Supplementary materials File

Unexpected result of KOH—MeOH-promoted Thorpe—Ziegler heterocyclization of *N*-[(3-cyanoquinolin-2-yl)thio]acetylphenothiazines

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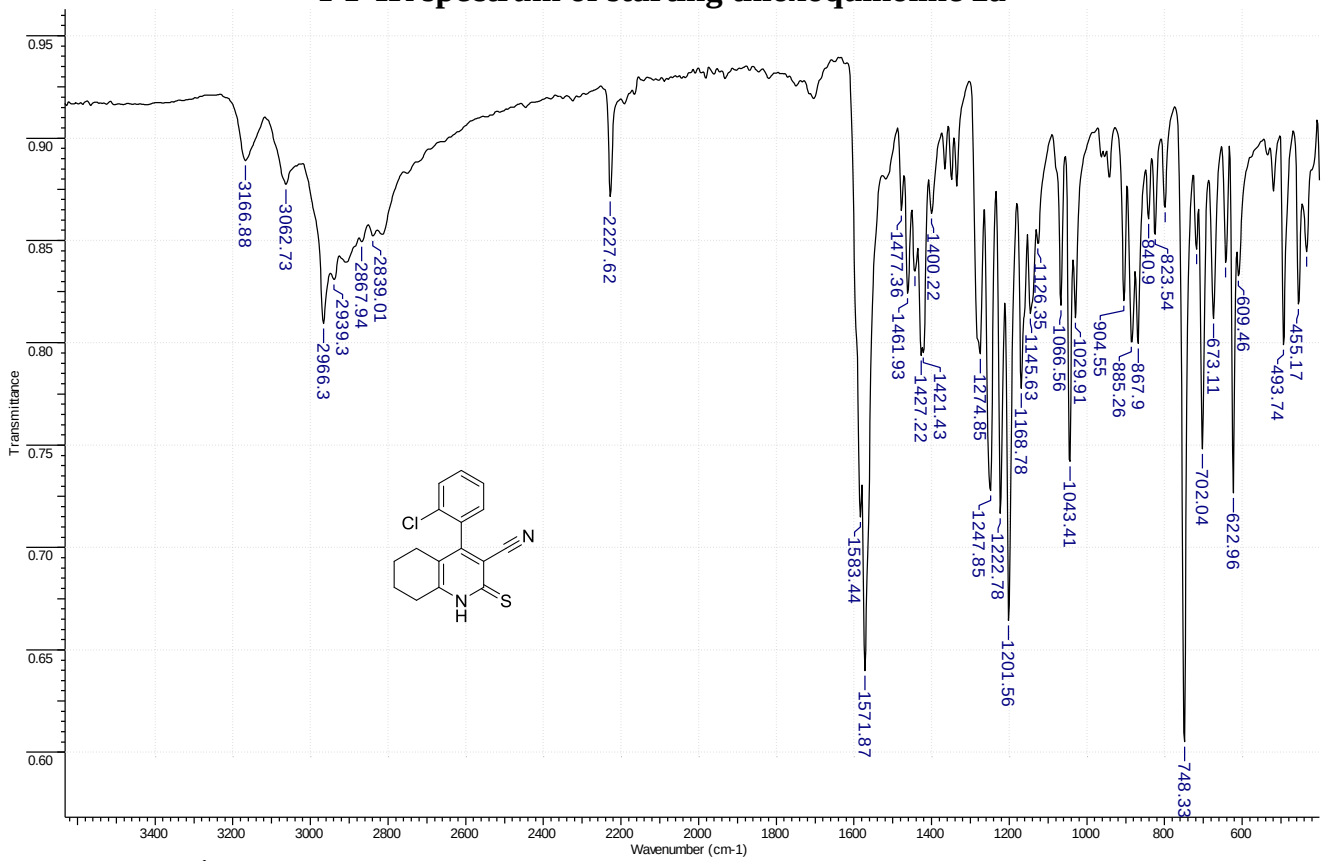
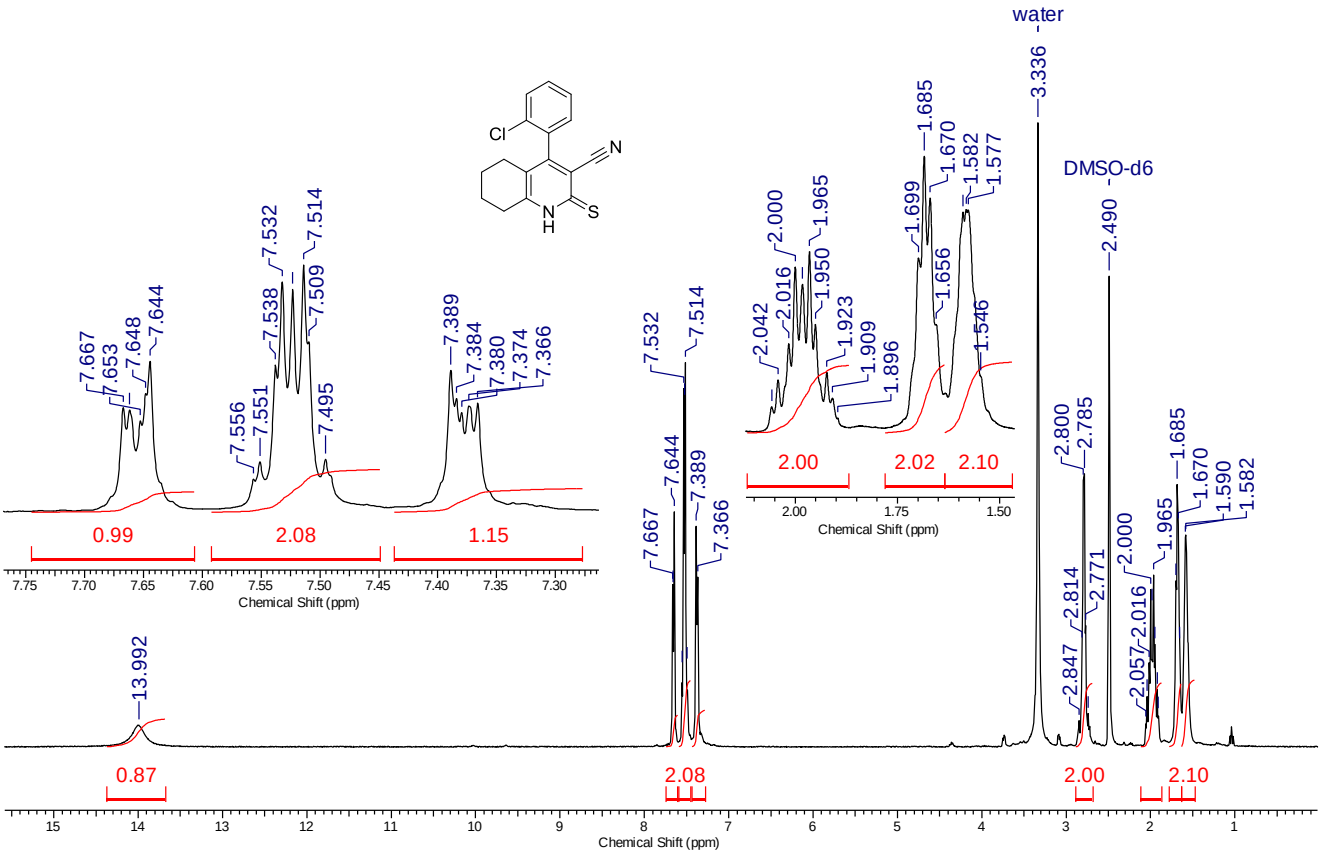
Contents. Selected spectral and X-ray data

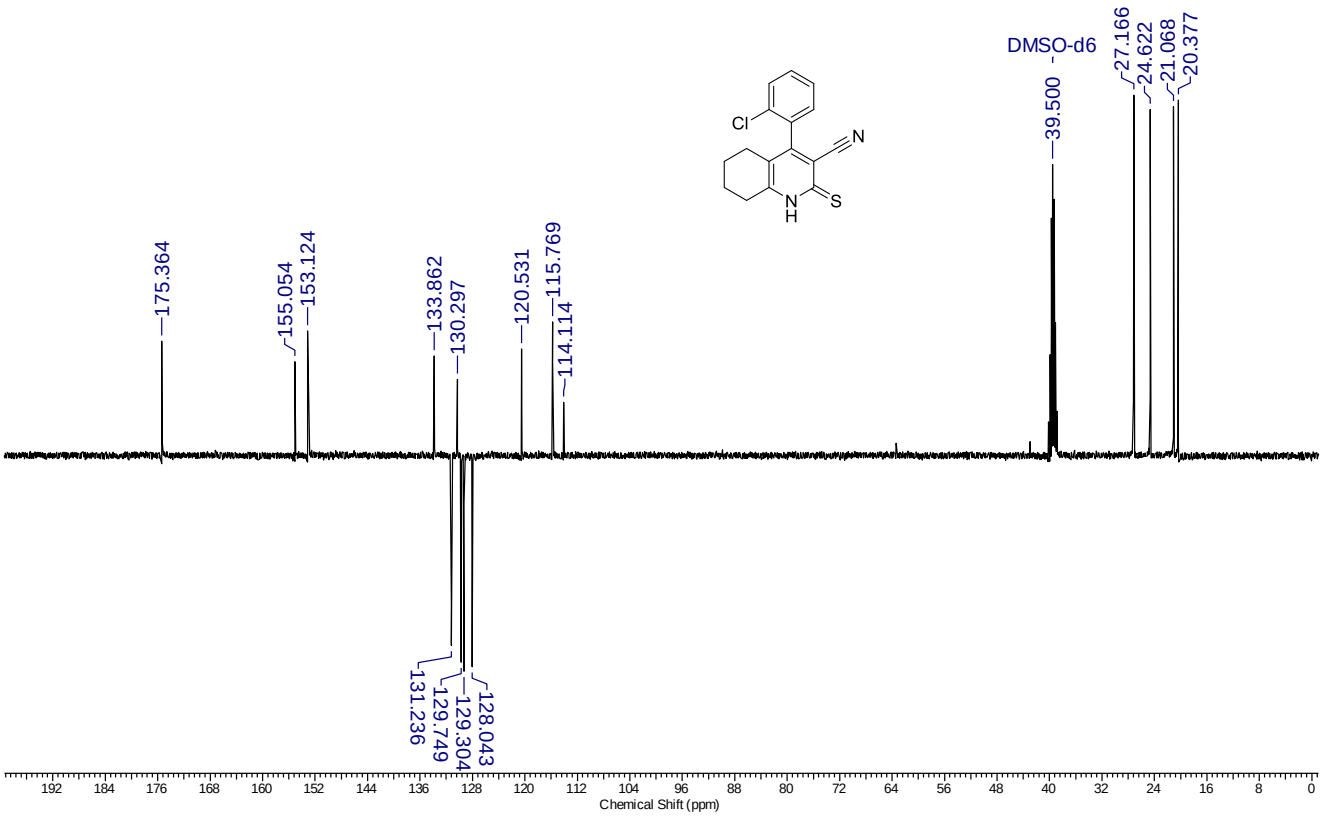
FT-IR spectrum of starting thioxoquinoline 2a



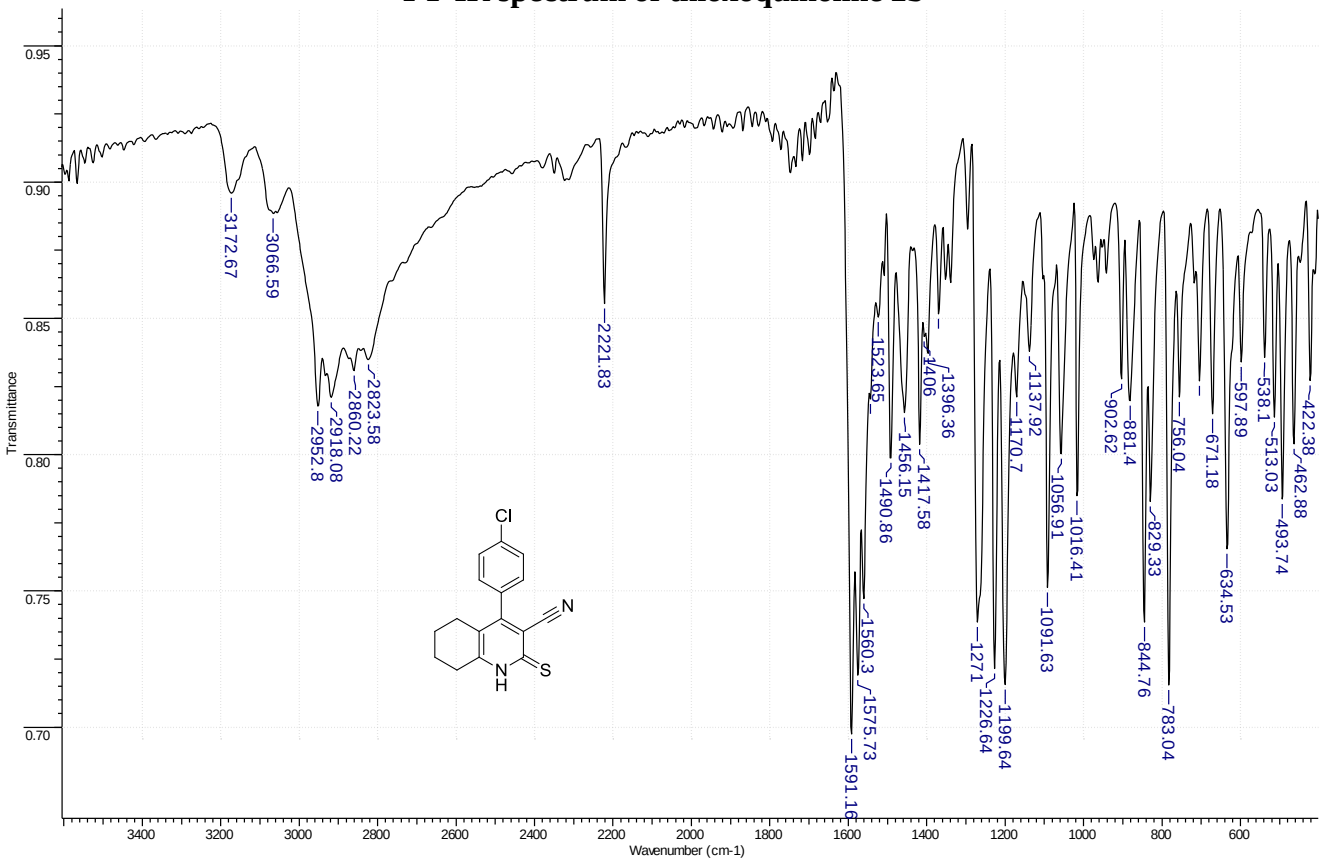
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of thioxoquinoline 2a



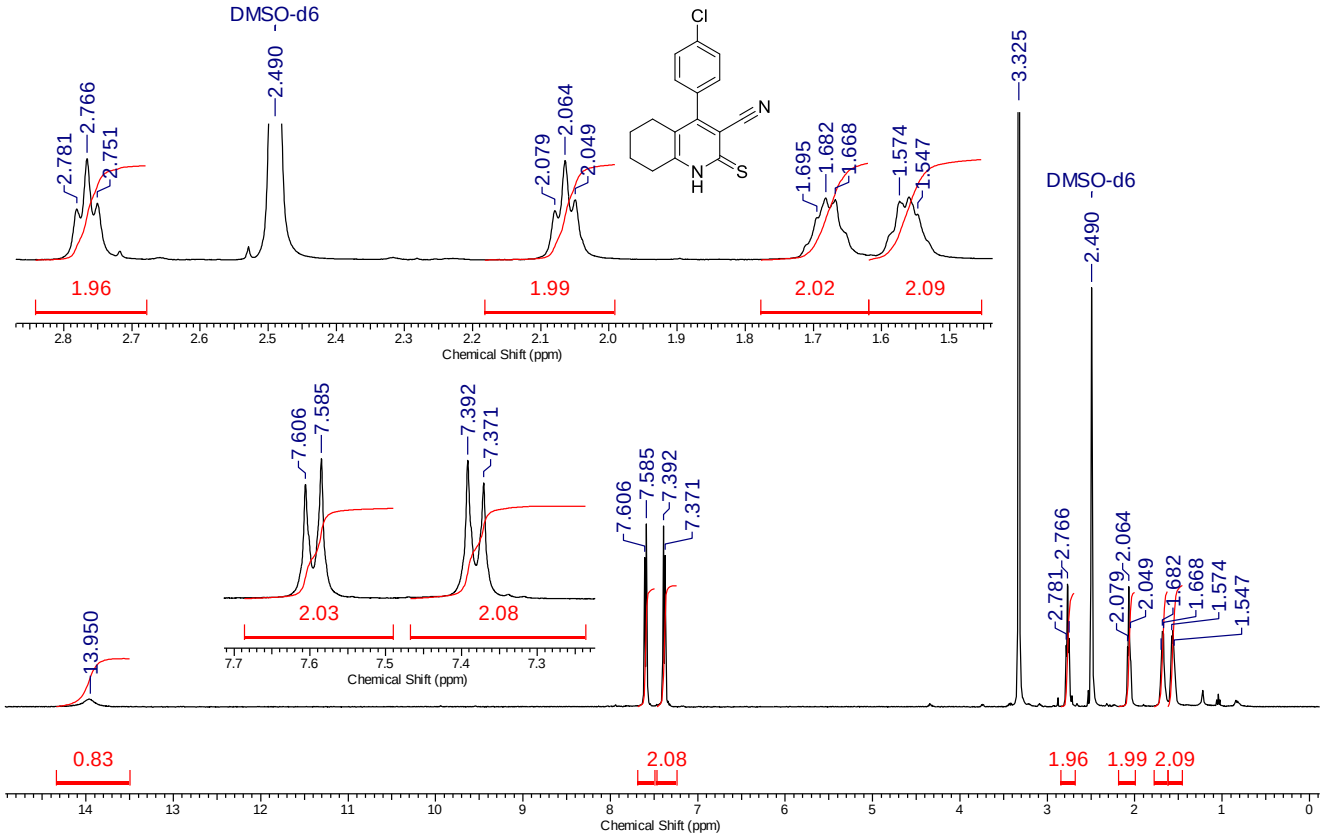
^{13}C DEPTQ NMR spectrum (101 MHz, DMSO-d_6) of thioxoquinoline 2a



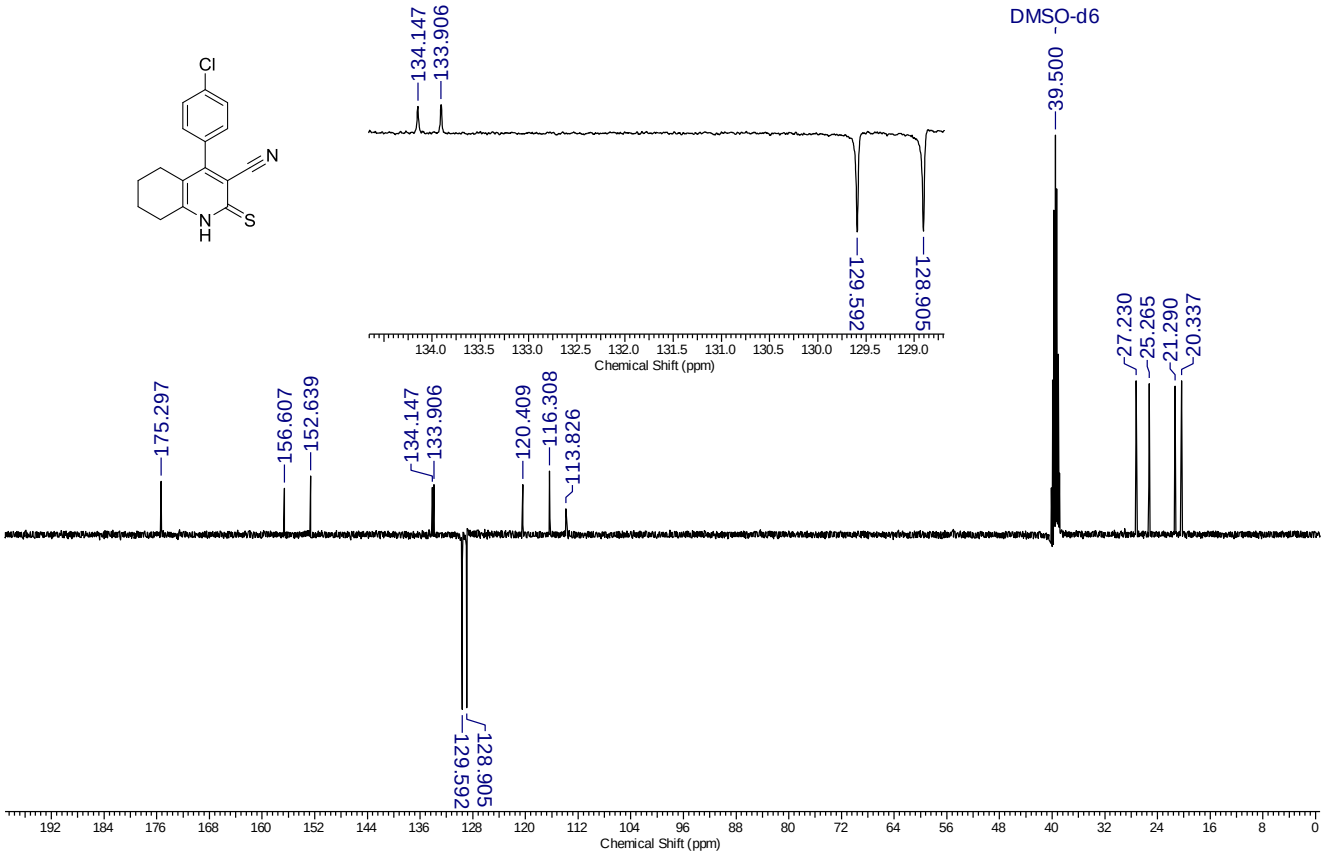
FT-IR spectrum of thioxoquinoline 2b



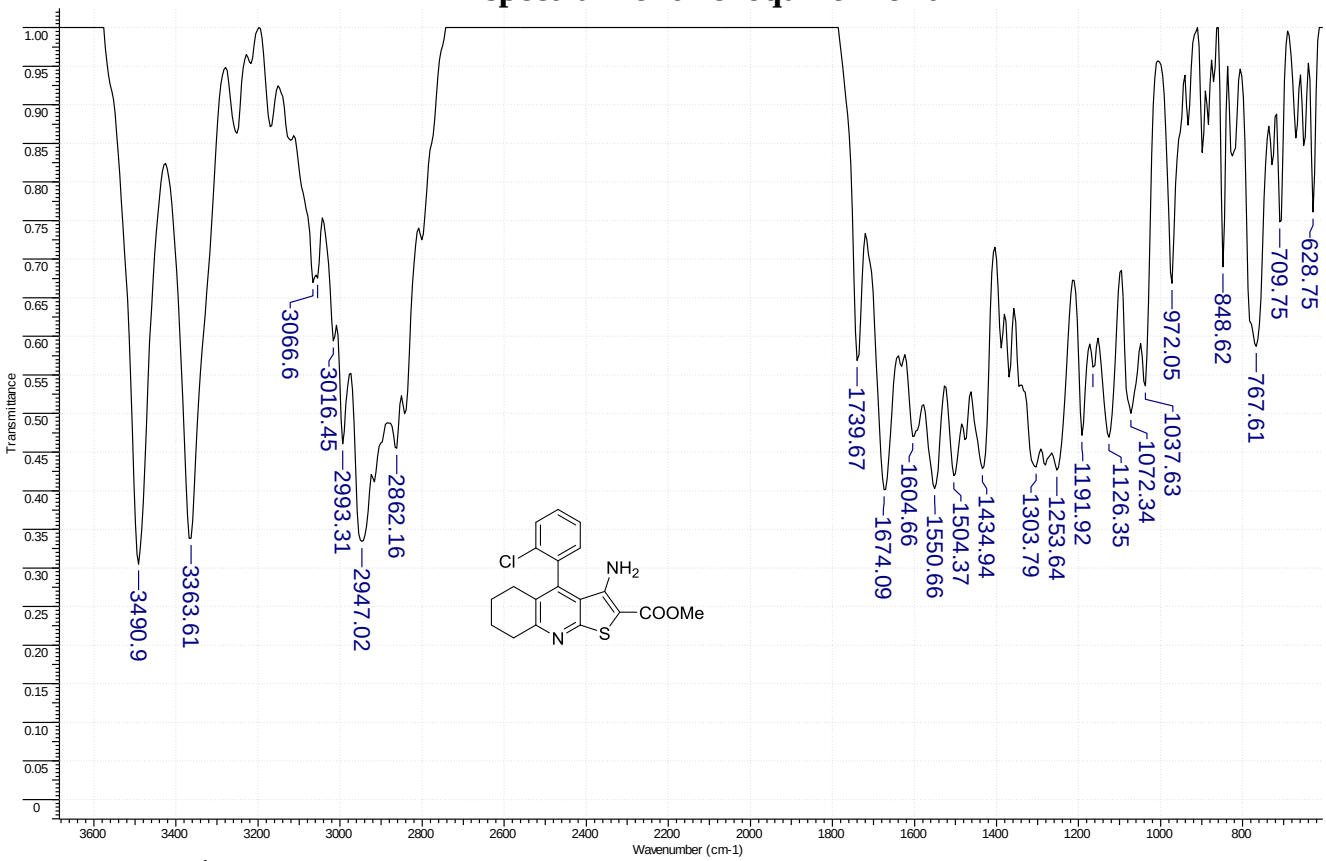
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of thioxoquinoline 2b



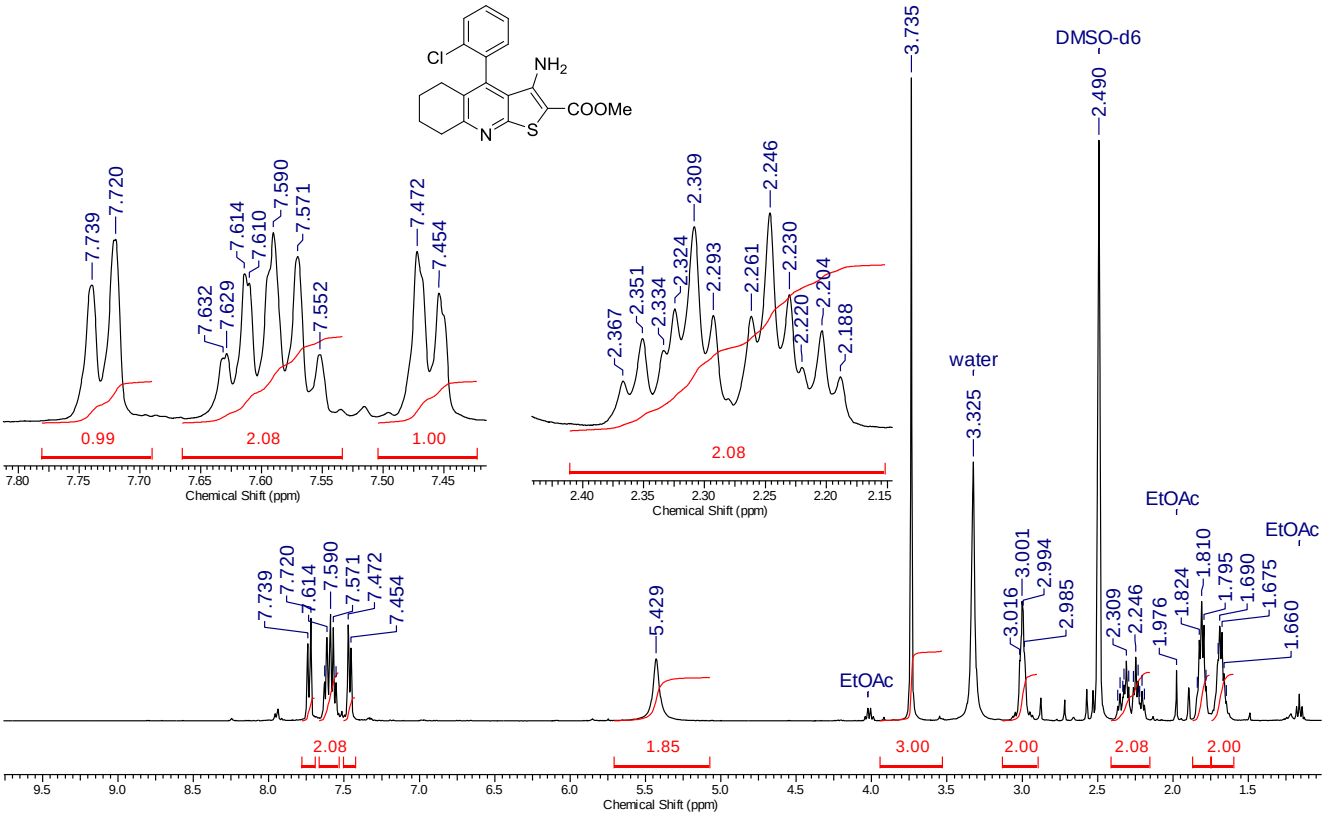
^{13}C DEPTQ NMR spectrum (101 MHz, DMSO-d_6) of thioxoquinoline 2b



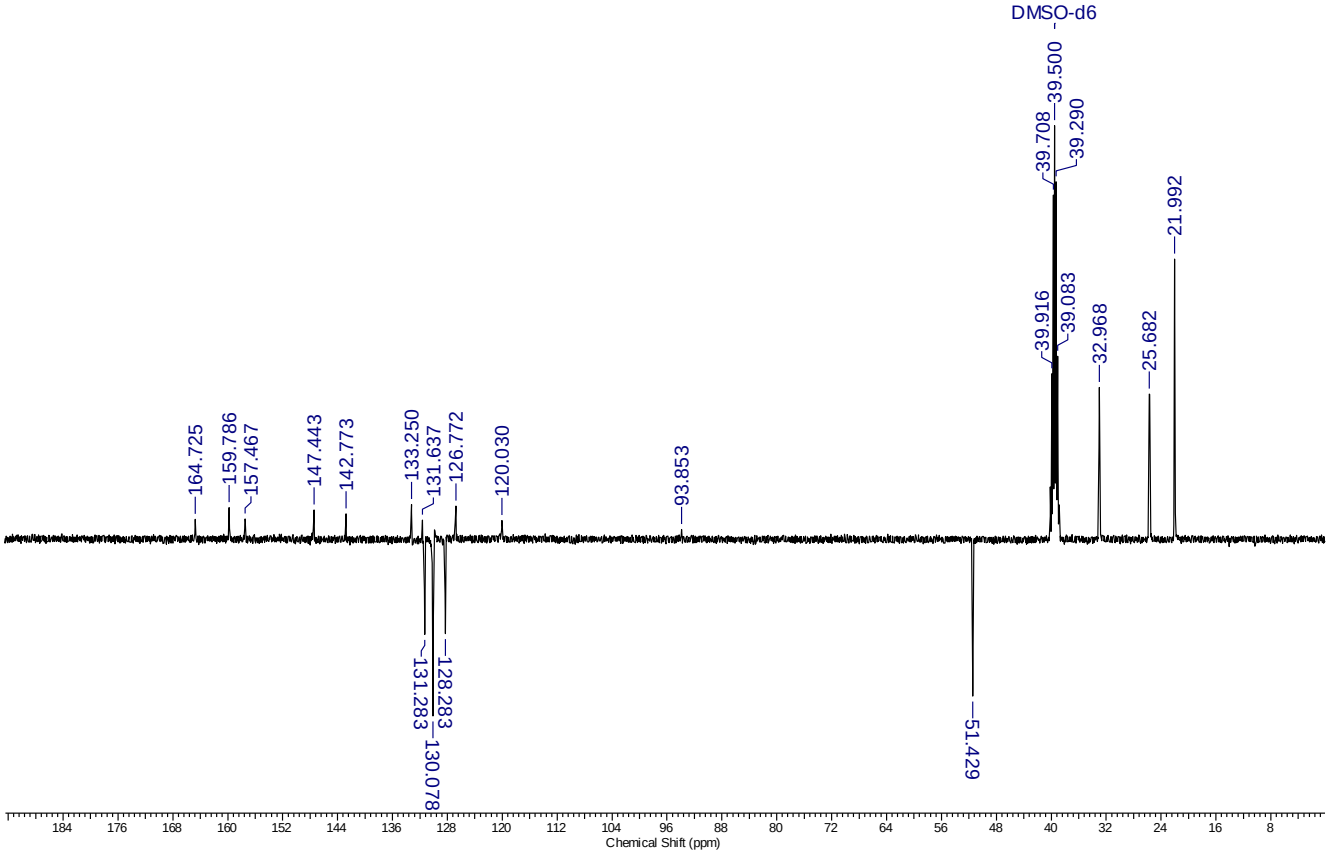
FT-IR spectrum of thienoquinoline 4a



^{1}H NMR spectrum (400 MHz, DMSO-d_6) of thienoquinoline 4a



^{13}C DEPTQ NMR spectrum (101 MHz, DMSO-d_6) of thienoquinoline 4a



X-Ray data for methyl 3-amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydrothieno[2,3-b]quinoline-2-carboxylate (4a)

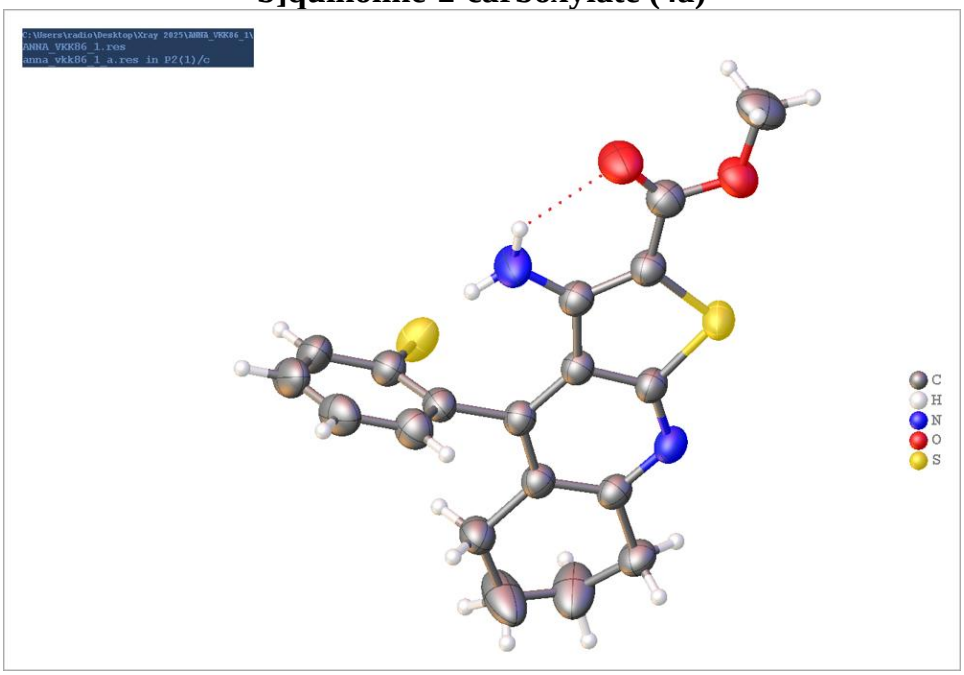


Fig. S1. ORTEP drawing of methyl 3-amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydrothieno[2,3-b]quinoline-2-carboxylate (4a) at the 50% probability level

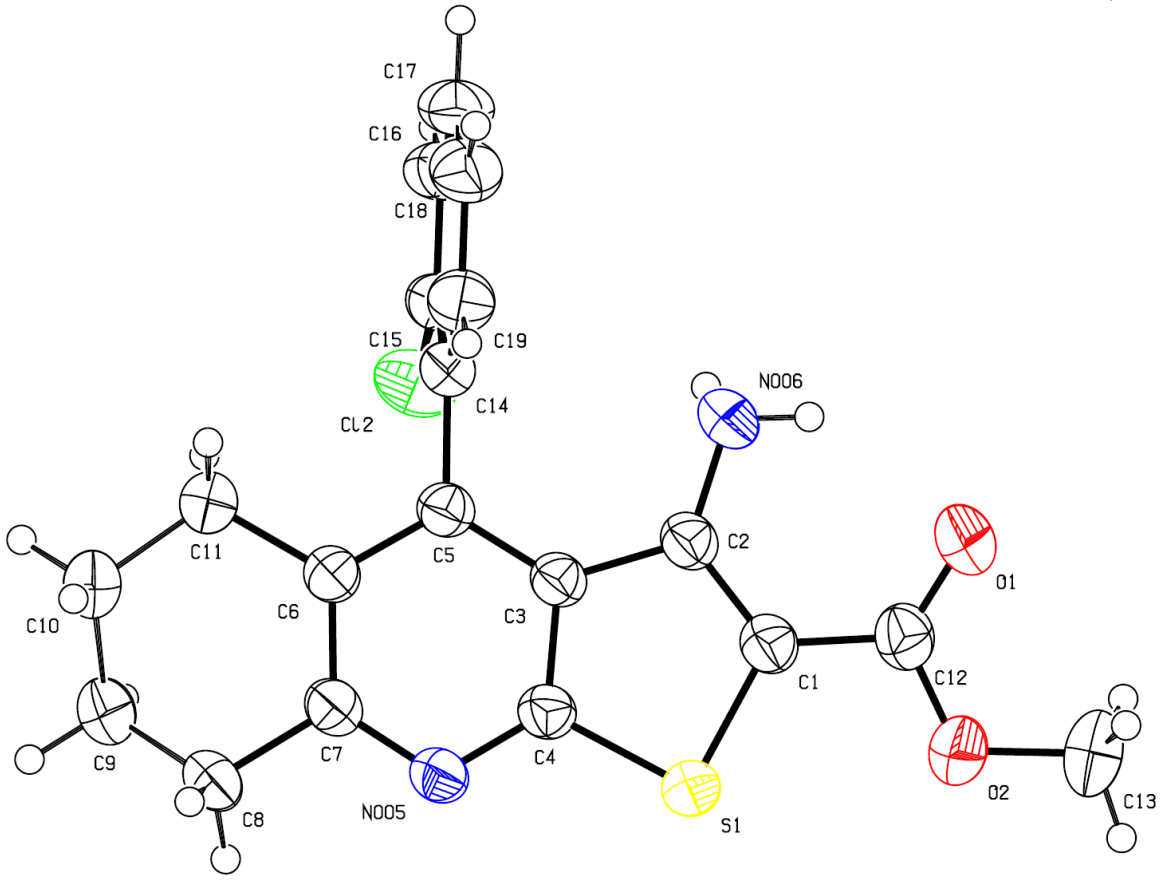


Table S1 Crystal data and structure refinement for thienoquinoline 4a

Identification code	ANNA_VKK86_1
Empirical formula	$C_{19}H_{17}ClN_2O_2S$
Formula weight	372.85
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.33120(10)
b/Å	7.93860(10)
c/Å	18.2034(2)
α/°	90
β/°	102.1520(10)
γ/°	90
Volume/Å^3	1742.05(3)
Z	4
ρ_{calc}g/cm^3	1.422
μ/mm^{-1}	3.188
F(000)	776.0
Crystal size/mm^3	0.61 × 0.35 × 0.25
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.334 to 152.258
Index ranges	$-15 \le h \le 15$, $-8 \le k \le 9$, $-22 \le l \le 21$

Reflections collected	18586
Independent reflections	3634 [R_{int} = 0.0254, R_{sigma} = 0.0151]
Data/restraints/parameters	3634/0/247
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1234
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1263
Largest diff. peak/hole / e Å^{-3}	0.47/-0.54

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for thienoquinoline 4a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	1122.6(4)	2313.5(6)	4791.1(3)	49.37(16)
Cl2	2727.8(4)	4176.2(8)	2081.3(3)	61.03(18)
O2	1954.6(12)	-940.7(18)	5333.8(8)	55.1(4)
O1	3672.5(13)	-780(2)	5100.2(11)	69.0(5)
N005	649.3(12)	5290(2)	4103.5(8)	43.0(3)
N006	4031.7(13)	2020(2)	4221.1(11)	57.7(5)
C3	2426.3(13)	3979(2)	4077.4(9)	37.2(3)
C7	935.4(14)	6573(2)	3709.2(9)	40.1(4)
C5	2709.1(13)	5346(2)	3661.8(9)	38.1(4)
C6	1957.8(14)	6663(2)	3476.8(9)	39.6(4)
C14	3796.4(14)	5394(2)	3421.8(10)	41.3(4)
C4	1384.6(14)	4050(2)	4279.0(9)	39.5(4)
C2	3015.0(14)	2444(2)	4347.2(10)	40.6(4)
C1	2406.6(15)	1453(2)	4737.7(10)	43.2(4)
C12	2758.3(16)	-162(3)	5067.2(11)	47.6(4)
C8	84.6(16)	7949(3)	3504.3(12)	49.8(4)
C15	3897.6(15)	4866(2)	2715.7(11)	45.1(4)
C11	2218.0(17)	8137(3)	3015.0(12)	52.1(5)
C19	4749.5(16)	5985(3)	3916.7(13)	52.1(5)
C17	5834.9(17)	5436(3)	3001.5(16)	63.0(6)
C16	4916.2(18)	4875(3)	2499.0(14)	57.7(5)
C18	5762.5(17)	5992(3)	3700.8(15)	60.6(6)
C13	2230(2)	-2558(3)	5680.4(14)	68.1(6)
C9	173(4)	8862(7)	2806(3)	53.3(10)
C10	1355(3)	9525(6)	2893(4)	55.1(11)
C9A	457(10)	9470(17)	3064(9)	58(3)
C10A	1208(8)	8943(18)	2538(8)	58(3)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for thienoquinoline 4a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1	47.4(3)	51.4(3)	54.6(3)	13.8(2)	22.6(2)	8.72(19)
Cl2	47.8(3)	75.6(4)	57.8(3)	-16.6(2)	6.9(2)	2.5(2)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for thienoquinoline 4a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	57.9(8)	51.4(8)	56.1(8)	15.3(6)	12.3(6)	2.9(6)
O1	53.8(9)	60.2(9)	93.3(12)	23.3(8)	16.0(8)	17.0(7)
N005	40.0(7)	47.7(8)	43.9(8)	5.2(6)	14.2(6)	9.1(6)
N006	42.8(9)	60.9(11)	72.1(11)	18.7(9)	18.0(8)	17.0(7)
C3	33.6(8)	41.1(9)	36.7(8)	1.6(6)	6.7(6)	3.7(6)
C7	38.8(8)	43.8(9)	37.6(8)	0.6(7)	8.2(6)	7.1(7)
C5	34.3(8)	42.2(9)	37.9(8)	1.0(7)	7.7(6)	2.0(6)
C6	39.0(8)	40.9(9)	39.3(8)	2.2(7)	9.4(6)	3.7(7)
C14	35.5(8)	39.7(9)	49.2(9)	5.8(7)	10.2(7)	3.5(6)
C4	38.3(8)	44.5(9)	37.2(8)	2.2(7)	11.3(6)	4.6(7)
C2	36.7(8)	43.5(9)	40.7(8)	2.4(7)	6.4(6)	5.2(7)
C1	41.0(8)	45.4(9)	43.1(9)	4.3(7)	8.6(7)	5.7(7)
C12	49.1(10)	48.2(10)	43.7(9)	5.2(8)	5.3(7)	5.0(8)
C8	45.1(9)	49.2(10)	57.1(11)	6.6(8)	14.7(8)	14.5(8)
C15	39.2(9)	43.7(9)	53.9(10)	0.3(8)	13.0(7)	2.4(7)
C11	51.4(10)	47.4(10)	61.0(12)	13.0(9)	19.6(9)	6.4(8)
C19	41.5(9)	55.2(11)	58.0(11)	2.5(9)	6.6(8)	-2.7(8)
C17	42.6(10)	53.9(12)	99.0(18)	-5.7(11)	29.3(11)	-5.0(9)
C16	53.1(11)	53.2(11)	74.3(13)	-10.2(10)	30.3(10)	-1.4(9)
C18	38.4(10)	57.3(12)	83.6(16)	-0.9(11)	7.3(10)	-7.1(9)
C13	87.3(17)	51.4(12)	63.0(13)	17.0(10)	9.8(12)	1.1(11)
C9	48.3(19)	52(2)	58(2)	12.0(17)	7.1(15)	9.4(17)
C10	55.5(19)	44.5(19)	66(3)	11.3(17)	14.7(18)	5.1(14)
C9A	55(6)	47(5)	72(7)	13(5)	11(5)	14(4)
C10A	56(4)	61(6)	56(6)	17(5)	10(4)	8(4)

Table S4. Bond Lengths for thienoquinoline 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C4	1.7325(18)	C6	C11	1.514(2)
S1	C1	1.7457(18)	C14	C15	1.382(3)
Cl2	C15	1.7360(19)	C14	C19	1.403(3)
O2	C12	1.342(2)	C2	C1	1.383(3)
O2	C13	1.440(3)	C1	C12	1.444(3)
O1	C12	1.219(2)	C8	C9	1.486(4)
N005	C7	1.335(2)	C8	C9A	1.570(11)
N005	C4	1.331(2)	C15	C16	1.394(3)
N006	C2	1.363(2)	C11	C10	1.516(4)
C3	C5	1.408(2)	C11	C10A	1.503(9)
C3	C4	1.409(2)	C19	C18	1.386(3)
C3	C2	1.450(2)	C17	C16	1.372(3)
C7	C6	1.413(2)	C17	C18	1.368(4)
C7	C8	1.506(2)	C9	C10	1.526(8)
C5	C6	1.390(2)	C9A	C10A	1.52(2)
C5	C14	1.496(2)			

Table S5. Bond Angles for thienoquinoline 4a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	S1	C1	90.42(8)	C1	C2	C3	111.40(15)
C12	O2	C13	116.44(18)	C2	C1	S1	113.76(13)
C4	N005	C7	116.69(15)	C2	C1	C12	124.83(17)
C5	C3	C4	116.81(15)	C12	C1	S1	121.41(14)
C5	C3	C2	131.81(15)	O2	C12	C1	112.28(17)
C4	C3	C2	111.38(15)	O1	C12	O2	122.87(19)
N005	C7	C6	123.55(15)	O1	C12	C1	124.85(19)
N005	C7	C8	115.92(15)	C7	C8	C9A	114.9(4)
C6	C7	C8	120.52(16)	C9	C8	C7	113.1(2)
C3	C5	C14	120.99(15)	C14	C15	Cl2	119.29(14)
C6	C5	C3	118.80(15)	C14	C15	C16	121.66(19)
C6	C5	C14	120.20(16)	C16	C15	Cl2	119.04(16)
C7	C6	C11	120.78(15)	C6	C11	C10	114.8(2)
C5	C6	C7	118.72(16)	C10A	C11	C6	113.8(4)
C5	C6	C11	120.48(15)	C18	C19	C14	120.1(2)
C15	C14	C5	121.74(16)	C18	C17	C16	121.25(19)
C15	C14	C19	118.12(17)	C17	C16	C15	118.7(2)
C19	C14	C5	120.15(17)	C17	C18	C19	120.1(2)
N005	C4	S1	121.53(13)	C8	C9	C10	108.7(4)
N005	C4	C3	125.43(16)	C11	C10	C9	113.0(4)
C3	C4	S1	113.04(13)	C10A	C9A	C8	113.0(10)
N006	C2	C3	124.28(16)	C11	C10A	C9A	107.0(11)
N006	C2	C1	124.31(17)				

Table S6. Torsion Angles for thienoquinoline 4a

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C12	O2	6.3(2)	C6	C11	C10	C9	-35.3(7)
S1	C1	C12	O1	-174.25(18)	C6	C11	C10A	C9A	56.6(15)
Cl2	C15	C16	C17	179.44(18)	C14	C5	C6	C7	179.67(16)
N005	C7	C6	C5	0.4(3)	C14	C5	C6	C11	1.5(3)
N005	C7	C6	C11	178.59(17)	C14	C15	C16	C17	-0.5(3)
N005	C7	C8	C9	-152.6(3)	C14	C19	C18	C17	0.6(3)
N005	C7	C8	C9A	178.1(8)	C4	S1	C1	C2	0.08(15)
N006	C2	C1	S1	-178.79(16)	C4	S1	C1	C12	-178.85(17)
N006	C2	C1	C12	0.1(3)	C4	N005	C7	C6	0.1(3)
C3	C5	C6	C7	-0.4(3)	C4	N005	C7	C8	178.97(16)
C3	C5	C6	C11	-178.55(16)	C4	C3	C5	C6	-0.1(2)
C3	C5	C14	C15	96.0(2)	C4	C3	C5	C14	179.85(16)
C3	C5	C14	C19	-84.1(2)	C4	C3	C2	N006	178.53(18)
C3	C2	C1	S1	0.2(2)	C4	C3	C2	C1	-0.5(2)
C3	C2	C1	C12	179.09(17)	C2	C3	C5	C6	179.54(17)
C7	N005	C4	S1	179.81(13)	C2	C3	C5	C14	-0.5(3)
C7	N005	C4	C3	-0.6(3)	C2	C3	C4	S1	0.53(19)
C7	C6	C11	C10	5.1(4)	C2	C3	C4	N005	-179.07(17)
C7	C6	C11	C10A	-27.9(8)	C2	C1	C12	O2	-172.49(17)
C7	C8	C9	C10	-54.9(6)	C2	C1	C12	O1	6.9(3)
C7	C8	C9A	C10A	34.1(16)	C1	S1	C4	N005	179.27(16)
C5	C3	C4	S1	-179.75(13)	C1	S1	C4	C3	-0.35(14)
C5	C3	C4	N005	0.6(3)	C8	C7	C6	C5	-178.43(17)
C5	C3	C2	N006	-1.1(3)	C8	C7	C6	C11	-0.3(3)
C5	C3	C2	C1	179.88(18)	C8	C9	C10	C11	60.5(7)
C5	C6	C11	C10	-176.7(3)	C8	C9A	C10A	C11	-60.0(18)
C5	C6	C11	C10A	150.2(8)	C15	C14	C19	C18	-1.6(3)
C5	C14	C15	Cl2	1.5(2)	C19	C14	C15	Cl2	-178.41(15)
C5	C14	C15	C16	-178.50(18)	C19	C14	C15	C16	1.6(3)
C5	C14	C19	C18	178.46(18)	C16	C17	C18	C19	0.4(4)
C6	C7	C8	C9	26.3(4)	C18	C17	C16	C15	-0.5(4)
C6	C7	C8	C9A	-3.0(8)	C13	O2	C12	O1	1.1(3)
C6	C5	C14	C15	-84.1(2)	C13	O2	C12	C1	-179.44(18)
C6	C5	C14	C19	95.9(2)					

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for thienoquinoline 4a.

Atom	*x*	*y*	*z*	U(eq)
H00A	4253.39	1108.03	4462.06	69
H00B	3979.26	1856.07	3747.61	69
H8AA	-650.59	7461.26	3439.18	60
H8AB	172.24	8748.71	3915.64	60
H8BC	-101.45	8374.54	3961.91	60
H8BD	-583.82	7465.88	3200.34	60
H11B	2299.91	7721.04	2528.61	63
H11A	2924.63	8614.57	3262.8	63
H11C	2619.86	8980.03	3351.57	63
H11D	2700.13	7752.51	2691.48	63
H19	4701.61	6374.36	4390.77	63
H17	6519.8	5438.85	2864.11	76
H16	4972.19	4507.92	2023.23	69
H18	6394.17	6374.52	4032.03	73
H13A	2488.77	-3291.1	5334.55	102
H13B	1582.84	-3038.89	5813.34	102
H13C	2800.98	-2423.67	6124.6	102
H9A	-349.31	9790.99	2721.42	64
H9B	-1.35	8106.61	2378.71	64
H10A	1410.24	10153.29	2445.36	66
H10B	1511.15	10294.65	3315.93	66
H9AA	-196.42	10019.3	2773.46	70
H9AB	847.14	10282.74	3422.72	70
H10C	826.63	8148.78	2166.74	69
H10D	1417.73	9917.08	2278.1	69

Table S8. Atomic Occupancy for thienoquinoline 4a.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H8AA	0.709(12)	H8AB	0.709(12)	H8BC	0.291(12)
H8BD	0.291(12)	H11B	0.709(12)	H11A	0.709(12)
H11C	0.291(12)	H11D	0.291(12)	C9	0.709(12)
H9A	0.709(12)	H9B	0.709(12)	C10	0.709(12)
H10A	0.709(12)	H10B	0.709(12)	C9A	0.291(12)
H9AA	0.291(12)	H9AB	0.291(12)	C10A	0.291(12)
H10C	0.291(12)	H10D	0.291(12)		

X-ray studies details

Single crystals of thienoquinoline **4a**, $C_{14}H_{12}N_2S_2$ were grown from EtOAc—petroleum ether mixture (1 : 1). A suitable crystal was selected and mounted on the glass stick by acrylic glue on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of thienoquinoline 4a

Crystal Data for $C_{19}H_{17}ClN_2O_2S$ (M =372.85 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.33120(10) Å, b = 7.93860(10) Å, c = 18.2034(2) Å, β = 102.1520(10)°, V = 1742.05(3) Å^3, Z = 4, T = 293(2) K, μ(Cu Kα) = 3.188 mm^{-1}, *Dcalc* = 1.422 g/cm^3, 18586 reflections measured (7.334° ≤ 2Θ ≤ 152.258°), 3634 unique (R_{int} = 0.0254, R_{sigma} = 0.0151) which were used in all calculations. The final R_1 was 0.0423 (I > 2σ(I)) and wR_2 was 0.1263 (all data). The complete structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC **2449120**) and can be obtained, free of charge, on request (http://www.ccdc.cam.ac.uk/data_request/cif).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups, All N(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Others
 Sof(H8BC)=Sof(H8BD)=Sof(H11C)=Sof(H11D)=Sof(C9A)=Sof(H9AA)=Sof(H9AB)=
 Sof(C10A)=Sof(H10C)=Sof(H10D)=1-FVAR(1)
 Sof(H8AA)=Sof(H8AB)=Sof(H11B)=Sof(H11A)=Sof(C9)=Sof(H9A)=Sof(H9B)=Sof(C10)=
 Sof(H10A)=Sof(H10B)=FVAR(1)
3.a Rotating group:
 N006(H00A,H00B)
3.b Secondary CH2 refined with riding coordinates:
 C8(H8AA,H8AB), C8(H8BC,H8BD), C11(H11B,H11A), C11(H11C,H11D), C9(H9A,H9B),
 C10(H10A,H10B), C9A(H9AA,H9AB), C10A(H10C,H10D)
3.c Aromatic/amide H refined with riding coordinates:
 C19(H19), C17(H17), C16(H16), C18(H18)
3.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C)
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