

Supplementary Material:

Multicomponent Electrocatalytic Selective Approach to Unsymmetrical Spiro[furo[3,2-c]pyran-2,5'-pyrimidine] Scaffold under a Column Chromatography-Free Protocol at Room Temperature

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1. The copies of ^1H NMR and ^{13}C NMR spectra for compounds 2a-i

Figure S1. ^1H NMR spectrum of 1',3',6-trimethyl-3-phenyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2a** in CDCl_3 .

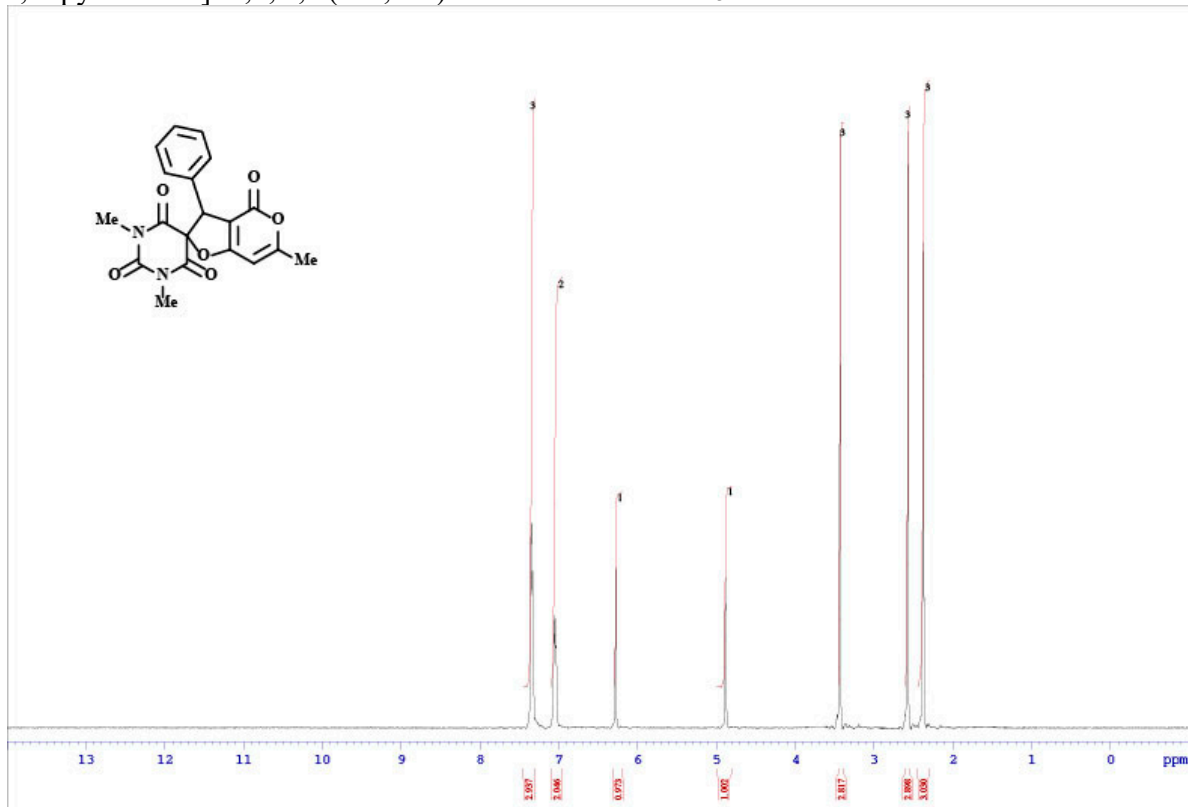


Figure S2. ^{13}C NMR spectrum of 1',3',6-trimethyl-3-phenyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2a** in CDCl_3 .

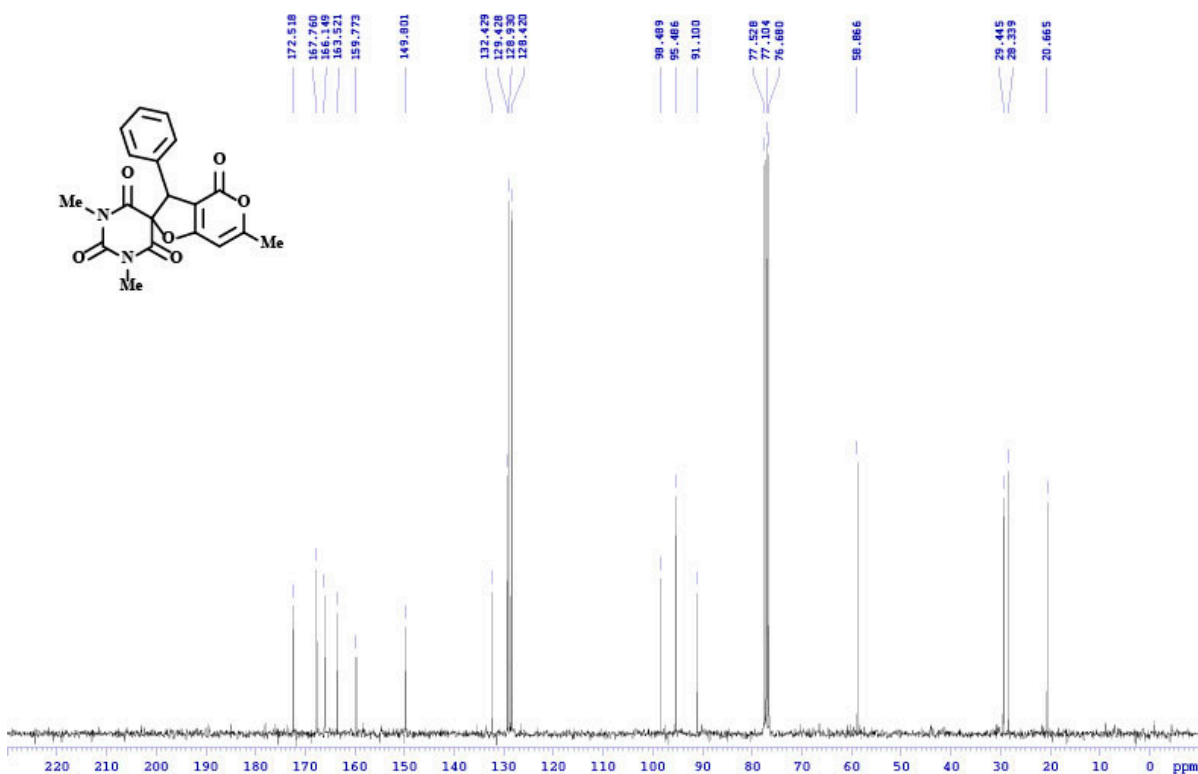


Figure S3. ^1H NMR spectrum of 3-(4-methyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2b** in CDCl_3 .

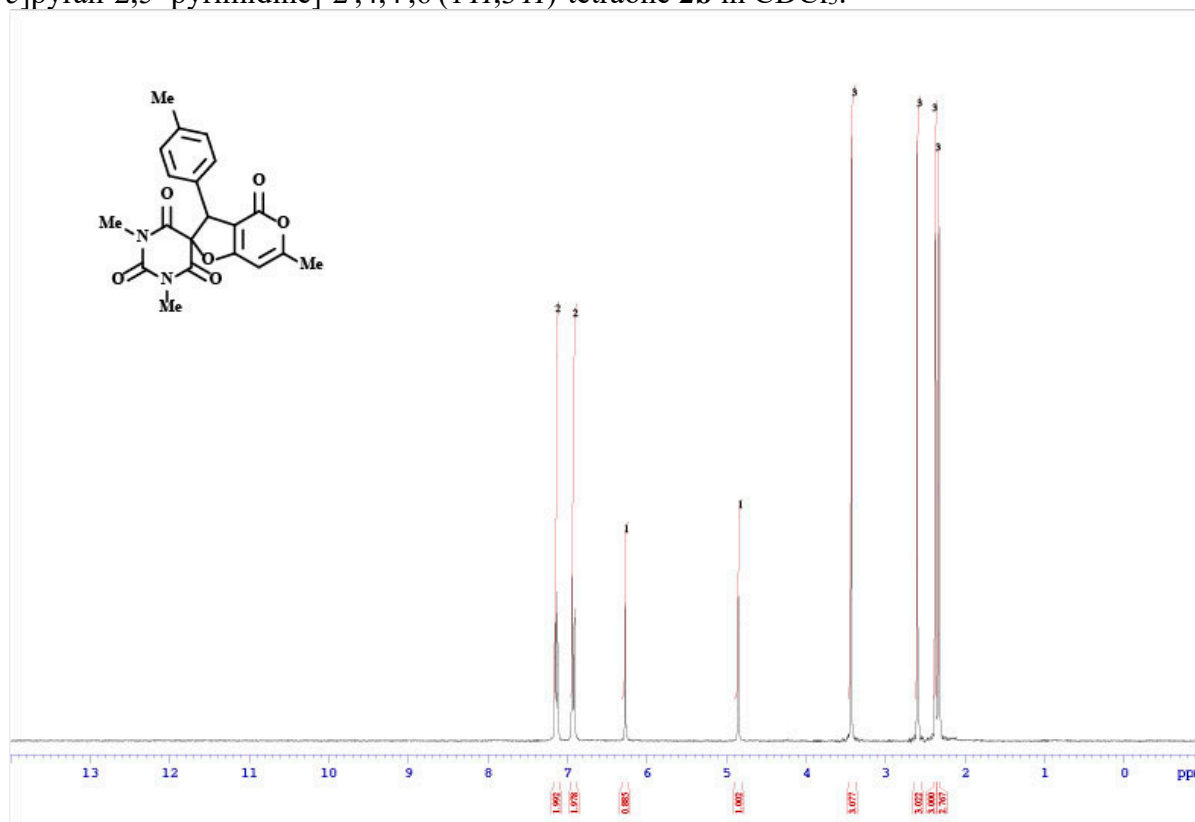


Figure S4. ^{13}C NMR spectrum of 3-(4-methyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2b** in CDCl_3 .

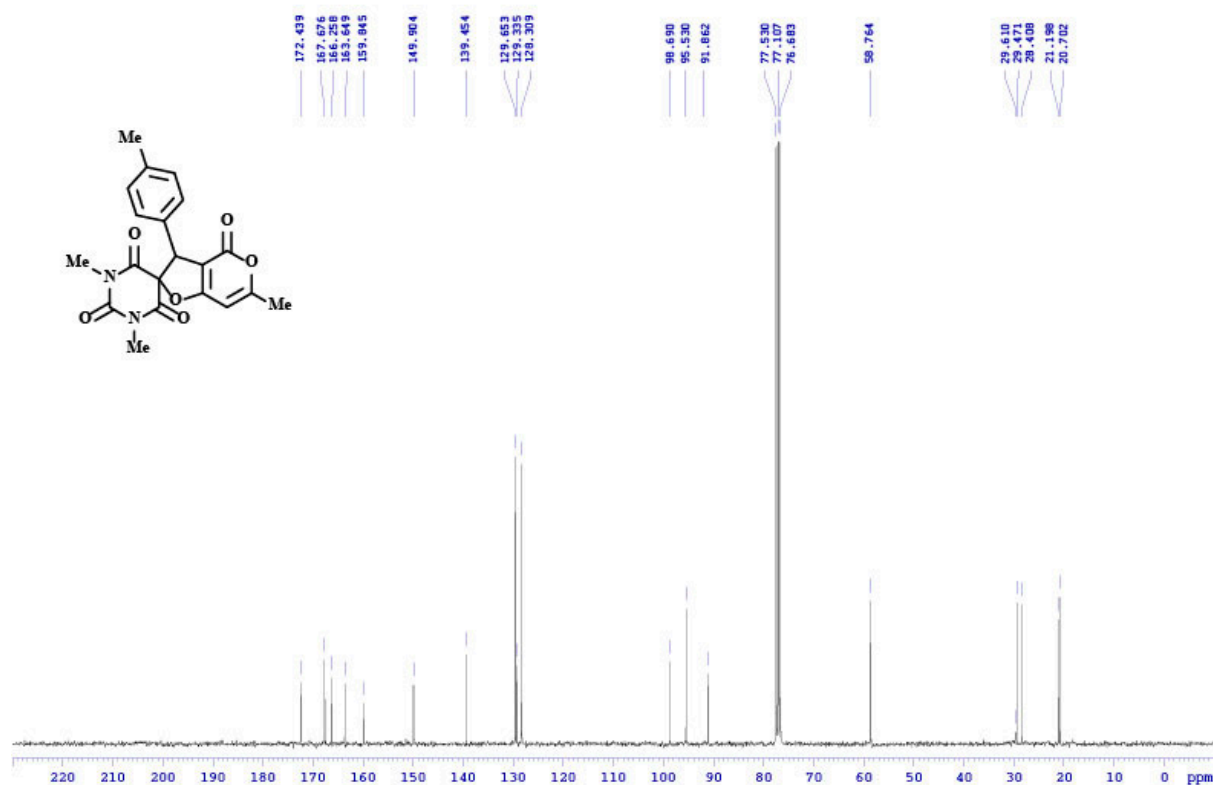


Figure S5. ^1H NMR spectrum of 3-(3-fluorophenyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2c** in CDCl_3 .

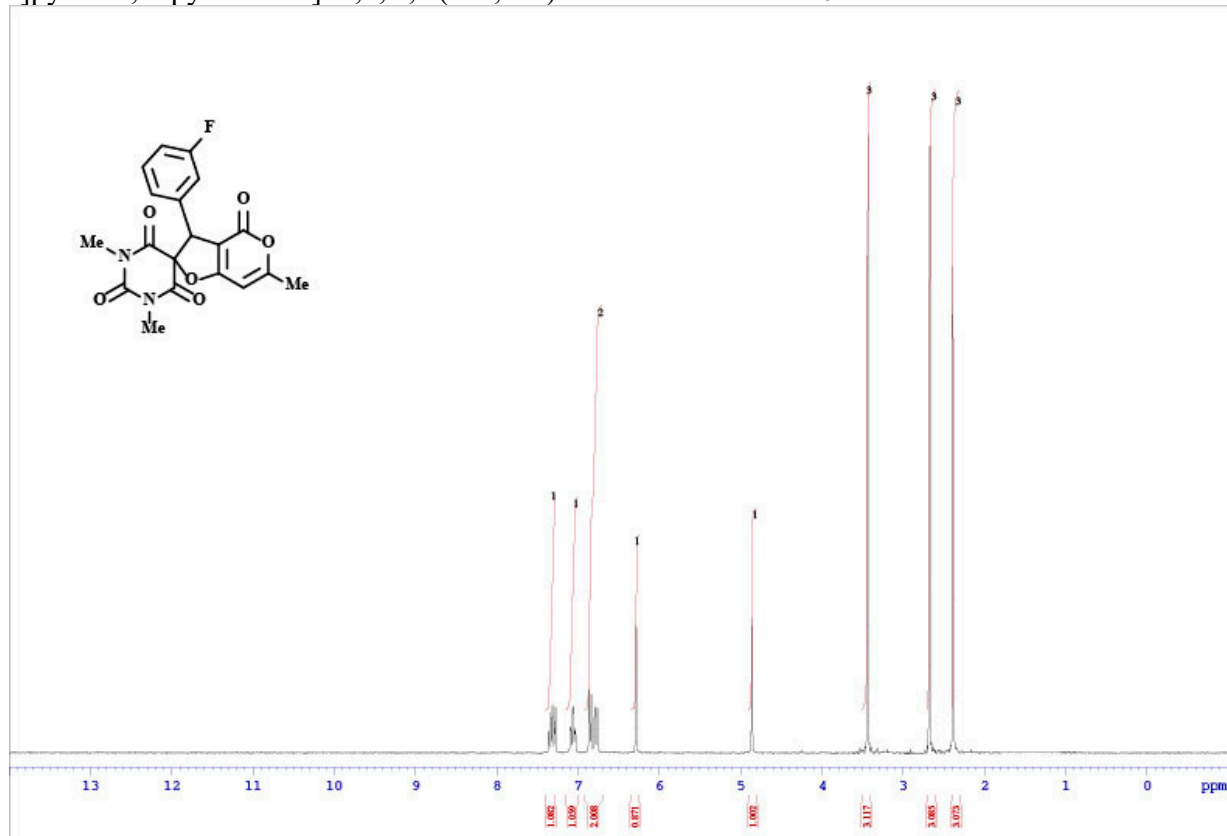


Figure S6. ^{13}C NMR spectrum of 3-(3-fluorophenyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2c** in CDCl_3 .

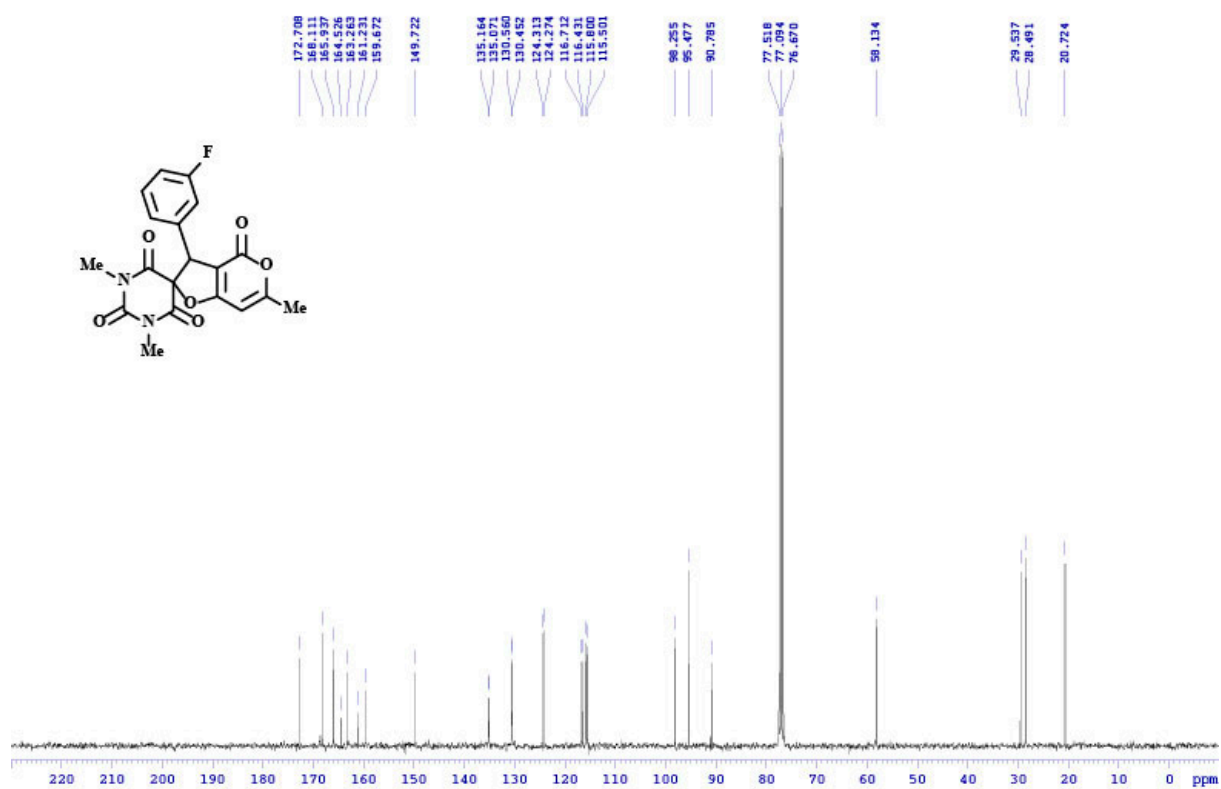


Figure S7. ^1H NMR spectrum of 3-(4-chlorophenyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2d** in CDCl_3 .

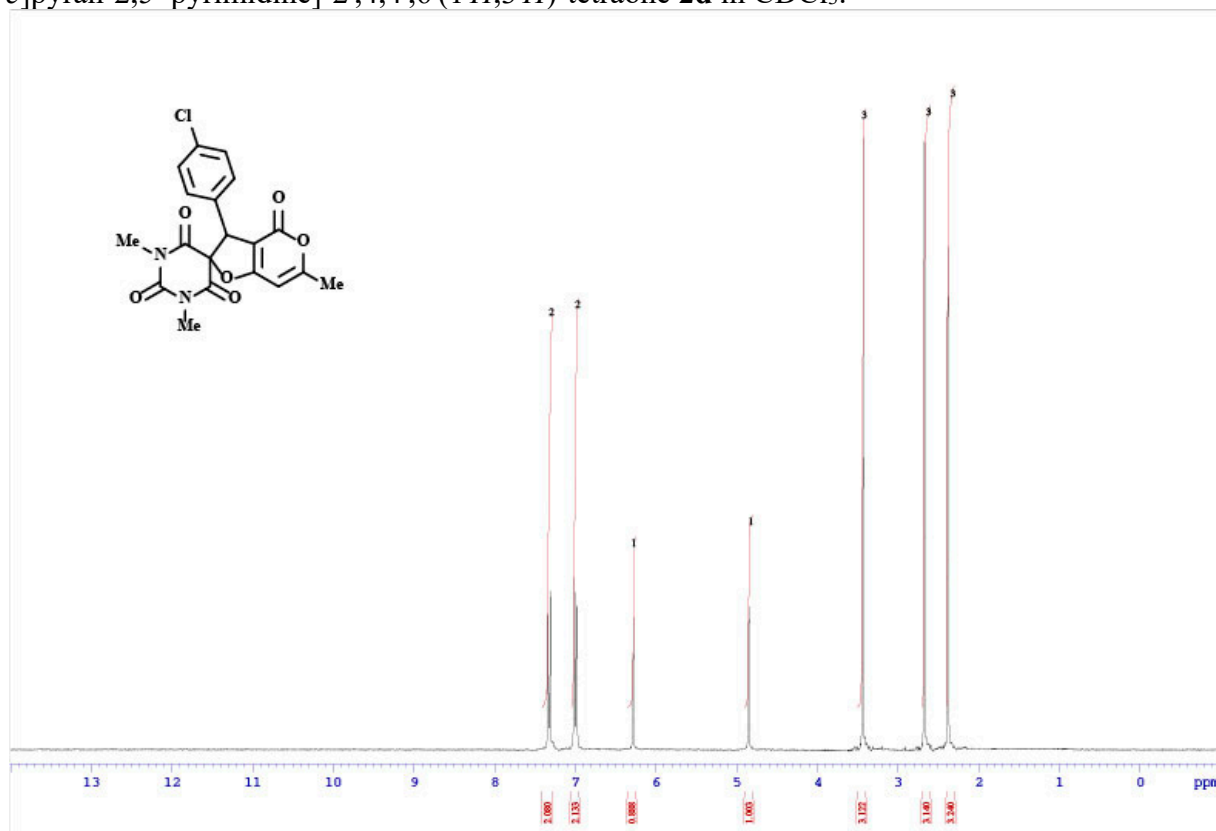


Figure S8. ^{13}C NMR spectrum of 3-(4-chlorophenyl)-1',3',6-trimethyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2d** in CDCl_3 .

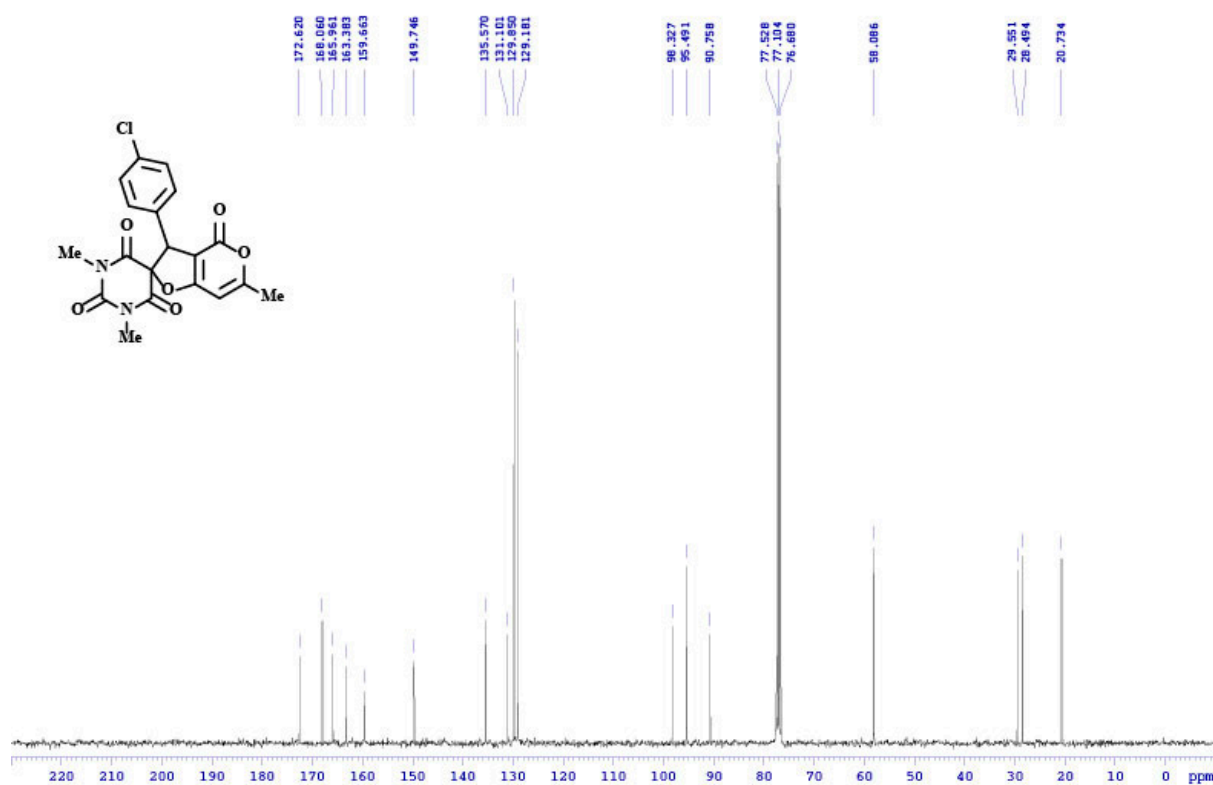


Figure S9. ^1H NMR spectrum of 1',3',6-trimethyl-3-(4-nitrophenyl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2e** in CDCl_3 .

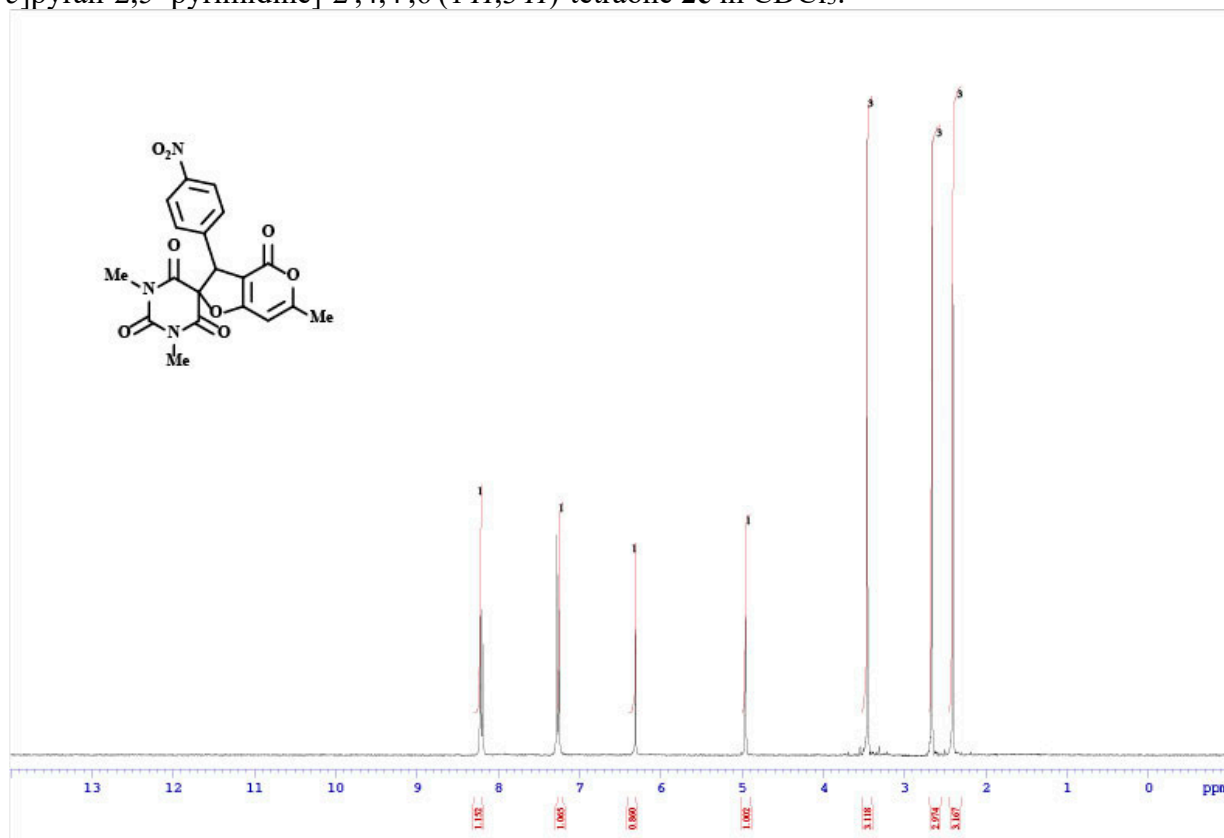


Figure S10. ^{13}C NMR spectrum of 1',3',6-trimethyl-3-(4-nitrophenyl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2e** in CDCl_3 .

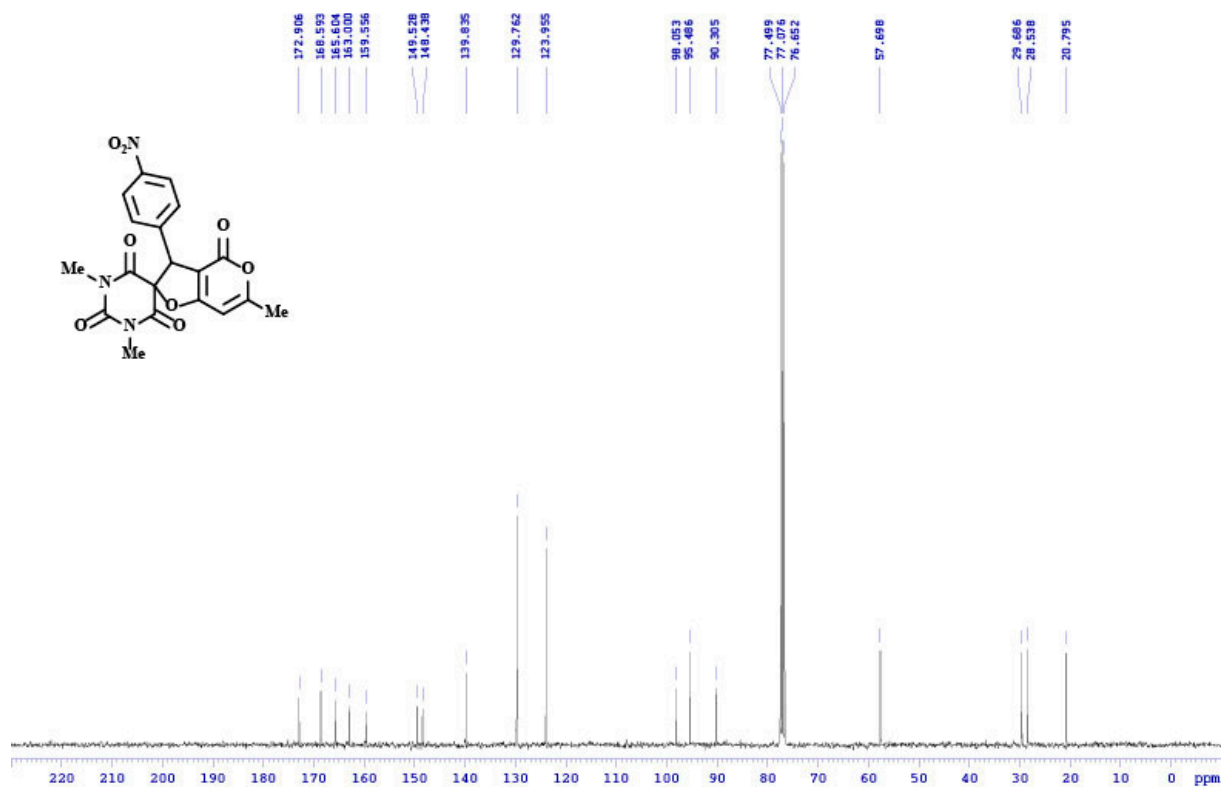


Figure S11. ^1H NMR spectrum of methyl 4-(1',3',6-trimethyl-2',4,4',6'-tetraoxo-1',3',4',6'-tetrahydro-2*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidin]-3-yl)benzoate **2f** in CDCl_3 .

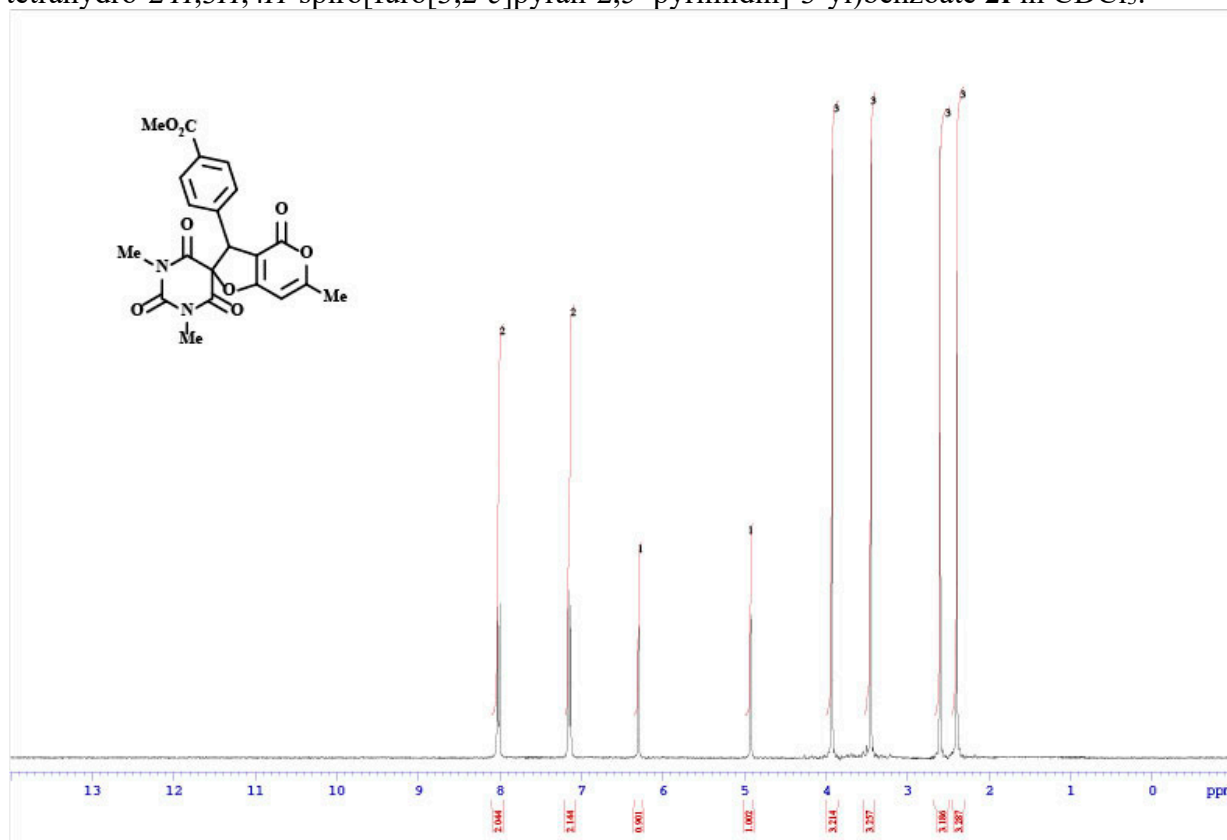


Figure S12. ^{13}C NMR spectrum of methyl 4-(1',3',6-trimethyl-2',4,4',6'-tetraoxo-1',3',4',6'-tetrahydro-2*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidin]-3-yl)benzoate **2f** in CDCl_3 .

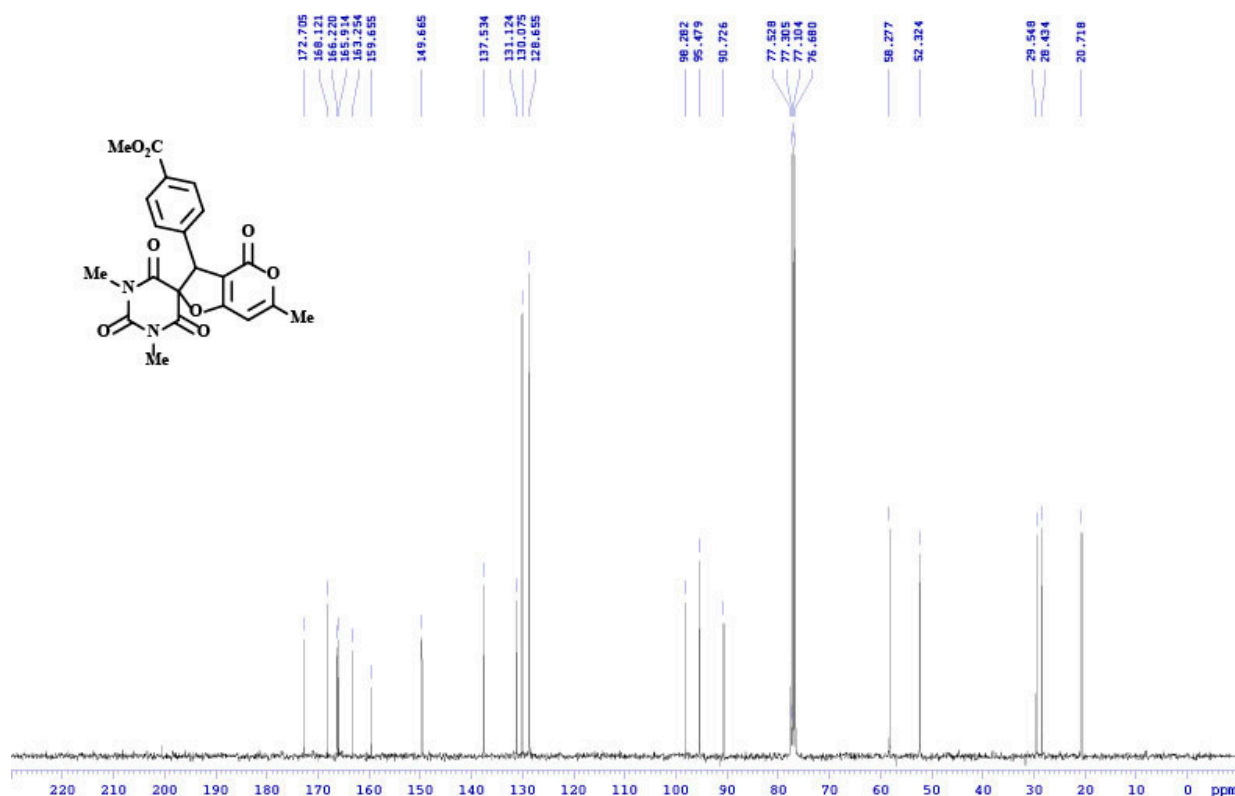


Figure S13. ^1H NMR spectrum of 1',3',6-trimethyl-3-(pyridin-3-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2g** in CDCl_3 .

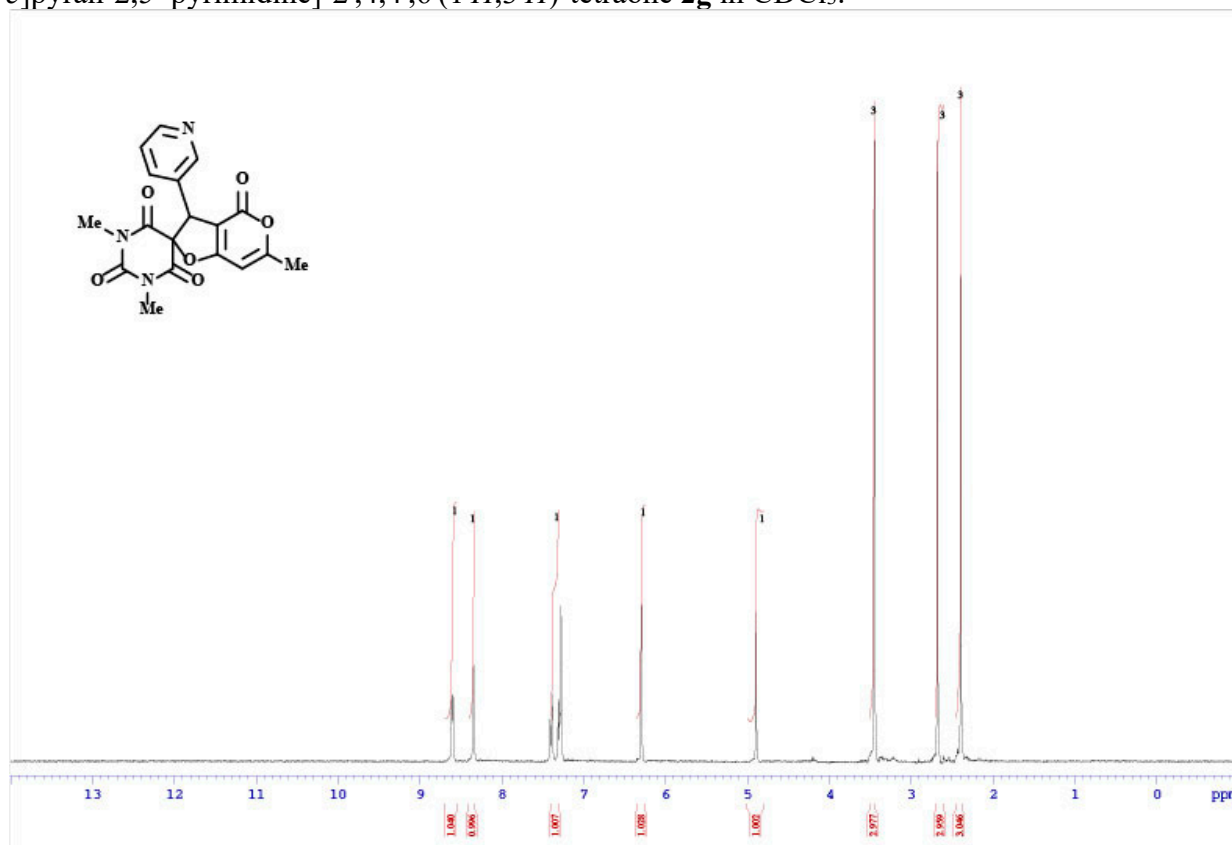


Figure S14. ^{13}C NMR spectrum of 1',3',6-trimethyl-3-(pyridin-3-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2g** in CDCl_3 .

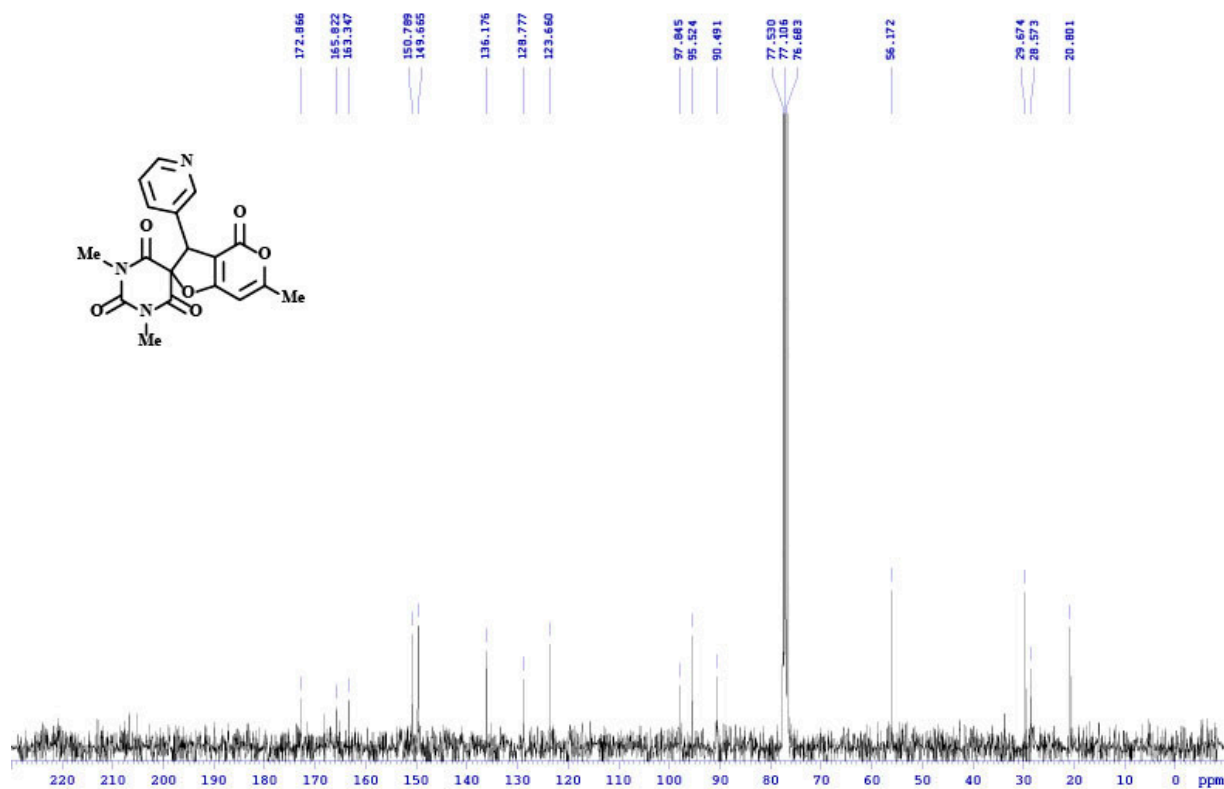


Figure S15. ^1H NMR spectrum of 1',3',6-trimethyl-3-(pyridin-4-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2h** in CDCl_3 .

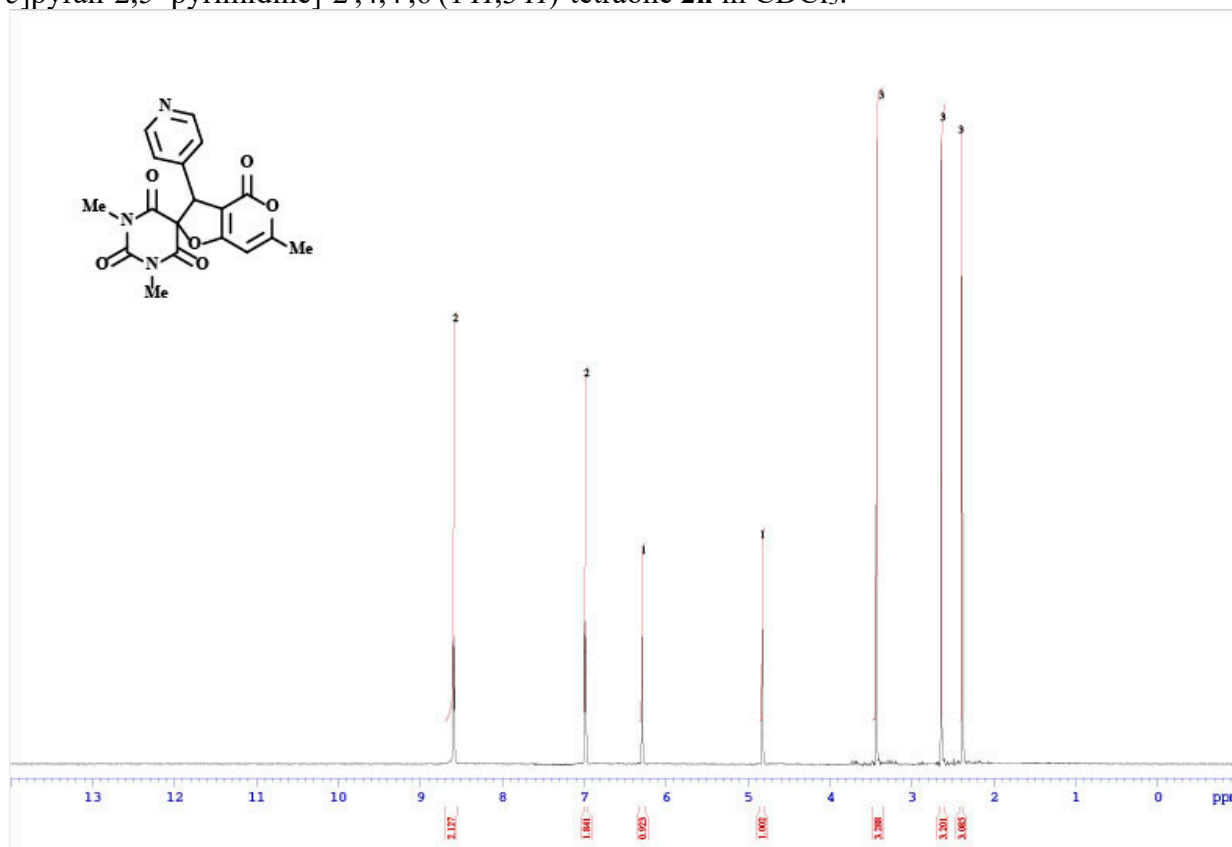


Figure S16. ^{13}C NMR spectrum of 1',3',6-trimethyl-3-(pyridin-4-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2h** in CDCl_3 .

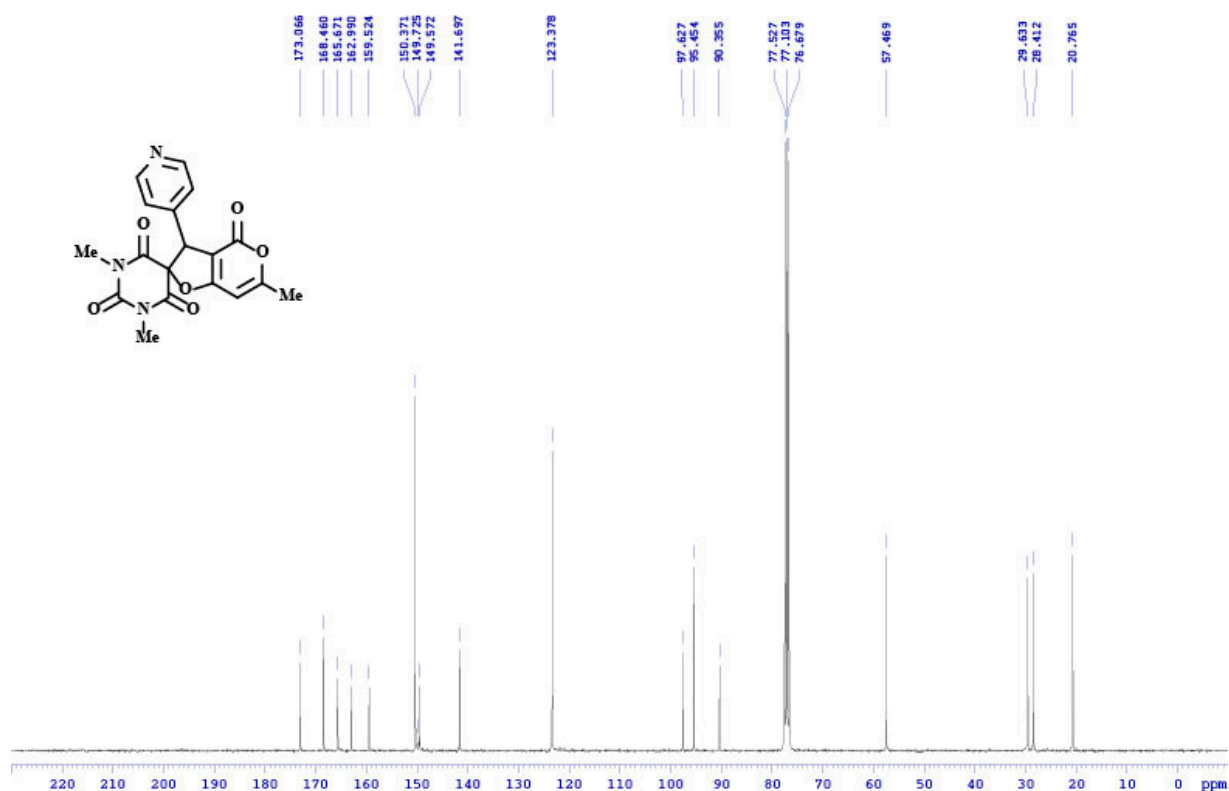


Figure S17. ^1H NMR spectrum of 1',3',6-trimethyl-3-(naphthalen-1-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2i** in CDCl_3 .

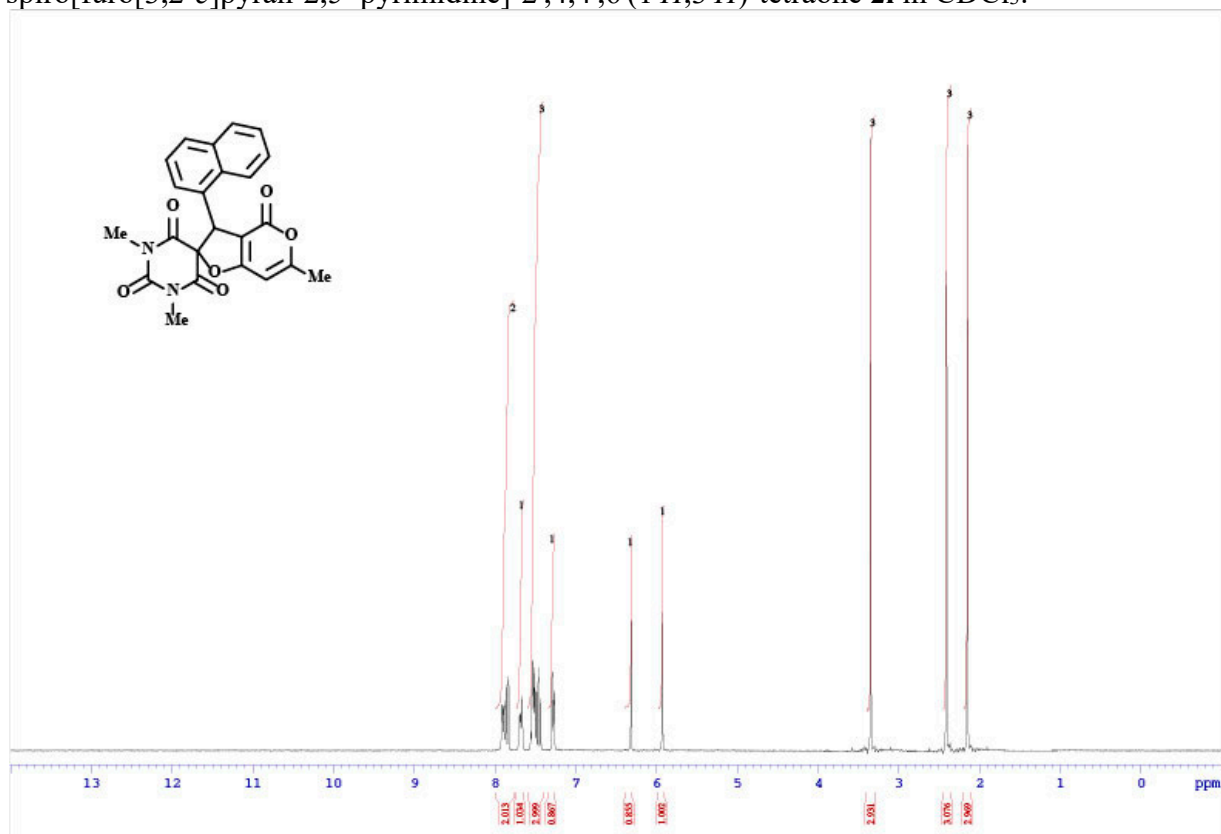
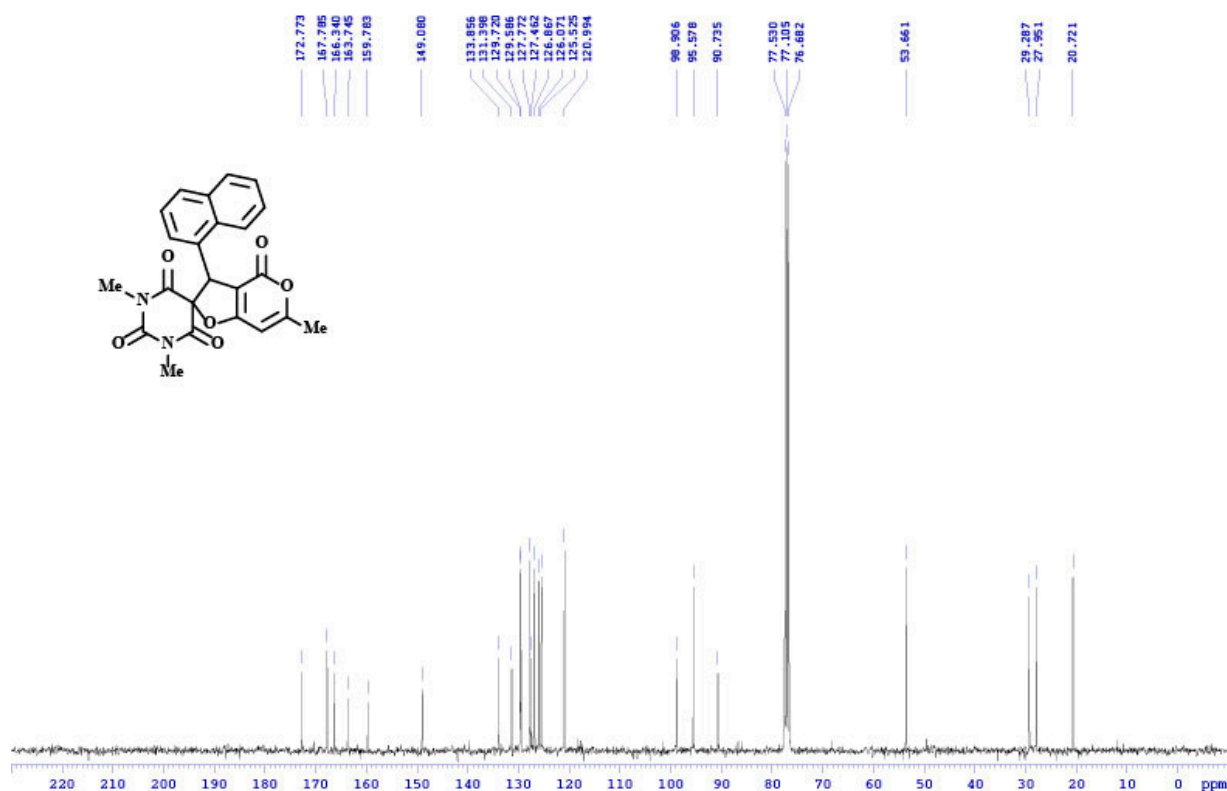
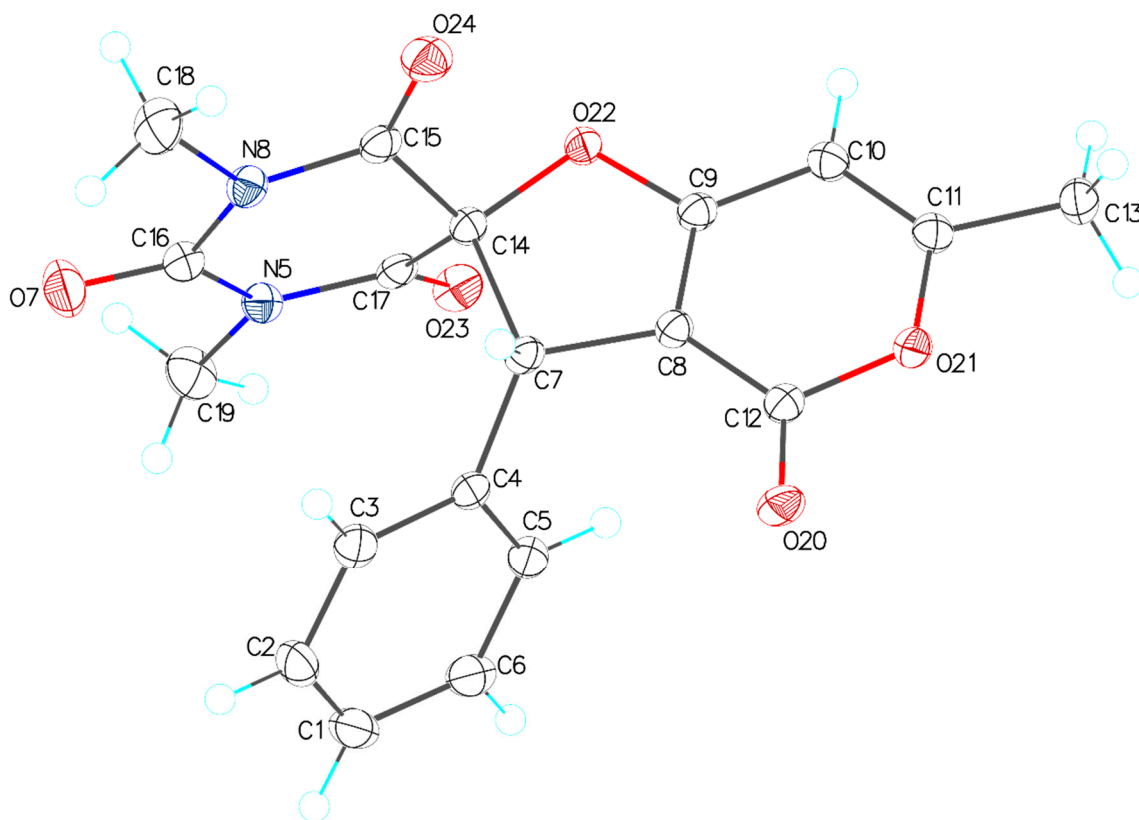


Figure S18. ^{13}C NMR spectrum of 1',3',6-trimethyl-3-(naphthalen-1-yl)-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2i** in CDCl_3 .



2. X-Ray data for compound **2a**

Figure S19. The general view of 1',3',6-trimethyl-3-phenyl-2'*H*,3*H*,4*H*-spiro[furo[3,2-*c*]pyran-2,5'-pyrimidine]-2',4,4',6'(1'*H*,3'*H*)-tetraone **2a** in crystal. Atoms are represented by thermal displacement ellipsoids ($p=50\%$).



Experimental

Single crystals of $C_{19}H_{16}N_2O_6$ **2a** were grown from EtOH. A suitable crystal was selected and placed on a Bruker APEX-II Duo diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the XL [2] refinement package using Least Squares minimization.

Crystal Data for $C_{19}H_{16}N_2O_6$ ($M=368.34$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 7.7339(4)$ Å, $b = 18.4269(11)$ Å, $c = 12.0713(7)$ Å, $\beta = 97.8430(10)^\circ$, $V = 1704.21(17)$ Å³, $Z = 4$, $T = 120$ K, $\mu(\text{MoK}\alpha) = 0.109$ mm⁻¹, $D_{\text{calc}} = 1.436$ g/cm³, 23459 reflections measured ($4.06^\circ \leq 2\theta \leq 61.202^\circ$), 5239 unique ($R_{\text{int}} = 0.0553$, $R_{\text{sigma}} = 0.0464$) which were used in all calculations. The final R_1 was 0.0455 ($I > 2\sigma(I)$) and wR_2 was 0.1146 (all data). CCDC 2152149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

Table S1. Crystal data and structure refinement for **2a**.

Identification code	2a
Empirical formula	C ₁₉ H ₁₆ N ₂ O ₆
Formula weight	368.34
Temperature/K	120
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	7.7339(4)
b/Å	18.4269(11)
c/Å	12.0713(7)
α /°	90
β /°	97.8430(10)
γ /°	90
Volume/Å ³	1704.21(17)
Z	4
ρ_{calc} /cm ³	1.436
μ /mm ⁻¹	0.109
F(000)	768.0
Crystal size/mm ³	0.3 × 0.2 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.06 to 61.202
Index ranges	-11 ≤ h ≤ 11, -26 ≤ k ≤ 26, -17 ≤ l ≤ 17
Reflections collected	23459
Independent reflections	5239 [R _{int} = 0.0553, R _{sigma} = 0.0464]
Data/restraints/parameters	5239/0/247
Goodness-of-fit on F ²	1.020
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0455, wR ₂ = 0.1015
Final R indexes [all data]	R ₁ = 0.0769, wR ₂ = 0.1146
Largest diff. peak/hole / e Å ⁻³	0.37/-0.28

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic DisplacementParameters ($\text{\AA}^2 \times 10^3$) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
O21	213.1(12)	4786.9(5)	1566.4(8)	17.5(2)
O20	-179.9(13)	5654.2(6)	2795.8(9)	21.5(2)
O23	6185.2(13)	6431.8(6)	1230.1(8)	22.1(2)
O22	5428.3(12)	5138.2(5)	2038.2(9)	18.9(2)
N5	7434.8(15)	6838.4(6)	2934.9(10)	16.4(2)
O24	6792.4(14)	4849.7(6)	4198.9(10)	25.7(2)
O7	8961.3(16)	7137.8(6)	4612.7(10)	29.4(3)
N8	7711.0(15)	6020.3(6)	4487.8(10)	17.5(2)
C7	3829.8(17)	5955.7(7)	3161.0(11)	15.6(3)
C17	6491.7(17)	6349.5(7)	2233.5(12)	16.1(3)
C8	2704.8(17)	5447.6(7)	2394.3(11)	15.1(3)
C9	3690.1(17)	5017.8(7)	1813.9(12)	16.0(3)
C16	8083.0(18)	6695.4(8)	4047.7(12)	18.4(3)
C11	1232.1(18)	4388.9(7)	949.6(12)	16.9(3)
C10	2976.2(18)	4482.2(8)	1039.5(12)	18.2(3)
C12	871.1(18)	5341.9(7)	2306.0(12)	16.1(3)
C15	6823.0(17)	5470.3(8)	3873.7(12)	17.3(3)
C5	2772.8(18)	7073.4(8)	2018.7(12)	19.5(3)
C13	174.7(19)	3861.1(8)	211.8(13)	20.6(3)
C4	3431.2(17)	6762.1(8)	3044.8(12)	16.4(3)
C14	5706.0(17)	5729.5(7)	2820.9(11)	15.6(3)
C6	2543.5(19)	7819.6(8)	1915.9(14)	23.1(3)
C3	3832.6(19)	7214.9(8)	3971.1(13)	20.9(3)
C2	3617(2)	7963.9(8)	3864.5(14)	25.1(3)
C18	8637(2)	5839.6(9)	5597.1(13)	29.1(4)
C1	2987(2)	8267.8(8)	2841.8(15)	26.1(3)
C19	7947(2)	7529.9(8)	2472.3(14)	26.6(3)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O21	14.1(5)	16.9(5)	21.7(5)	-0.5(4)	2.4(4)	-1.0(4)
O20	15.1(5)	24.2(5)	25.9(5)	-0.7(4)	5.7(4)	3.0(4)
O23	21.9(5)	28.8(6)	15.8(5)	0.9(4)	3.2(4)	3.5(4)
O22	12.3(5)	19.7(5)	25.1(5)	-7.8(4)	3.4(4)	-0.2(4)
N5	16.0(5)	15.4(5)	18.1(6)	1.0(4)	3.8(4)	-0.7(4)
O24	24.0(6)	19.7(5)	32.9(6)	6.1(5)	2.4(5)	1.1(4)
O7	34.2(6)	23.4(6)	28.2(6)	-4.2(5)	-4.0(5)	-6.2(5)
N8	17.7(6)	19.0(6)	15.4(6)	1.1(5)	0.2(4)	0.6(4)
C7	12.7(6)	18.7(6)	15.6(6)	-1.0(5)	3.0(5)	1.5(5)
C17	11.1(6)	19.3(6)	18.1(7)	-0.5(5)	3.2(5)	3.2(5)
C8	13.4(6)	15.5(6)	16.4(6)	0.1(5)	2.1(5)	0.0(5)
C9	13.7(6)	16.4(6)	18.3(6)	1.1(5)	2.9(5)	0.3(5)
C16	16.4(6)	18.7(7)	20.0(7)	-1.3(5)	2.1(5)	1.1(5)
C11	18.6(7)	14.5(6)	17.3(6)	1.8(5)	1.1(5)	-0.3(5)
C10	17.6(7)	17.2(6)	20.0(7)	-3.0(5)	3.9(5)	0.7(5)
C12	15.1(6)	16.1(6)	17.1(6)	2.1(5)	2.0(5)	-0.1(5)
C15	11.9(6)	19.1(7)	21.3(7)	0.8(5)	4.1(5)	1.3(5)
C5	16.8(6)	21.1(7)	20.5(7)	-3.5(6)	1.4(5)	0.2(5)
C13	19.9(7)	18.2(7)	22.6(7)	-0.8(6)	-0.7(6)	-2.9(5)
C4	11.1(6)	18.4(6)	20.3(7)	-2.4(5)	4.7(5)	-0.1(5)
C14	12.6(6)	16.8(6)	17.5(6)	-2.1(5)	2.6(5)	-0.3(5)
C6	19.7(7)	21.7(7)	28.2(8)	2.7(6)	4.3(6)	3.3(6)
C3	17.1(7)	25.5(7)	20.5(7)	-4.9(6)	4.0(5)	0.7(5)
C2	21.4(7)	23.8(8)	30.8(8)	-12.2(6)	6.4(6)	-1.8(6)
C18	34.9(9)	29.9(8)	19.6(7)	3.6(6)	-6.5(6)	-0.5(7)
C1	21.7(7)	17.2(7)	40.7(9)	-3.5(7)	9.2(7)	1.3(6)
C19	30.0(8)	20.2(7)	30.0(8)	5.2(6)	5.7(7)	-4.9(6)

Table S4. Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O21	C11	1.3687(17)	C7	C4	1.5202(19)
O21	C12	1.4064(17)	C7	C14	1.6156(18)
O20	C12	1.2135(16)	C17	C14	1.5150(19)
O23	C17	1.2115(17)	C8	C9	1.3580(19)
O22	C9	1.3529(16)	C8	C12	1.4210(19)
O22	C14	1.4389(16)	C9	C10	1.418(2)
N5	C17	1.3755(18)	C11	C10	1.3494(19)
N5	C16	1.3934(18)	C11	C13	1.486(2)
N5	C19	1.4672(18)	C15	C14	1.513(2)
O24	C15	1.2103(17)	C5	C4	1.397(2)
O7	C16	1.2101(18)	C5	C6	1.390(2)
N8	C16	1.3981(18)	C4	C3	1.396(2)
N8	C15	1.3817(18)	C6	C1	1.394(2)
N8	C18	1.4679(19)	C3	C2	1.394(2)
C7	C8	1.5069(19)	C2	C1	1.382(2)

Table S5. Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O21	C12	123.34(11)	C10	C11	O21	122.10(13)
C9	O22	C14	108.10(10)	C10	C11	C13	126.42(13)
C17	N5	C16	124.08(12)	C11	C10	C9	115.88(13)
C17	N5	C19	118.85(12)	O21	C12	C8	114.73(11)
C16	N5	C19	116.79(12)	O20	C12	O21	116.47(12)
C16	N8	C18	116.64(12)	O20	C12	C8	128.79(13)
C15	N8	C16	124.18(12)	O24	C15	N8	123.32(13)
C15	N8	C18	117.90(12)	O24	C15	C14	122.44(13)
C8	C7	C4	117.25(11)	N8	C15	C14	113.83(12)
C8	C7	C14	98.45(10)	C6	C5	C4	120.81(14)
C4	C7	C14	113.99(11)	C5	C4	C7	121.88(12)
O23	C17	N5	123.26(13)	C3	C4	C7	119.36(13)
O23	C17	C14	121.74(13)	C3	C4	C5	118.64(13)

N5	C17	C14	114.75(12)	O22	C14	C7	107.67(10)
C9	C8	C7	111.20(11)	O22	C14	C17	107.28(11)
C9	C8	C12	120.39(13)	O22	C14	C15	109.23(11)
C12	C8	C7	128.17(12)	C17	C14	C7	110.85(11)
O22	C9	C8	114.41(12)	C15	C14	C7	107.32(11)
O22	C9	C10	122.19(12)	C15	C14	C17	114.31(11)
C8	C9	C10	123.39(13)	C5	C6	C1	120.00(15)
N5	C16	N8	117.97(12)	C2	C3	C4	120.48(14)
O7	C16	N5	121.09(13)	C1	C2	C3	120.44(14)
O7	C16	N8	120.93(13)	C2	C1	C6	119.61(14)
O21	C11	C13	111.47(12)				

Table S6. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **2a**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H7	3784	5810	3937	19
H10	3668	4212	619	22
H5	2484	6778	1397	23
H13A	-155	3464	653	31
H13B	851	3682	-340	31
H13C	-855	4097	-154	31
H6	2094	8020	1230	28
H3	4247	7016	4664	25
H2	3899	8261	4486	30
H18A	9813	5700	5530	44
H18B	8052	5445	5910	44
H18C	8650	6255	6077	44
H1	2860	8768	2772	31
H19A	9197	7569	2578	40
H19B	7460	7924	2848	40
H19C	7520	7549	1688	40

3. References

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