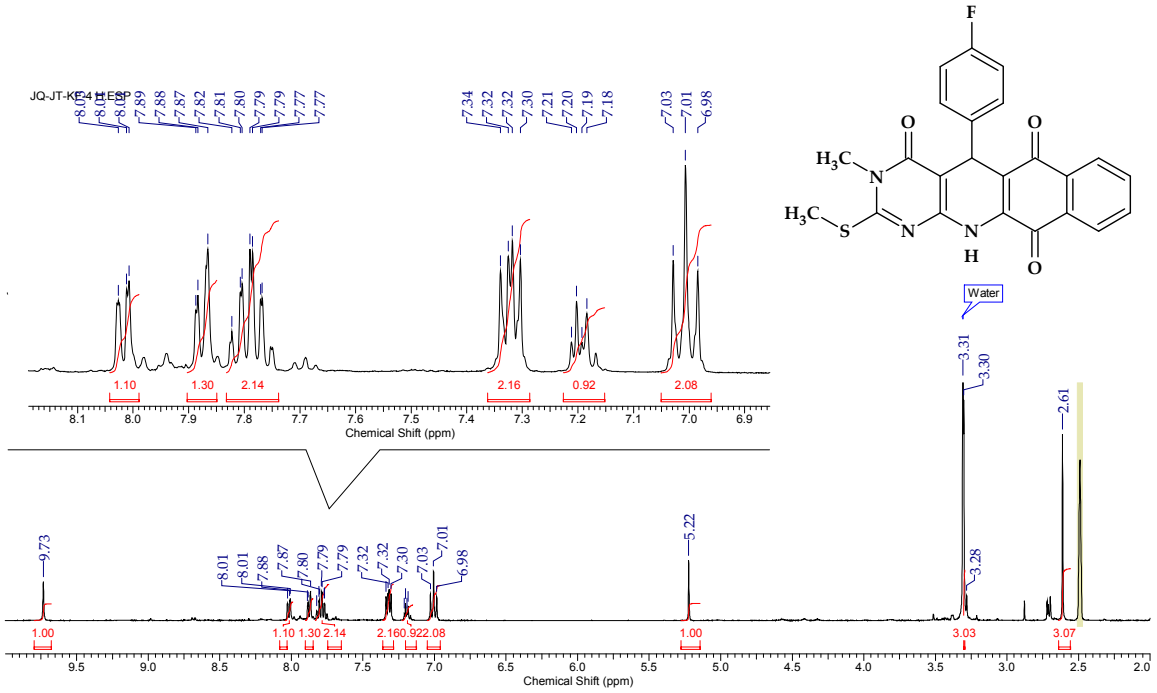


Figure S15. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4o**.

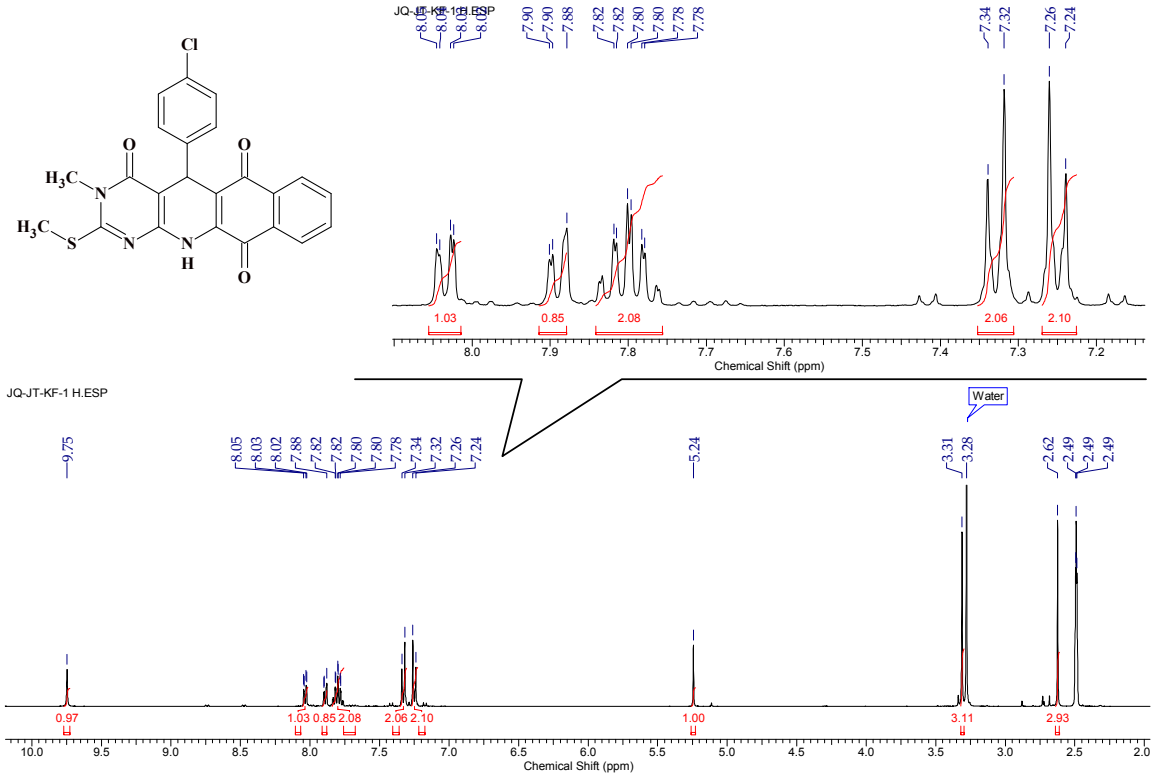


Figure S16. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4p**.

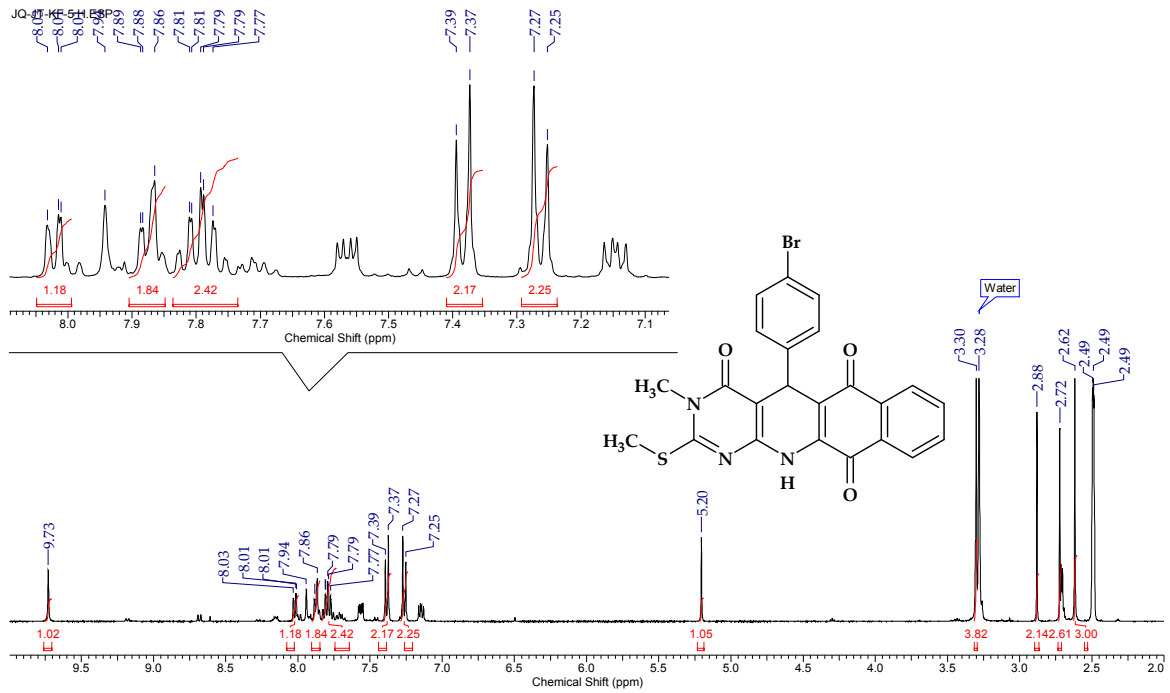


Figure S17. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of compound **4q**.

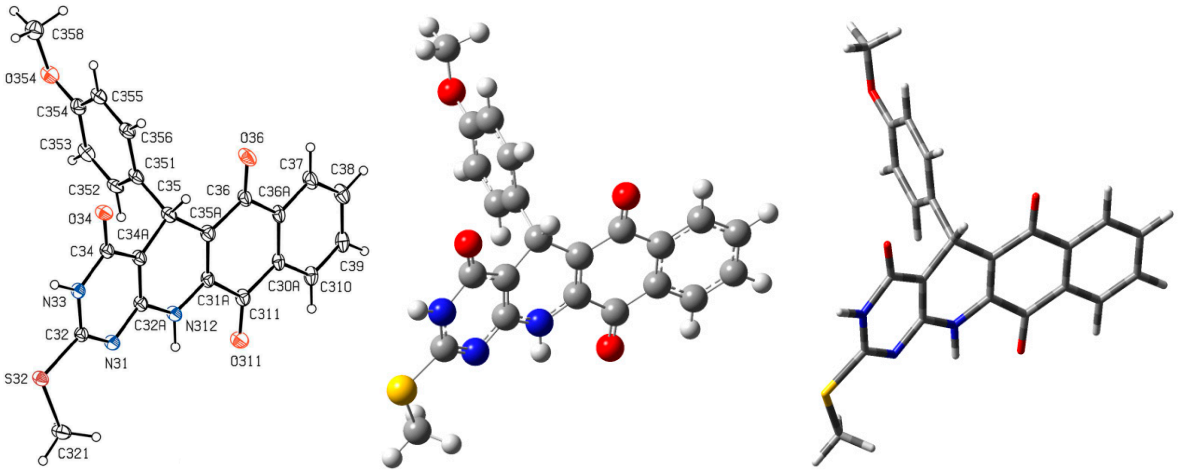


Figure S18. X-ray structure of 5-(4-methoxyphenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione **4c**: (Left) ORTEP diagram, displacement ellipsoids are drawn at the 30% probability level. (Right) The optimized structure with B3LYP/6-31G(d,p) level.

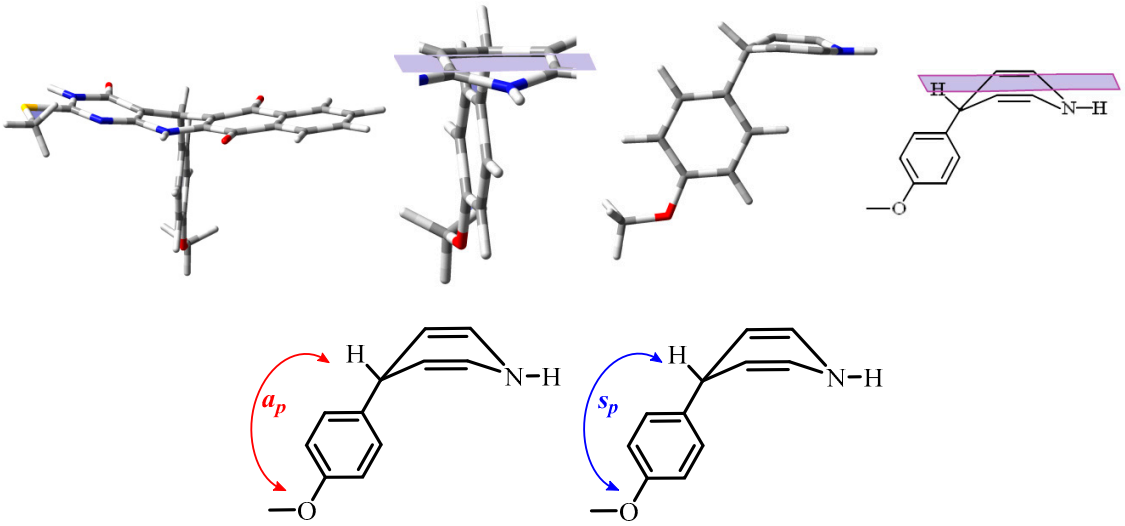


Figure S19. Conformation of the dihydropyridine ring in the structure of compound **4c**.

Table S1. X-ray data and calculated bond lengths, bond angles and dihedral angles of **4c** at DFT method.

Parameter			**Parameter**		
Bond Length (Å)	**Experimental X-ray**	**6-31G(d,p)**	**Bond Length (Å)**	**Experimental X-ray**	**6-31G(d,p)**
N_1-C_2	1.31 (4)	1.33	C_{11}-C_{17}	1.50 (4)	1.49
N_1-C_{13}	1.37 (4)	1.40	C_{11}-C_{18}	1.50 (4)	1.51
C_2-N_3	1.36 (4)	1.38	C_{11}-O_{23}	1.22 (4)	1.21
C_2-S_{19}	1.75 (3)	1.76	N_{12}-C_{13}	1.38 (4)	1.40
N_3-C_4	1.39 (4)	1.47	N_{12}-C_{18}	1.37 (4)	1.41
C_4-C_{14}	1.43 (4)	1.44	C_{13}-C_{14}	1.37 (4)	1.39
C_4-O_{21}	1.24 (4)	1.21	C_{15}-C_{18}	1.34 (4)	1.36
C_5-C_{14}	1.52 (4)	1.51	C_{16}-C_{17}	1.39 (4)	1.41
C_5-C_{15}	1.52 (4)	1.52	S_{19}-C_{20}	1.79 (3)	1.80
C_5-C_{24}	1.54 (5)	1.52	C_{24}-C_{25}	1.39 (4)	1.41
C_6-C_{15}	1.47 (4)	1.49	C_{24}-C_{29}	1.38 (5)	1.40
C_6-C_{16}	1.50 (4)	1.50	C_{25}-C_{26}	1.38 (5)	1.39
C_6-O_{22}	1.22 (4)	1.21	C_{26}-C_{27}	1.38 (5)	1.41
C_7-C_8	1.38 (4)	1.40	C_{27}-C_{28}	1.40 (5)	1.40
C_7-C_{16}	1.39 (4)	1.40	C_{27}-O_{44}	1.37 (4)	1.38

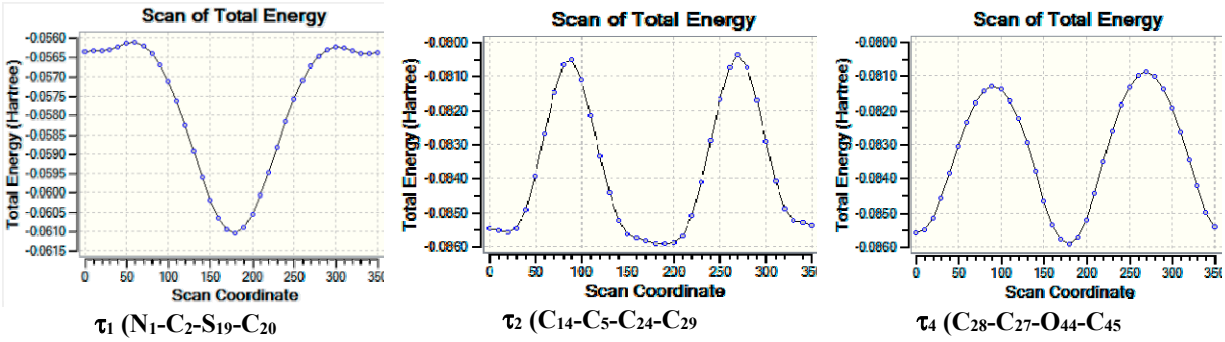
C_8-C_9	1.39 (5)	1.39	C_{28}-C_{29}	1.37 (5)	1.40
C_9-C_{10}	1.38 (5)	1.40	O_{44}-C_{45}	1.44 (4)	1.45
C_{10}-C_{17}	1.40 (4)	1.40			

Parameter			**Parameter**		
Bond angles °	**Experimental X-ray**	**6-31G(d,p)**	**Bond angles °**	**Experimental X-ray**	**6-31G(d,p)**
C_2-N_1-C_{13}	115.2 (3)	116.7	C_5-C_{14}-C_{13}	124.0 (3)	121.5
N_1-C_2-N_3	123.4 (3)	124.3	C_5-C_{15}-C_6	117.4 (3)	116.6
N_1-C_2-S_{19}	122.6 (2)	119.5	C_5-C_{15}-C_{18}	122.1 (3)	122.0
N_3-C_2-S_{19}	114.0 (2)	116.2	C_6-C_{15}-C_{18}	120.4 (3)	121.4
C_2-N_3-C_4	123.1 (2)	121.1	C_6-C_{16}-C_7	119.0 (3)	118.9
N_3-C_4-C_{14}	114.8 (3)	113.8	C_6-C_{16}-C_{17}	121.5 (3)	121.4
N_3-C_4-O_{21}	120.0 (3)	114.7	C_7-C_{16}-C_{17}	119.4 (3)	119.8
C_{14}-C_4-O_{21}	125.2 (3)	131.5	C_{10}-C_{17}-C_{11}	119.8 (3)	118.9
C_{14}-C_5-C_{15}	109.0 (3)	110.7	C_{10}-C_{17}-C_{16}	120.4 (3)	120.0
C_{15}-C_5-C_{24}	110.7 (3)	108.4	C_{11}-C_{17}-C_{16}	119.8 (3)	121.0
C_{15}-C_6-C_{16}	117.7 (3)	116.5	C_{11}-C_{18}-N_{12}	113.4 (3)	114.8
C_{15}-C_6-O_{22}	120.9 (3)	122.5	C_{11}-C_{18}-C_{15}	123.3 (3)	123.1
C_{16}-C_6-O_{22}	121.3 (3)	120.9	N_{12}-C_{18}-C_{15}	123.2 (3)	122.1
C_8-C_7-C_{16}	119.9 (3)	120.1	C_2-S_{19}-C_{20}	101.5 (15)	104.5
C_7-C_8-C_9	120.7 (3)	120.1	C_5-C_{24}-C_{25}	121.9 (3)	118.8
C_8-C_9-C_{10}	120.1 (3)	120.0	C_5-C_{24}-C_{29}	120.2 (3)	121.6
C_9-C_{10}-C_{17}	119.5 (3)	120.0	C_{25}-C_{24}-C_{29}	117.8 (3)	119.6
C_{17}-C_{11}-C_{18}	117.0 (3)	115.8	C_{24}-C_{25}-C_{26}	121.4 (3)	120.7
C_{17}-C_{11}-O_{23}	123.9 (3)	123.9	C_{25}-C_{26}-C_{27}	119.9 (3)	118.6
C_{18}-C_{11}-O_{23}	119.1 (3)	120.2	C_{26}-C_{27}-C_{28}	119.1 (3)	121.8
C_{13}-N_{12}-C_{18}	120.6 (3)	118.9	C_{27}-C_{28}-C_{29}	119.9 (3)	118.4
N_1-C_{13}-N_{12}	114.2 (3)	115.0	C_{24}-C_{29}-C_{28}	121.9 (3)	121.0

N_1-C_{13}-C_{14}	126.1 (3)	123.6	C_{27}-O_{44}-C_{45}	117.9 (3)	117.8
N_{12}-C_{13}-C_{14}	119.7 (3)	121.4	O_{44}-C_{27}-C_{26}	124.5 (3)	123.2
C_4-C_{14}-C_5	118.8 (3)	118.0	O_{44}-C_{27}-C_{28}	116.4 (3)	116.0
C_4-C_{14}-C_{13}	117.2 (3)	120.4			

Parameter			**Parameter**		
Dihedral angles °	**Experimental X-ray**	**6-31G(d,p)**	**Dihedral angles °**	**Experimental X-ray**	**6-31G(d,p)**
N_1-C_2-N_3-C_4	−0.7 (5)	1.3	C_{16}-C_{17}-C_{11}-C_{18}	−0.9 (5)	4.3
C_{13}-N_1-C_2-N_3	1.5 (5)	-1.3	C_{10}-C_{17}-C_{11}-C_{18}	177.8 (3)	-175.5
C_{13}-N_1-C_2-S_{19}	−178.9 (2)	179.2	C_6-C_{15}-C_{18}-N_{12}	179.5 (3)	174.5
S_{19}-C_2-N_3-C_4	179.7 (2)	-179.2	C_5-C_{15}-C_{18}-N_{12}	2.7 (5)	-6.1
C_2-N_3-C_4-O_{21}	176.3 (3)	-178.1	C_6-C_{15}-C_{18}-C_{11}	2.2 (5)	-5.2
C_2-N_3-C_4-C_{14}	−2.4 (5)	1.2	C_5-C_{15}-C_{18}-C_{11}	−174.6 (3)	174.2
O_{21}-C_4-C_{14}-C_{13}	−174.1 (3)	175.6	O_{24}-C_{11}-C_{18}-$_{15}$	178.7 (3)	178.5
N_3-C_4-C_{14}-C_{13}	4.6 (5)	-3.6	C_{17}-C_{11}-C_{18}-$_{15}$	1.1 (5)	-2.1
O_{21}-C_4-C_{14}-C_5	6.7 (5)	-5.8	O_{24}-C_{11}-C_{18}-N_{12}	1.2 (5)	-1.2
N_3-C_4-C_{14}-C_5	−174.7 (3)	175.0	C_{17}-C_{11}-C_{18}-N_{12}	−176.4 (3)	178.1
C_{13}-C_{14}-C_5-C_{15}	12.7 (5)	-18.2	C_{15}-C_{18}-N_{12}-C_{13}	5.7 (5)	-8.5
C_4-C_{14}-C_5-C_{15}	−168.1 (3)	163.1	C_{11}-C_{18}-N_{12}-C_{13}	−176.8 (3)	171.2
C_{13}-C_{14}-C_5-C_{24}	−109.7 (4)	102.8	C_2-N_1-C_{13}-C_{14}	1.1 (5)	-1.3
C_4-C_{14}-C_5-C_{24}	69.5 (4)	-75.9	C_2-N_1-C_{13}-N_{12}	−177.8 (3)	178.1
C_{14}-C_5-C_{15}-C_{18}	−10.8 (5)	18.4	C_4-C_{14}-C_{13}-N_1	−4.2 (5)	3.9
C_{24}-C_5-C_{15}-C_{18}	111.8 (4)	-104.7	C_5-C_{14}-C_{13}-N_1	174.9 (3)	-174.6
C_{14}-C_5-C_{15}-C_6	172.3 (3)	-162.1	C_4-C_{14}-C_{13}-N_{12}	174.7 (3)	-175.5
C_{24}-C_5-C_{15}-C_6	−65.1 (4)	74.8	C_5-C_{14}-C_{13}-N_{12}	−6.2 (5)	5.9
C_{18}-C_{15}-C_6-O_{22}	174.9 (3)	-168.9	C_{18}-N_{12}-C_{13}-N_1	175.1 (3)	-170.9
C_5-C_{15}-C_6-O_{22}	−8.1 (5)	11.6	C_{18}-N_{12}-C_{13}-C_{14}	−3.9 (5)	8.5
C_{18}-C_{15}-C_6-C_{16}	−5.5 (5)	10.1	N_1-C_2-S_{19}-C_{20}	−8.6 (3)	0.1

C_5-C_{15}-C_6-C_{16}	171.4 (3)	-169.4	N_3-C_2-S_{19}-C_{20}	171.1 (3)	-179.4
O_{22}-C_6-C_{16}-C_7	6.3 (5)	-8.4	C_{14}-C_5-C_{24}-C_{29}	71.1 (3)	-39.3
C_{15}-C_6-C_{16}-C_7	−173.2 (3)	172.6	C_{14}-C_5-C_{24}-C_{29}	−50.3 (4)	83.1
O_{22}-C_6-C_{16}-C_{17}	−174.7 (3)	171.1	C_{14}-C_5-C_{24}-C_{25}	−110.0 (3)	141.4
C_{15}-C_6-C_{16}-C_{17}	5.7 (5)	-7.9	C_{15}-C_5-C_{24}-C_{25}	128.7 (3)	-96.2
C_{17}-C_{16}-C_7-C_8	1.0 (5)	0.1	C_{25}-C_{24}-C_{29}-C_{28}	−0.1 (5)	-0.5
C_6-C_{16}-C_7-C_8	180.0 (3)	179.6	C_5-C_{24}-C_{29}-C_{28}	178.9 (3)	-179.8
C_{16}-C_3-C_3-C_9	0.4 (6)	-0.2	C_{24}-C_{29}-C_{28}-C_{27}	−0.5 (5)	0.1
C_7-C_8-C_9-C_{10}	−0.5 (6)	0.1	C_{29}-C_{28}-C_{27}-O_{44}	−178.6 (3)	179.9
C_8-C_9-C_{10}-C_{17}	−0.7 (5)	0.1	C_{29}-C_{28}-C_{27}-C_{26}	0.5 (5)	0.3
C_7-C_{16}-C_{17}-C_{10}	−2.2 (5)	0.2	O_{44}-C_{27}-C_{26}-C_{25}	179.1 (3)	180.0
C_6-C_{16}-C_{17}-C_{10}	178.8 (3)	-179.4	C_{35}-C_{27}-C_{26}-C_{25}	0.0 (4)	-0.4
C_7-C_{16}-C_{17}-C_{11}	176.5 (3)	-179.7	C_{27}-C_{26}-C_{25}-C_{24}	−0.6 (5)	0
C_6-C_{16}-C_{17}-C_{11}	−2.5 (5)	0.8	C_{29}-C_{24}-C_{25}-C_{26}	0.7 (4)	0.4
C_9-C_{10}-C_{17}-C_{16}	2.1 (5)	-0.3	C_{35}-C_{24}-C_{25}-C_{26}	−178.3 (3)	179.8
C_9-C_{10}-C_{17}-C_{11}	−176.6 (3)	179.6	C_{26}-C_{27}-O_{44}-C_{45}	9.9 (4)	-0.1
C_{16}-C_{17}-C_{11}-O_{24}	−178.4 (3)	-176.4	C_{28}-C_{27}-O_{44}-C_{45}	−171.0 (3)	179.9
C_{10}-C_{17}-C_{11}-O_{24}	0.3 (5)	3.8			



τ_1 (N_1-C_2-S_{19}-C_{20}) τ_2 (C_{14}-C_5-C_{24}-C_{29}) τ_4 (C_{28}-C_{27}-O_{44}-C_{45})

Figure S20. One-dimensional potential energy surface (PES) scan of the calculated energies *vs*. dihedral angles (τ) using DFT/B3LYP/6-31G (d,p) for 5-(4-methoxyphenyl)-2-methylthio-5,12-dihydrobenzo[*g*]pyrimido[4,5-*b*]quinoline-4,6,11(3*H*)-trione 4c.

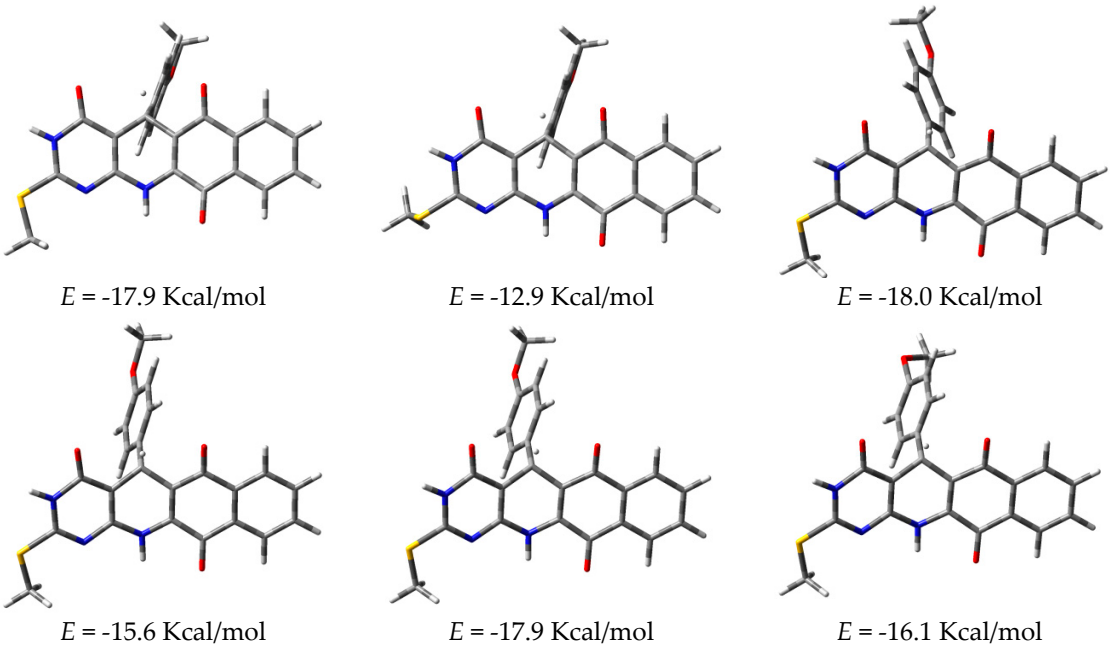


Figure S21. Highest and lowest energy conformations using DFT/B3LYP/6-31G(d,p) for 4c.

Table S2. Experimental FT-IR and computed vibrational bands for 4c and their assignments at B3LYP/6-31G(d,p) level.

ν	Experimental	Calculate		Assignment
		Un-scaled	Scaled	
1	3272	3459	3334	N_{12}-H stretching
		3450	3325	N_3-H stretching
		3141	3027	O-CH_3 bending symmetric
		3127	3014	O-CH_3 stretching asymmetric
2	2841	3108	2996	S-CH_3 stretching asymmetric
		3039	2929	O-CH_3 stretching symmetric
		3018	2909	S-CH_3 stretching symmetric
3	1674	1851	1784	C_4=O_{21} stretching
4	1650	1822	1756	C_{11}=O_{23} stretching
5	1620	1811	1745	C_6=O_{22} stretching
6	1496	1495	1436	C=N stretching
7	1450	1467	1409	C=N stretching
8	1390	1350	1297	C-N stretching

9	1332	1185	1138	C-N stretching
10	1247	1126	1082	C-N stretching

Table S3. Occupation of natural orbitals and hybrids for 4c calculated by the DFT/B-3LYP/6-31G (d,p) method for the representative atoms.

Donor Lewis NBOs	Type	Electronic Density	Hybridization	Contribution of natural atomic orbitals (%)			
					s	*p*	*d*
C_4 - O_{21}	**σ**	1.99441	0.5952($sp^{2.01}$)C + 0.8036($sp^{1.43}$)O	C:	33.23	66.68	0.09
				O:	41.00	58.65	0.34
C_4 - O_{21}	**π**	1. 98431	0.5492 ($sp^{1.00}$)C + 0.835 ($sp^{1.00}$)O	C:	0.01	99.81	0.18
				O:	0.01	99.69	0.31
C_6 - O_{22}	**σ**	1.99483	0.5895 ($sp^{2.31}$)C + 0.8078 ($sp^{1.38}$)O	C:	30.22	69.68	0.11
				O:	41.88	57.80	0.01
C_6 - O_{22}	**π**	1.94776	0.5813 ($sp^{99.99}$)C + 0.8137 ($sp^{99.99}$)O	C:	0.01	99.84	0.14
				O:	0.02	99.67	0.31
C_{11} - O_{23}	**σ**	1.99525	0.5885 ($sp^{2.30}$)C + 0.8085 ($sp^{1.38}$)O	C:	30.26	69.63	0.11
				O:	41.89	57.79	0.32
C_{11} - O_{23}	**π**	1.95767	0.5756 ($sp^{1.00}$)C + 0.8177 ($sp^{1.00}$)O	C:	0.00	99.85	0.15
				O:	0.00	99.69	0.31
C_{15} - C_{18}	**σ**	1.97340	0.7021 ($sp^{1.83}$)C + 0.7121 ($sp^{1.51}$)C	C:	35.30	64.66	0.04
				C:	39.87	60.10	0.03
C_{15} - C_{18}	**π**	1.77932	0.7191 ($sp^{1.00}$)C + 0.6949 ($sp^{1.00}$)C	C:	0.00	99.94	0.06
				C:	0.00	99.95	0.05
C_2 - S_{19}	**σ**	1.97646	0.7439 ($sp^{2.38}$)C + 0.6683 ($sp^{5.04}$)S	C:	29.51	70.38	0.10
				S:	16.44	82.84	0.73
C_{27} - O_{44}	**σ**	1.99168	0.5705 ($sp^{3..02}$)C + 0.8213 ($sp^{2.01}$)O	C:	24.82	74.97	0.21
				O:	33.17	66.76	0.07
N_{12} - H_{31}	**σ**	1.98356	0.8596 ($sp^{2.52}$)N + 0.5110 ($s^{99.89}$)H	N:	28.02	71.96	0.02
				H:	99.89	0.11	
N_3 - H_{30}	**σ**	1.98394	0.8551 ($sp^{2.61}$)N + 0.5184 ($s^{99.90}$)H	N:	27.68	72.29	0.02
				H:	99.90	0.10	
N_1	LP[a] (1)	1.89271	$sp^{2.45}$	N:	28.94	70.90	0.16
N_3	LP[a] (1)	1.61063	$p^{1.00}$	N:	0.00	98.99	0.01
N_{12}	LP[a] (1)	1.73427	$sp^{.90.58}$	N:	1.09	98.89	0.01
O_{21}	LP[a] (1)	1.97642	$p^{1.00}$	O:	58.92	41.03	0.04
O_{21}	LP[a] (2)	1.84939	$p^{.99.99}$	O:	0.03	99.73	0.24
O_{22}	LP[a] (1)	1.97885	$sp^{0.72}$	O:	58.07	41.88	0.04
O_{22}	LP[a] (2)	1.88965	$p^{1.00}$	O:	0.00	99.80	0.20
O_{23}	LP[a] (1)	1.97850	$sp^{0.72}$	O:	58.02	41.93	0.05
O_{23}	LP[a] (2)	1.88503	$p^{1.00}$	O:	0.05	99.74	0.20
O_{44}	LP[a] (1)	1.96389	$sp^{1.59}$	O:	38.53	61.41	0.06
O_{44}	LP[a] (2)	1.84157	$p^{1.00}$	O:	0.00	99.91	0.09
S_{19}	LP[a] (1)	1.98246	$sp^{0.48}$	N:	67.55	32.43	0.02
S_{19}	LP[a] (2)	1.82875	$p^{1.00}$	N:	0.00	99.94	0.05

[a]Lone pair on natural Lewis structure.

Table S4. Occupation of natural orbitals (NBO) no Lewis and hybrids for 4c calculated by the DFT/B-3LYP/6-31G (d,p) method for the representative atoms.

Acceptor not Lewis	Type	Electronic Density	Hybridization	Contribution of natural atomic orbitals (%)			
					s	*p*	*d*
C_4 - O_{21}	σ*	0.00892	0.8036 ($sp^{2.01}$)C - 0.5952 ($sp^{1.43}$)O	C:	33.23	66.68	0.09
				O:	41.00	58.65	0.34
C_4 - O_{21}	π*	0.35268	0.8357 ($p^{1.00}$)C - 0.5492 ($p^{1.00}$)O	C:	0.01	99.81	0.18
				O:	0.01	99.69	0.31
C_6 - O_{22}	σ*	0.00782	0.8078 ($sp^{2.31}$)C - 0.5895 ($sp^{1.38}$)O	C:	30.22	69.68	0.11
				O:	41.88	57.80	0.01
C_6 - O_{22}	π*	0.20945	0.8137 ($p^{99.99}$)C - 0.5813 ($p^{99.99}$)O	C:	0.01	99.84	0.14
				O:	0.02	99.67	0.31
C_{11} - O_{23}	σ*	0.00754	0.8085 ($sp^{2.30}$)C - 0.5885 ($sp^{1.38}$)O	C:	30.26	69.63	0.11
				O:	41.89	57.79	0.32
C_{11} - O_{23}	π*	0.19366	0.8177 ($p^{1.00}$)C - 0.5756 ($p^{1.00}$)O	C:	0.00	99.85	0.15
				O:	0.00	99.69	0.310
C_{15} - C_{18}	σ*	0.02406	0.7121 ($sp^{1.83}$)C - 0.7021 ($sp^{1.51}$)C	C:	35.30	64.66	0.04
				C:	39.87	60.10	0.03
C_{15} - C_{18}	π*	0.24133	0.6949 ($p^{1.00}$)C - 0.7191 ($p^{1.00}$)C	C:	0.00	99.94	0.06
				C:	0.00	99.95	0.05
C_2 - S_{19}	σ*	0.05230	0.6683 ($sp^{2.38}$)C - 0.7439 ($sp^{5.04}$)S	C:	29.51	70.38	0.10
				S:	16.44	82.84	0.73
C_{27} - O_{44}	σ	0.02955	0.8213 ($sp^{3..02}$)C - 0.5705 ($sp^{2.01}$)O	C:	24.82	74.97	0.21
				O:	33.17	66.76	0.07
N_{12} - H_{31}	σ*	0.02603	0.5110 ($sp^{2.52}$)N - 0.8596 ($s^{99.89}$)H	N:	28.02	71.96	0.02
				H:	99.89	0.11	
N_3 - H_{30}	σ	0.01822	0.5184 ($sp^{2.61}$)N + 0.8551 ($s^{99.90}$)H	N:	27.68	72.29	0.02
				H:	99.90	0.10	

Table S5. Analysis perturbation theory second order in Fock matrix in NBO by level calculation B3LYP/6-31G (d,p) for compound 4c.

Donor NBO (*i*)	Acceptor NBO (*j*)	E_2	E_j-E_i	*F(i,j)*
		Kcal/mol	a.u	a.u
LP N_3	π* N_1-C_2	65.72	0.26	0.116
LP N_3	π* C_4-O_{21}	44.57	0.30	0.104
LP N_{12}	π* C_{13}-C_{14}	41.73	0.30	0.101
LP N_{12}	π* C_{15}-C_{18}	39.97	0.30	0.101
π* C_4-O_{21}	π* C_{13}-C_{14}	256.96	0.01	0.080
π* C_6-O_{22}	π* C_{15}-C_{18}	94.72	0.02	0.076
π* C_{11}-O_{23}	π* C_{15}-C_{18}	41.82	0.04	0.075
π* C_{11}-O_{23}	π* C_{16}-C_{17}	76.69	0.03	0.075

Table S6. Electrical dipole moment, polarizability and first order hyperpolarizability of 4c at the level DFT/B3LYP/6-31G (d,p).

Dipole Moment		**Polarizability**			**First Order Hyperpolarizability**		
Parameter	**D**	**Parameter**	**au**	**esu (10^{-24})**	**Parameter**	**au**	**esu (10^{-33})**
μ_x	-0.28	α_{xx}	373.29	55.26	β_{xxx}	1497.24	12941.0
μ_y	-1.34	α_{xy}	7.513	1.11	β_{xxy}	-165.57	-1431.10
μ_z	-1.28	α_{yy}	336.29	49.78	β_{xyy}	665.94	5755.80
μ_0	1.88	α_{xz}	12.913	1.91	β_{yyy}	-3426.60	-29616.0
		α_{yz}	55.10	8.15	β_{xxz}	420.33	3633.0
		α_{zz}	211.86	31.36	β_{xyz}	72.03	622.60
		α_0	307.15	45.46	β_{yyz}	438.54	3790,30
		$\Delta\alpha$	207.15	30.66	β_{xzz}	20.44	176.73
					β_{yzz}	-87.92	-759.93
					β_{zzz}	-25.13	-217.26
					β_0 3768.07 x 10^{-33}		

Table S7. Enthalpy, Gibbs free energy and entropy calculated for 4c and 5c compounds.

THERMODYNAMIC PARAMETERS	**4c**	**5c**
Enthalpy (*H*/*a.u*)	-549.949	-1181.96
Gibbs free energy (*G*/*a.u*)	-549.994	-1182.04
Entropy (*S*/*cal* $mol^{-1}K^{-1}$)	93.941	172.531
ZEP vibrational energy (Kcal/Mol)	226.975	226.194
ZEP + electronic energy	-1749.749	-1749.758