Supporting Information for

Synthesis of hydroxy-thiazoline substituted pyridine derivatives *via* [3 + 2] cycloaddition of 1,4-dithiane-2,5-diol with cyanopyridine

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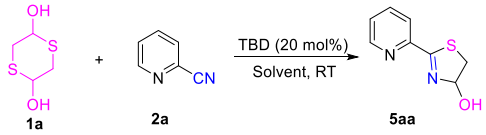
Contents

1. General information.

All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. 1H and 13C NMR spectra were measured on a JNM-ECZ600R/S3 (Jeol, Japan) (600 and 150 MHz for 1H and 13C NMR, respectively) using $CDCl_3$ or DMSO-*D6* as the solvent. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; m = multiplet, etc.), coupling constants (Hz), integration. Enantiomer excesses were determined by chiral HPLC analysis on in comparison with the authentic racemates. Singlecrystal X-ray diffraction was performed on the title crystals. The diffractometer is a Bruker D8 Venture（IμS3.0）. And it is equipped with graphite-monochromated MoKα radiation, at 296 K. High resolution mass spectra (HRMS (ESI)) were obtained via ESI mode by using a MicrOTOF mass spectrometer.

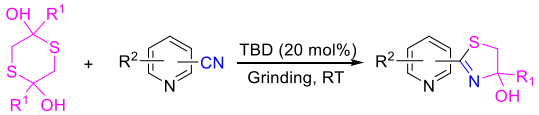
2. Optimization of reaction conditions.



Entry	Solvent	T (°C)	Yield (%)[b]
1	DCM	50	82(78)[c]
2	$CHCl_3$	50	60
3	PhCl	50	47
4	CH_3OH	50	22
5	THF	50	16
6	EtOH	50	37
7	CH_3CN	60	19
8	DMSO	70	21

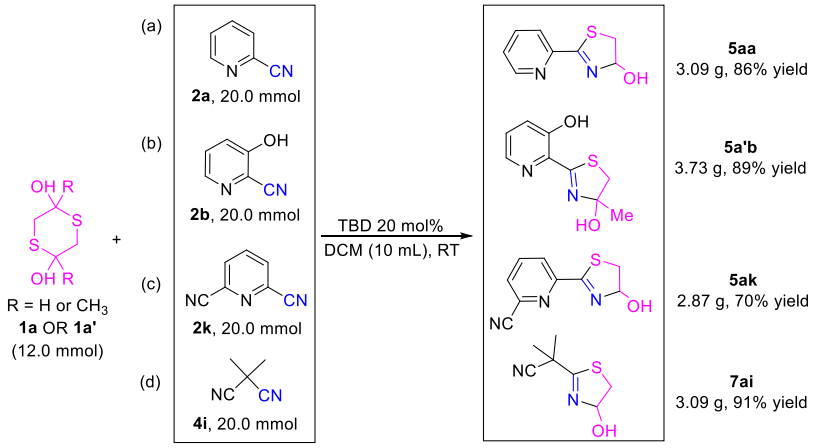
[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.12 mmol), **2a** (0.2 mmol), and in solvent (1 mL) for 12 h, TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene. [b]The yield was determined by ^{1}H NMR spectra of the crude product using 1,3,5-trimethylbenzene as an internal standard. [c]Isolated yields.

3. General procedure for the synthesis of pyridine hydroxy thiazoline compounds.



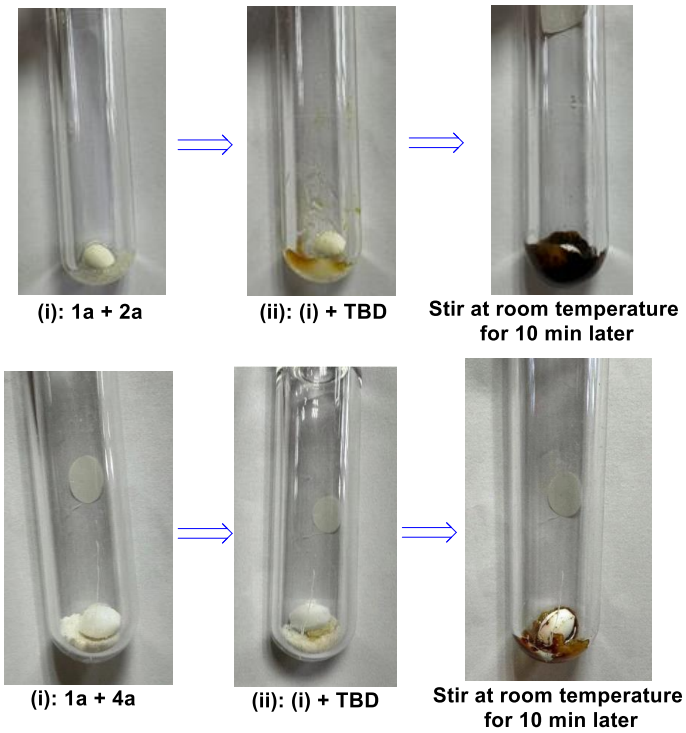
To the dry mortar, add **1a** or **1a'** (0.12 mmol), **2/3/4** (0.2 mmol), and grind the compound to mix well. Then 20 mol% **TBD** is added to the mixture and grinding continues for 10-15 min. After grinding, the mixture was dissolved in methanol or dichloromethane, and petroleum ether was gradually added to the mixture, so that the solid was recrystallized and purified. After crystallization, the mother liquor mixture was purified by silica gel column chromatography, and the product was separated in the ethyl acetate petroleum ether system (EA / PE = 3/1 to 1/1).

Gram-scale experiment：



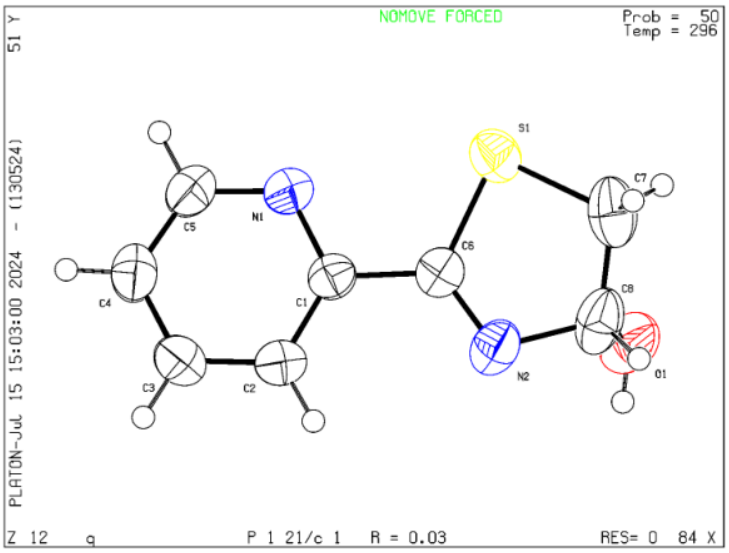
To a Schlenk tube equipped with a magnetic stir bar, **1a** or **1a'** (12.0 mmol), **2a/2b/2k/4i** (20.0 mmol), DCM (10.0 mL) was added to the reaction mixture, TBD (20 mol%) were added, and stir the mixture at room temperature. The reaction process was analyzed by TLC. After the reaction is completed, the solid solvent is heated and petroleum ether is slowly dropped into the solution to recrystallize the target product. The remaining mixture was purified by silica gel column chromatography in an ethyl acetate petroleum ether system (EA / PE = 3/1-1/1).

4. The state of compounds and color change



5. The X-ray crystallographic data of 5aa.

X-Ray crystal structure of **5aa** (The crystal was obtained by slow evaporation of **5aa** in a mixture of CH_2Cl_2/petroleum ether/ethyl acetate) (CCDC 2371473):



Table

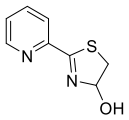
Identification code	**5aa**
Empirical formula	$C_8H_8N_2OS$
Formula weight	180.22
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.0399(3)
b/Å	15.0255(11)
c/Å	11.3318(9)
α/°	90
β/°	93.975(2)
γ/°	90
Volume/Å3	856.06(11)
Z	4
ρcalcg/cm3	1.398
μ/mm-1	0.327
F(000)	376.0
Crystal size/mm3	0.13 ×0.11 ×0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.51 to 56.658
Index ranges	-6 ⩽ h ⩽ 6, -20 ⩽ k ⩽ 20, -15 ⩽ l ⩽ 15
Reflections collected	12362
Independent reflections	2110 [Rint = 0.0192, Rsigma = 0.0145]
Data/restraints/parameters	2110/0/110
Goodness-of-fit on F2	1.069
Final R indexes [I>=2σ (I)]	R1 = 0.0337, wR2 = 0.0922

Final R indexes [all data] R1 = 0.0400, wR2 = 0.0969

Largest diff. peak/hole / e Å-3 0.22/-0.18

6. The analytical and spectral characterization data for the products.

2-(pyridin-2-yl)-4,5-dihydrothiazol-4-ol



5aa, White solid, m.p. = 122.9-125.2 ℃. 158.4 mg, 88% yield.

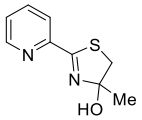
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 – 8.62 (dd, *J* = 4.8, 0.6 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.81 (td, *J* = 7.8, 1.2 Hz, 1H), 7.41 (ddd, *J* = 7.8, 4.8, 1.2 Hz, 1H), 6.38 (dd, *J* = 6.6, 5.4 Hz, 1H), 5.34 (s, 1H), 3.60 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.35 (dd, *J* = 12.0, 7.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8, 150.4, 149.6, 137.0, 126.2, 121.9, 99.7, 38.4.

HRMS (ESI): calcd for $C_8H_9N_2OS^+$ $[M+H]^+$ requires m/z 181.0431, found m/z 181.0439

4-methyl-2-(pyridin-2-yl)-4,5-dihydrothiazol-4-ol



5a'a, White solid, m.p. = 127.7-129.4 ℃. 166.8 mg, 86% yield.

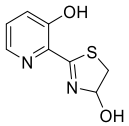
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.61 (d, *J* = 4.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.56 – 7.44 (m, 1H), 6.28 (s, 1H), 3.27 (d, *J* = 11.4 Hz, 1H), 3.18 (d, *J* = 11.4 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (150 MHz, DMSO- D_6) δ 166.3, 150.3, 149.3, 137.1, 126.1, 121.2, 107.2, 42.7, 27.6.

HRMS (ESI): calcd for $C_9H_{11}N_2OS^+$ $[M+N]^+$ requires m/z 195.0587, found m/z 195.0595.

2-(3-hydroxypyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ab, White solid, m.p. = 101.7-103.5 ℃. 139.1 mg, 71% yield.

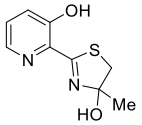
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, DMSO-*D6*) δ 12.53 (s, 1H), 8.17 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.50 – 7.36 (m, 2H), 6.68 (d, *J* = 6.4 Hz, 1H), 6.30 – 6.14 (m, 1H), 3.52 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.06 (dd, *J* = 12.0, 4.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-*D6*) δ 175.1, 155.8, 141.5, 133.9, 128.5, 125.3, 98.6, 37.5.

HRMS (ESI): calcd for $C_8H_9N_2O_2S^+$ $[M+H]^+$ requires m/z 197.0379, found m/z 197.0386.

2-(3-hydroxypyridin-2-yl)-4-methyl-4,5-dihydrothiazol-4-ol



5a'b, White solid, m.p. = 129.7-131.5 ℃. 186.9 mg, 89% yield.

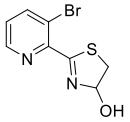
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 12.47 (s, 1H), 8.25 – 8.15 (m, 1H), 7.58 – 7.30 (m, 2H), 6.57 (s, 1H), 3.36 (s, 1H), 3.24 (d, *J* = 11.4 Hz, 1H), 1.59 (s, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 172.2, 155.6, 141.4, 134.0, 128.3, 125.1, 106.6, 41.9, 28.4.

HRMS (ESI): calcd for $C_9H_{11}N_2O_2S^+$ $[M+H]^+$ requires m/z 211.0536, found m/z 211.0537.

2-(3-bromopyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ac, Pale yellow solid, m.p. = 112.2-114.5 ℃. 234.7 mg, 91% yield.

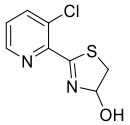
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 8.66 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.2, 4.2 Hz, 1H), 6.64 (s, 1H), 6.20 (t, *J* = 6.6 Hz, 1H), 3.53 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.05 (dd, *J* = 11.4, 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 166.7, 148.4, 143.4, 127.1, 118.5, 101.6, 38.9.

HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9535.

2-(3-chloropyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ad, Yellow solid, m.p. = 126.2-128.9 ℃. 196.8 mg, 92% yield.

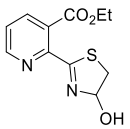
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 8.64 (d, *J* = 5.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.65 (d, *J* = 5.4 Hz, 1H), 6.28 – 6.16 (m, 1H), 3.51 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.03 (dd, *J* = 11.4, 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 166.3, 148.0, 147.1, 140.2, 130.0, 127.1, 101.8, 38.5.

HRMS (ESI): calcd for $C_8H_8ClN_2OS^+$ $[M+H]^+$ requires m/z 215.0041, found m/z 215.0047.

ethyl 2-(4-hydroxy-4,5-dihydrothiazol-2-yl)nicotinate



5ae, Pale yellow solid, m.p. = 115.4-118.2 ℃. 183.9 mg, 73% yield.

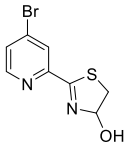
TLC: R_f = 0.25 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.75 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.11 (t, *J* = 7.2 Hz, 1H), 4.40 – 4.15 (m, 2H), 3.56 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.07 (dd, *J* = 11.4, 7.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 167.6, 166.9, 150.8, 147.6, 136.6, 129.4, 126.1, 100.7, 62.0, 38.8, 14.2.

HRMS (ESI): calcd for $C_{11}H_{13}N_2O_3S^+$ $[M+H]^+$ requires m/z 253.0642, found m/z 253.0649.

2-(4-bromopyridin-2-yl)-4,5-dihydrothiazol-4-ol



5af, White solid, m.p. = 131.4-133.7 ℃. 224.4 mg, 87% yield.

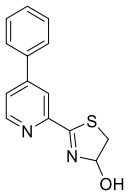
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.57 (d, *J* = 5.4 Hz, 1H), 8.20 (s, 1H), 7.87 (d, *J* = 5.4 Hz, 1H), 6.55 (d, *J* = 6.0 Hz, 1H), 6.17 (q, *J* = 6.0 Hz, 1H), 3.57 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.09 (dd, *J* = 11.4, 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 168.3, 151.9, 151.3, 133.4, 129.7, 124.6, 100.3, 38.9.

HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9530.

2-(4-phenylpyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ag, White solid, m.p. = 127.9-129.6 ℃. 225.2 mg, 88% yield.

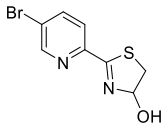
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 3:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.78 – 8.68 (m, 1H), 8.30 (d, *J* = 1.2 Hz, 1H), 7.90 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.50 (m, 1H), 6.54 (d, *J* = 6.6 Hz, 1H), 6.25 – 6.14 (m, 1H), 3.57 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.09 (dd, *J* = 12.0, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 169.5, 151.5, 150.7, 148.6, 137.1, 130.2, 129.9, 127.5, 124.2, 118.9, 100.5, 38.9.

HRMS (ESI): calcd for $C_{14}H_{13}N_2OS^+$ $[M+H]^+$ requires m/z 257.0477, found m/z 257.0472.

2-(5-bromopyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ah, White solid, m.p. = 128.6-130.5 ℃. 229.6 mg, 89% yield.

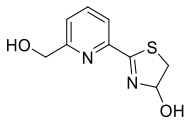
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.82 (s, 1H), 8.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 6.0 Hz, 1H), 6.16 (q, *J* = 6.0 Hz, 1H), 3.56 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.08 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 168.4, 150.8, 149.5, 140.5, 123.4, 100.5, 39.0.

HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9531.

2-(6-(hydroxymethyl)pyridin-2-yl)-4,5-dihydrothiazol-4-ol



5ai, Pale yellow solid, m.p. = 134.4-135.9 ℃. 96.6 mg, 46% yield.

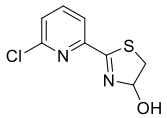
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 7.97 – 7.90 (m, 2H), 7.63 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 6.0 Hz, 1H), 6.15 (q, *J* = 6.0 Hz, 1H), 5.52 (t, *J* = 5.4 Hz, 1H), 4.60 (d, *J* = 5.4 Hz, 2H), 3.52 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.04 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 169.4, 162.7, 149.8, 138.1, 123.2, 120.1, 100.4, 64.5, 38.7.

HRMS (ESI): calcd for $C_9H_{11}N_2O_2S^+$ $[M+H]^+$ requires m/z 211.0536, found m/z 211.0532.

2-(6-chloropyridin-2-yl)-4,5-dihydrothiazol-4-ol



5aj, White solid, m.p. = 130.2-132.5 ℃. 181.9 mg, 85% yield.

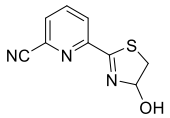
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.08 – 7.98 (m, 2H), 7.71 (d, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 6.0 Hz, 1H), 6.17 (q, *J* = 6.6 Hz, 1H), 3.58 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.10 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 167.7, 151.3, 150.2, 141.4, 127.5, 121.1, 100.4, 39.0.

HRMS (ESI): calcd for $C_8H_8ClN_2OS^+$ $[M+H]^+$ requires m/z 215.0041, found m/z 215.0048.

6-(4-hydroxy-4,5-dihydrothiazol-2-yl)picolinonitrile



5ak, White solid, m.p. = 109.8-111.2 ℃. 147.6 mg, 72% yield.

HPLC CHIRALPAK OD-3, n-hexane/2-propanol = 80/20, flow rate 1.2 mL/min, λ = 254 nm, retention time: 6.078 min, 8.294 min.

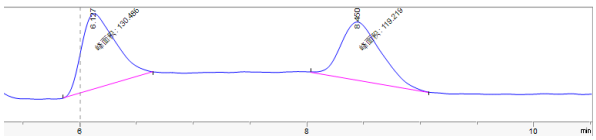
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.43 – 8.29 (m, 1H), 8.21 (d, *J* = 4.8 Hz, 2H), 6.63 (d, *J* = 6.6 Hz, 1H), 6.19 (q, *J* = 6.0 Hz, 1H), 3.61 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.13 (dd, *J* = 12.0, 7.2 Hz, 1H), 2.55 – 2.43 (m, 2H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 167.7, 152.1, 139.9, 132.8, 131.9, 125.8, 117.4, 100.4, 39.1.

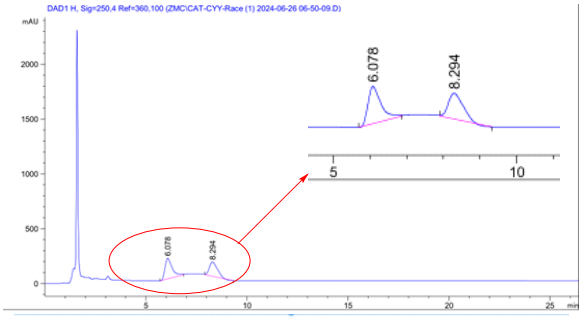
HRMS (ESI): calcd for $C_9H_8N_3OS^+$ $[M+H]^+$ requires m/z 206.0383, found m/z 206.0388.

5ak Race



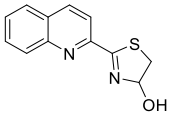
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.127	MM	0.3467	130.48593	6.27360	52.2561
2	8.450	MM	0.4119	119.21854	4.82406	47.7439

5ak Cat



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.078	BB	0.3571	4560.87549	186.61723	56.7913
2	8.294	BB	0.4172	3470.06592	127.64752	43.2087

2-(quinolin-2-yl)-4,5-dihydrothiazol-4-ol



5al, White solid, m.p. = 121.0-123.2 ℃. 181.7 mg, 79% yield.

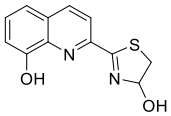
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 9.38 (s, 1H), 8.58 (s, 1H), 8.18 (dd, *J* = 19.8, 6.8 Hz, 2H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 6.49 (s, 1H), 6.22 (s, 1H), 3.58 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.11 (dd, *J* = 11.4, 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 169.6, 152.8, 144.5, 135.5, 131.9, 129.7, 128.4, 128.3, 119.2, 100.4, 38.9.

HRMS (ESI): calcd for $C_{12}H_{11}N_2OS^+$ $[M+H]^+$ requires m/z 231.0587, found m/z 231.0582.

2-(8-hydroxyquinolin-2-yl)-4,5-dihydrothiazol-4-ol



5am, White solid, m.p. = 127.4-130.5 ℃. 186.9 mg, 76% yield.

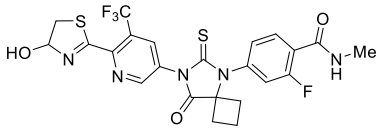
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 9.77 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 6.6 Hz, 1H), 6.22 (q, *J* = 6.6 Hz, 1H), 3.59 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.11 (dd, *J* = 11.4, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 169.8, 154.1, 149.2, 138.4, 137.5, 130.3, 129.6, 119.4, 118.5, 113.1, 100.5, 38.9.

HRMS (ESI): calcd for $C_{12}H_{11}N_2O_2S^+$ $[M+H]^+$ requires m/z 247.0536, found m/z 247.0539.

2-fluoro-4-(7-(6-(4-hydroxy-4,5-dihydrothiazol-2-yl)-5-(trifluoromethyl)pyridin-3-yl)-8-oxo-6-thioxo-5,7-diazaspiro[3.4]octan-5-yl)-N-methylbenzamide



5an, White solid, m.p. = 139.4-142.2 ℃. 331.8 mg, 60% yield.

TLC: R_f = 0.35 (petroleum ether/ethyl acetate = 1:1) [UV].

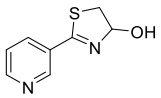
^{1}H NMR (600 MHz, DMSO- D_6) δ 9.06 (s, 1H), 8.61 (s, 1H), 8.48 – 8.41 (m, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 12.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.21 (q, *J* = 6.6 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 1H), 3.64 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.18 (dd, *J* = 11.4, 7.2 Hz, 1H), 2.82 (d, *J* = 4.2 Hz, 3H), 2.27 – 2.61 (m, 2H), 2.02 – 1.95 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 180.8, 175.2, 170.8, 165.0, 164.0, 160.5, 158.8, 152.1, 149.2, 138.9 (d, *J* = 39.5 Hz), 136.8 (d, J_{C-F} = 16.9 Hz), 131.9, 131.6 (d, J_{C-F} = 11.3 Hz), 126.9 (d, J_{C-F} = 11.3 Hz), 125.9, 125.8 (d, J_{C-F} = 56.5 Hz), 125.7, 124.3, 124.1, 123.8, 123.6, 122.0, 120.2, 118.9, 118.7, 101.4, 68.2, 60.3, 39.5, 31.7, 26.8, 21.2, 14.6, 13.9.

^{19}F NMR (565 MHz, DMSO-D_6) δ -57.91, -112.11, -112.12, -112.14.

HRMS (ESI): calcd for $C_{23}H_{20}F_4N_5O_3S_2^+$ $[M+H]^+$ requires m/z 554.0938, found m/z 554..0946.

2-(pyridin-3-yl)-4,5-dihydrothiazol-4-ol



6aa, White solid, m.p. = 116.3-118.9 ℃. 167.4 mg, 93% yield.

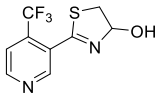
TLC: R_f = 0.35 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.96 (s, 1H), 8.73 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.43 (m, 1H), 6.53 (d, *J* = 6.0 Hz, 1H), 6.14 (q, *J* = 6.0 Hz, 1H), 3.67 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.21 (dd, *J* = 11.4, 6.6 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.6, 152.9, 148.9, 136.0, 129.1, 124.6, 99.9.

HRMS (ESI): calcd for $C_8H_9N_2OS^+$ $[M+H]^+$ requires m/z 181.0431, found m/z 181.0436.

2-(4-(trifluoromethyl)pyridin-3-yl)-4,5-dihydrothiazol-4-ol



6ab, White solid, m.p. = 120.9-123.7 ℃. 186.0 mg, 75% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

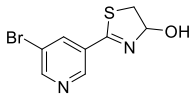
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.97 (d, *J* = 5.4 Hz, 1H), 8.90 (s, 1H), 7.89 (d, *J* = 5.4 Hz, 1H), 6.70 – 6.65 (m, 1H), 6.13 (q, *J* = 6.0 Hz, 1H), 3.75 (dd, *J* = 12.0, 7.8 Hz, 1H), 3.30 (dd, *J* = 11.4, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 161.9, 153.1, 150.7, 135.1, 134.7 (d, J_{C-F} = 124.3 Hz), 134.4, 127.9, 123.8, 121.9, 120.9 (d, J_{C-F} = 16.9 Hz), 100.8, 41.6.

^{19}F NMR (565 MHz, DMSO-D_6) δ -59.16.

HRMS (ESI): calcd for $C_9H_8F_3N_2OS^+$ $[M+H]^+$ requires m/z 249.0304, found m/z 249.0309.

2-(5-bromopyridin-3-yl)-4,5-dihydrothiazol-4-ol

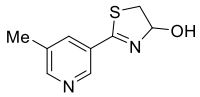


6ac, White solid, m.p. = 131.2-133.9 ℃. 245.1 mg, 95% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.92 (s, 1H), 8.89 (s, 1H), 8.31 (s, 1H), 6.60 – 6.55 (m, 1H), 6.14 (s, 1H), 3.70 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.24 (dd, *J* = 12.0, 7.2 Hz, 1H).
^{13}C NMR (150 MHz, DMSO-D_6) δ 163.4, 153.6, 147.5, 137.8, 130.7, 120.9, 99.7.
HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9539.

2-(5-methylpyridin-3-yl)-4,5-dihydrothiazol-4-ol

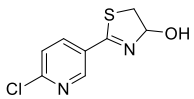


6ad, White solid, m.p. = 119.1-121.5 ℃. 131.9 mg, 68% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.76 (s, 1H), 8.57 (s, 1H), 7.95 (s, 1H), 6.51 (d, *J* = 6.0 Hz, 1H), 6.13 (q, *J* = 6.6 Hz, 1H), 3.66 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.20 (dd, *J* = 11.4, 5.4 Hz, 1H), 2.37 (s, 3H).
^{13}C NMR (150 MHz, DMSO-D_6) δ 164.6, 153.3, 146.2, 136.1, 134.0, 128.7, 99.8, 18.2.
HRMS (ESI): calcd for $C_9H_{11}N_2OS^+$ $[M+H]^+$ requires m/z 195.0587, found m/z 195.0580.

2-(6-chloropyridin-3-yl)-4,5-dihydrothiazol-4-ol

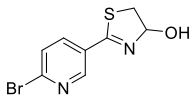


6ae, White solid, m.p. = 139.7-141.5 ℃. 194.7 mg, 91% yield.

TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.78 (s, 1H), 8.25 – 8.15 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 6.14 (s, 1H), 3.69 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.23 (dd, *J* = 12.0, 5.4 Hz, 1H).
^{13}C NMR (150 MHz, DMSO-D_6) δ 163.5, 153.5, 149.3, 139.3, 128.5, 125.3, 99.8.
HRMS (ESI): calcd for $C_8H_8ClN_2OS^+$ $[M+H]^+$ requires m/z 215.0041, found m/z 215.0048.

2-(6-bromopyridin-3-yl)-4,5-dihydrothiazol-4-ol

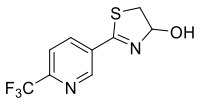


6af, White solid, m.p. = 135.5-137.2 ℃. 242.5 mg, 94% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.74 (d, *J* = 1.8 Hz, 1H), 8.06 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.79 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.57 (d, *J* = 6.0 Hz, 1H), 6.16 – 6.10 (m, 1H), 3.68 (dd, *J* = 11.4, 6.6 Hz, 1H), 3.23 (dd, *J* = 11.4, 6.0 Hz, 1H).
^{13}C NMR (150 MHz, DMSO-D_6) δ 163.7, 149.6, 144.8, 138.9, 129.0, 128.8, 99.9.
HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9530.

2-(6-(trifluoromethyl)pyridin-3-yl)-4,5-dihydrothiazol-4-ol



6ag, White solid, m.p. = 137.1-139.4 ℃. 190.9 mg, 77% yield.

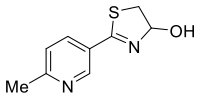
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 9.13 (s, 1H), 8.40 (d, J = 9.6 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 6.0 Hz, 1H), 6.18 (q, J = 6.0 Hz, 1H), 3.73 (dd, J = 11.4, 7.2 Hz, 1H), 3.27 (dd, J = 11.4, 5.6 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 163.6, 149.3, 148.8 (d, $J_{C\text{-}F}$ = 124.3 Hz), 148.6, 138.4, 132.0, 124.6, 122.7, 121.7, 120.9, 119.1, 99.9.

HRMS (ESI): calcd for $C_9H_8F_3N_2OS^+$ $[M+H]^+$ requires m/z 249.0304, found m/z 249.0307.

2-(6-methylpyridin-3-yl)-4,5-dihydrothiazol-4-ol



6ah, White solid, m.p. = 121.0-123.2 ℃. 139.68 mg, 72% yield.

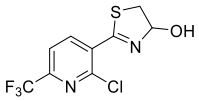
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.79 (d, J = 1.8 Hz, 1H), 7.99 (dd, J = 7.8, 2.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 6.45 (s, 1H), 6.09 (t, J = 6.0 Hz, 1H), 3.61 (dd, J = 11.4, 7.2 Hz, 1H), 3.15 (dd, J = 11.4, 5.4 Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.5, 162.0, 148.4, 136.2, 126.5, 123.8, 99.8, 24.6.

HRMS (ESI): calcd for $C_9H_{11}N_2OS^+$ $[M+H]^+$ requires m/z 195.0587, found m/z 195.0588.

2-(2-chloro-6-(trifluoromethyl)pyridin-3-yl)-4,5-dihydrothiazol-4-ol



6ai, White solid, m.p. = 125.7-128.3 ℃, 211.5 mg, 75% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

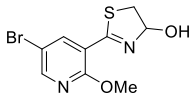
^{1}H NMR (600 MHz, DMSO- D_6) δ 8.38 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 6.0 Hz, 1H), 6.16 (q, J = 6.0 Hz, 1H), 3.75 (dd, J = 11.4, 7.2 Hz, 1H), 3.29 (dd, J = 11.4, 6.0 Hz, 2H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 162.6, 148.5, 147.6 (d, $J_{C\text{-}F}$ = 129.9 Hz), 142.7, 133.5, 121.9, 121.1 (d, $J_{C\text{-}F}$ = 5.6 Hz), 120.1, 99.9, 41.3.

^{19}F NMR (565 MHz, DMSO-D_6) δ -66.79.

HRMS (ESI): calcd for $C_9H_7ClF_3N_2OS^+$ $[M+H]^+$ requires m/z 282.9915, found m/z 282.9917.

2-(5-bromo-2-methoxypyridin-3-yl)-4,5-dihydrothiazol-4-ol



6aj, White solid, m.p. = 119.1-121.4 ℃. 184.3 mg, 64% yield.

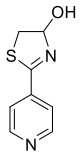
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.47 (d, J = 1.8 Hz, 1H), 8.31 (d, J = 2.4 Hz, 1H), 6.38 (d, J = 6.0 Hz, 1H), 6.02 (q, J = 6.0 Hz, 1H), 3.96 (s, 3H), 3.53 (dd, J = 11.4, 7.2 Hz, 1H), 3.10 (dd, J = 12.0, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 162.2, 160.2, 150.5, 141.1, 118.2, 111.8, 97.9, 54.8.

HRMS (ESI): calcd for $C_9H_{10}BrN_2O_2S^+$ $[M+H]^+$ requires m/z 288.9641, found m/z 288.9648.

2-(pyridin-4-yl)-4,5-dihydrothiazol-4-ol



7aa, White solid, m.p. = 109.3-111.5 ℃. 165.6 mg, 92% yield.

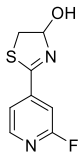
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.81 – 8.64 (m, 2H), 7.79 – 7.59 (m, 2H), 6.59 (d, J = 6.0 Hz, 1H), 6.16 (q, J = 6.0 Hz, 1H), 3.69 (dd, J = 11.4, 7.2 Hz, 1H), 3.23 (dd, J = 12.0, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 165.5, 151.1, 140.1, 122.2, 100.1.

HRMS (ESI): calcd for $C_8H_9N_2OS^+$ $[M+H]^+$ requires m/z 181.0431, found m/z 181.0439.

2-(2-fluoropyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ab, Pale yellow solid, m.p. = 131.5-133.7 ℃. 176.2 mg, 89% yield.

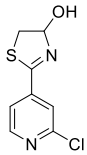
TLC: R_f = 0.35 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.41 (d, J = 5.4 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.45 (s, 1H), 6.65 (d, J = 5.4 Hz, 1H), 6.16 (d, J = 6.6 Hz, 1H), 3.72 (dd, J = 11.4, 7.2 Hz, 1H), 3.26 (dd, J = 12.0, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.8, 164.4 (d, J_{C-F} = 16.9 Hz), 163.2, 149.5, 149.4, 145.9, 145.9, 120.9, 108.4 (d, J_{C-F} = 146.9 Hz), 99.9.

HRMS (ESI): calcd for $C_8H_8FN_2OS^+$ $[M+H]^+$ requires m/z 199.0336, found m/z 199.0331.

2-(2-chloropyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ac, White solid, m.p. = 128.4-130.8 ℃. 168.8 mg, 92% yield.

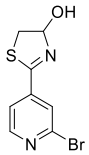
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.82 – 7.66 (m, 2H), 6.64 (d, *J* = 6.0 Hz, 1H), 6.22 – 6.09 (m, 1H), 3.72 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.25 (dd, *J* = 12.0, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.4, 151.6, 143.5, 122.5, 121.9, 99.9.

HRMS (ESI): calcd for $C_8H_8ClN_2OS^+$ $[M+H]^+$ requires m/z 215.0041, found m/z 215.0047.

2-(2-bromopyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ad, White solid, m.p. = 116.1-118.3 ℃. 234.7 mg, 91% yield.

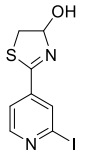
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 2:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.56 (dd, *J* = 4.8, 0.6 Hz, 1H), 8.08 – 8.05 (m, 1H), 7.76 (dd, *J* = 5.4, 1.2 Hz, 1H), 6.64 (d, *J* = 6.0 Hz, 1H), 6.26 – 6.04 (m, 1H), 3.72 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.25 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.2, 152.1, 143.1, 142.5, 126.0, 122.1, 99.9.

HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9537.

2-(2-iodopyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ae, Tawny solid, m.p. = 141.7-143.5 ℃. 275.4 mg, 90% yield.

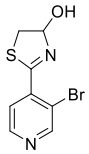
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 8.55 – 8.46 (m, 1H), 7.84 – 7.82 (m, 1H), 7.72 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.61 (d, *J* = 6.0 Hz, 1H), 6.14 (q, *J* = 6.0 Hz, 1H), 3.70 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.24 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 164.2, 152.6, 141.7, 132.4, 122.1, 119. 7, 99.9.

HRMS (ESI): calcd for $C_8H_8IN_2OS^+$ $[M+H]^+$ requires m/z 306.9397, found m/z 306.9391.

2-(3-bromopyridin-4-yl)-4,5-dihydrothiazol-4-ol



7af, Pale yellow oil, m.p. = 139.1-141.5 ℃. 219.3 mg, 85% yield.

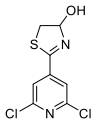
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 8.87 (s, 1H), 8.65 (d, *J* = 4.8 Hz, 1H), 7.59 (d, *J* = 4.8 Hz, 1H), 6.14 (t, *J* = 6.0 Hz, 1H), 3.72 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.27 (dd, *J* = 11.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 163.9, 153.2, 149.4, 142.3, 124.8, 118.7, 100.1, 41.2.

HRMS (ESI): calcd for $C_8H_8BrN_2OS^+$ $[M+H]^+$ requires m/z 258.9536, found m/z 258.9532.

2-(2,6-dichloropyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ag, White solid, m.p. = 139.4-141.5 ℃. 183.5 mg, 74% yield.

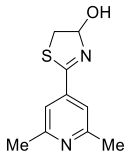
TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 7.79 (s, 2H), 6.69 (s, 1H), 6.16 (s, 1H), 3.74 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.27 (dd, *J* = 12.0, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 163.4, 150.7, 146.1, 122.1, 99.8.

HRMS (ESI): calcd for $C_8H_7Cl_2N_2OS^+$ $[M+H]^+$ requires m/z 248.9651, found m/z 248.9652.

2-(2,6-dimethylpyridin-4-yl)-4,5-dihydrothiazol-4-ol



7ah, White solid, m.p. = 125.7-127.7 ℃. 145.6 mg, 70% yield.

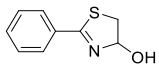
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 7.37 (s, 2H), 6.55 (d, *J* = 5.4 Hz, 1H), 6.14 (q, *J* = 6.0 Hz, 1H), 3.67 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.20 (dd, *J* = 11.4, 5.4 Hz, 1H), 2.49 (s, 6H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 165.8, 158.9, 140.8, 118.7, 99.9, 24.4.

HRMS (ESI): calcd for $C_{10}H_{13}N_2OS^+$ $[M+H]^+$ requires m/z 209.0744, found m/z 209.0747.

2-phenyl-4,5-dihydrothiazol-4-ol



7ai, White solid, m.p. = 102.2-105.7 ℃. 111.6 mg, 62% yield.

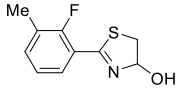
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D6) δ 7.87 – 7.76 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 6.44 (d, *J* = 6.0 Hz, 1H), 6.14 – 6.08 (m, 1H), 3.62 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.16 (dd, *J* = 12.0, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-D6) δ 166.6, 133.3, 132.3, 129.3, 128.5, 100.0.

HRMS (ESI): calcd for $C_9H_{10}NOS^+$ $[M+H]^+$ requires m/z 180.0478, found m/z 180.0471.

2-(2-fluoro-3-methylphenyl)-4,5-dihydrothiazol-4-ol



7aj, White solid, m.p. = 114.2-116.8 ℃. 93.3 mg, 44% yield.

TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 2:1) [UV].

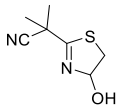
^{1}H NMR (600 MHz, DMSO-D_6) δ 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 – 7.40 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.45 (s, 1H), 6.07 (t, *J* = 6.0 Hz, 1H), 3.59 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.14 (dd, *J* = 11.4, 5.4 Hz, 1H), 2.28 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 161.9 (d, $J_{C\text{-}F}$ = 6.0 Hz), 159.8, 158.1, 135.0 (d, $J_{C\text{-}F}$ = 6.0 Hz), 128.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 126.2, 126.1, 124.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.0 (d, $J_{C\text{-}F}$ = 12.0 Hz), 98.9, 14.7.

^{19}F NMR (565 MHz, DMSO-D_6) δ -115.86.

HRMS (ESI): calcd for $C_9H_{11}FNOS^+$ $[M+H]^+$ requires m/z 212.0540, found m/z 212.0543.

2-(4-hydroxy-4,5-dihydrothiazol-2-yl)-2-methylpropanenitrile



7ak, Yellow oil. 158.1 mg, 93% yield.

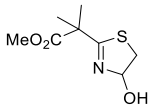
TLC: R_f = 0.33 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 6.51 (d, J = 5.4 Hz, 1H), 5.96 (q, J = 5.4 Hz, 1H), 3.60 (dd, J = 11.4, 7.2 Hz, 1H), 3.13 (dd, J = 12.0, 6.0 Hz, 1H), 1.60 (s, 3 H), 1.59 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 170.4, 122.4, 99.5, 40.7, 38.3, 26.5, 26.4.

HRMS (ESI): calcd for $C_7H_{11}N_2OS^+$ $[M+H]^+$ requires m/z 171.0587, found m/z 171.0580.

methyl 2-(4-hydroxy-4,5-dihydrothiazol-2-yl)-2-methylpropanoate



7al, Colorless oil. 143.6 mg, 84% yield.

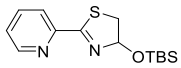
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 1:1) [UV].

^{1}H NMR (600 MHz, DMSO-d_6) δ 6.34 (d, J = 6.0 Hz, 1H), 5.87 – 5.81 (m, 1H), 3.60 (s, 3H), 3.43 (dd, J = 11.4, 7.2 Hz, 1H), 2.95 (dd, J = 12.0, 6.0 Hz, 1H), 1.37 (s, 6H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 173.7, 172.6, 99.5, 52.9, 48.7, 24.5.

HRMS (ESI): calcd for $C_8H_{14}NO_3S^+$ $[M+H]^+$ requires m/z 204.0689, found m/z 204.0684.

4-((tert-butyldimethylsilyl)oxy)-2-(pyridin-2-yl)-4,5-dihydrothiazole



8aa, White solid, m.p. = 101.5-103.8 ℃. 56.4 mg, 96% yield.

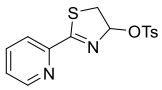
TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, DMSO-D_6) δ 8.64 -8.61 (m, 1H), 8.04 – 8.0 (m, 1H), 7.91 (td, J = 7.2, 1.2 Hz, 1H), 7.52 (ddd, J = 7.8, 4.8, 1.2 Hz, 1H), 6.28 (dd, J = 7.2, 5.4 Hz, 1H), 3.55 (dd, J = 11.4, 7.2 Hz, 1H), 3.06 (dd, J = 12.0, 4.8 Hz, 1H), 0.84 (s, 10H), 0.13 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 170.9, 150.6, 149.98, 137.7, 126.9, 121.9, 101.1, 39.6, 26.3, 18.3, -3.5, -4.1.

HRMS (ESI): calcd for $C_{14}H_{23}N_2OSSi^+$ $[M+H]^+$ requires m/z 295.1295, found m/z 295.1299.

2-(pyridin-2-yl)-4,5-dihydrothiazol-4-yl 4-methylbenzenesulfonate



9aa, White solid, m.p. = 98.2-100.7 ℃. 58.1 mg, 87% yield.

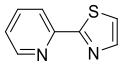
TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, DMSO- D_6) δ 8.70 – 8.54 (m, 1H), 8.02 – 7.93 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.60 (q, *J* = 4.8 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.34 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.87 – 3.72 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 177.3, 150.1, 149.8, 145.6, 138.0, 134.3, 130.2, 129.8, 127.5, 122.1, 96.3, 66.9, 31.1, 21.7.

HRMS (ESI): calcd for $C_8H_7N_2OS^+$ $[M+H]^+$ requires m/z 335.0519, found m/z 335.0525.

2-(pyridin-2-yl)thiazole



10aa, White solid, m.p. = 97.1-99.5 ℃. 31.7 mg, 98% yield.

TLC: R_f = 0.30 (petroleum ether/ethyl acetate = 5:1) [UV].

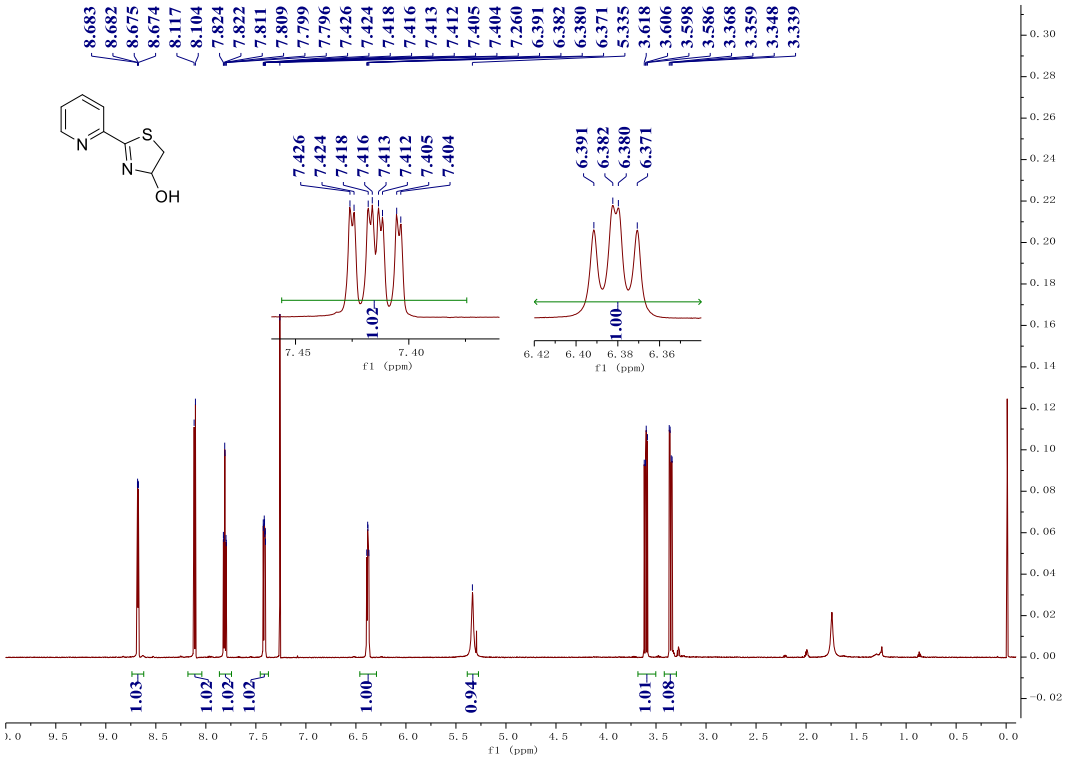
^{1}H NMR (600 MHz, DMSO- D_6) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.03 – 7.91 (m, 2H), 7.86 (d, *J* = 3.0 Hz, 1H), 7.55 – 7.44 (m, 1H).

^{13}C NMR (150 MHz, DMSO-D_6) δ 168.9, 151.1, 150.2, 144.8, 138.3, 125.6, 123.2, 119.7.

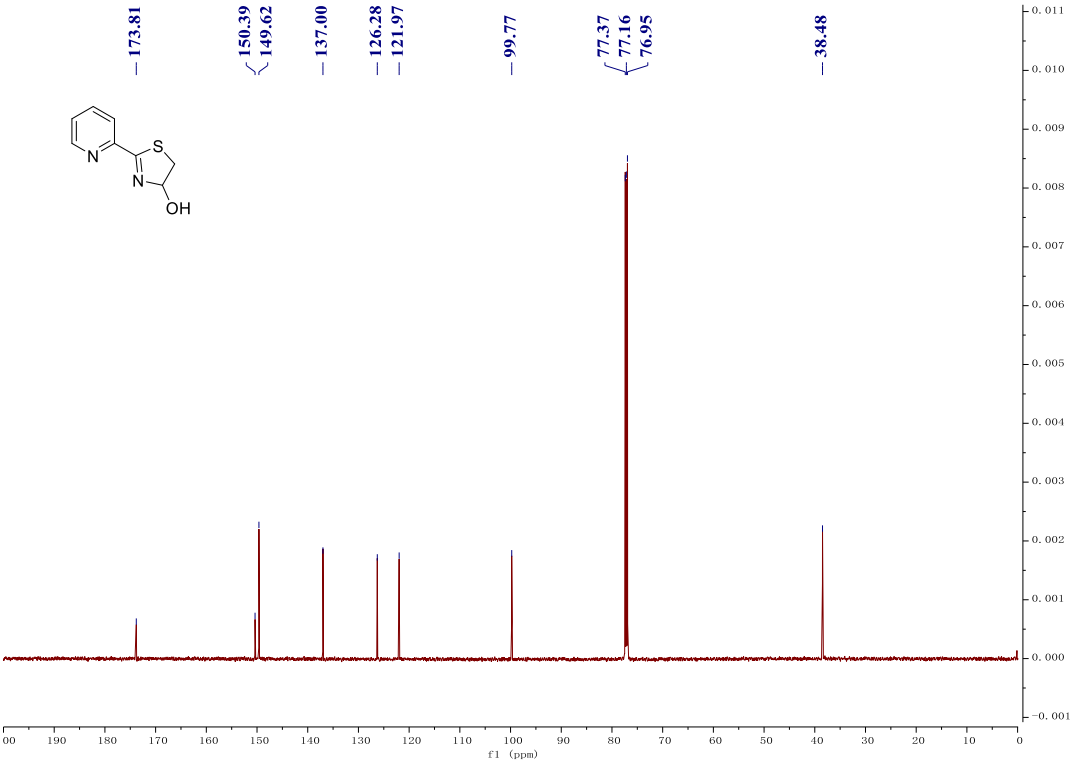
HRMS (ESI): calcd for $C_8H_7N_2S^+$ $[M+H]^+$ requires m/z 163.0324, found m/z 163.0233.

7. Copies of NMR spectra.

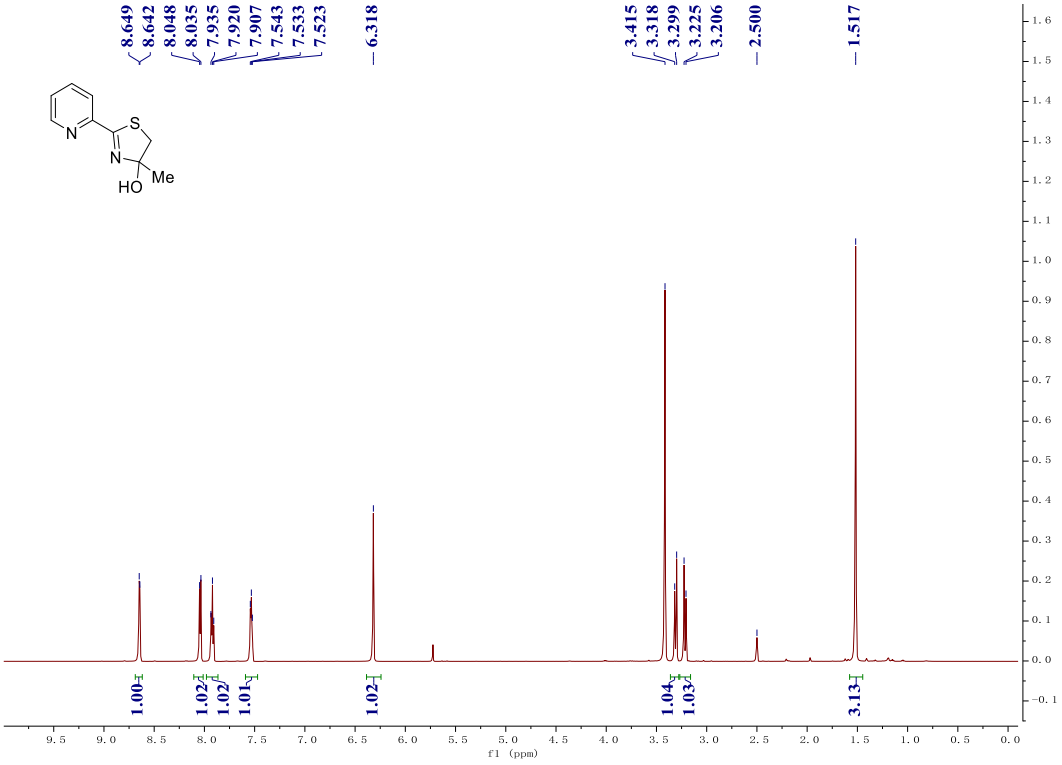
^{1}H NMR Spectrum of **5aa** (600 MHz, DMSO-D6)



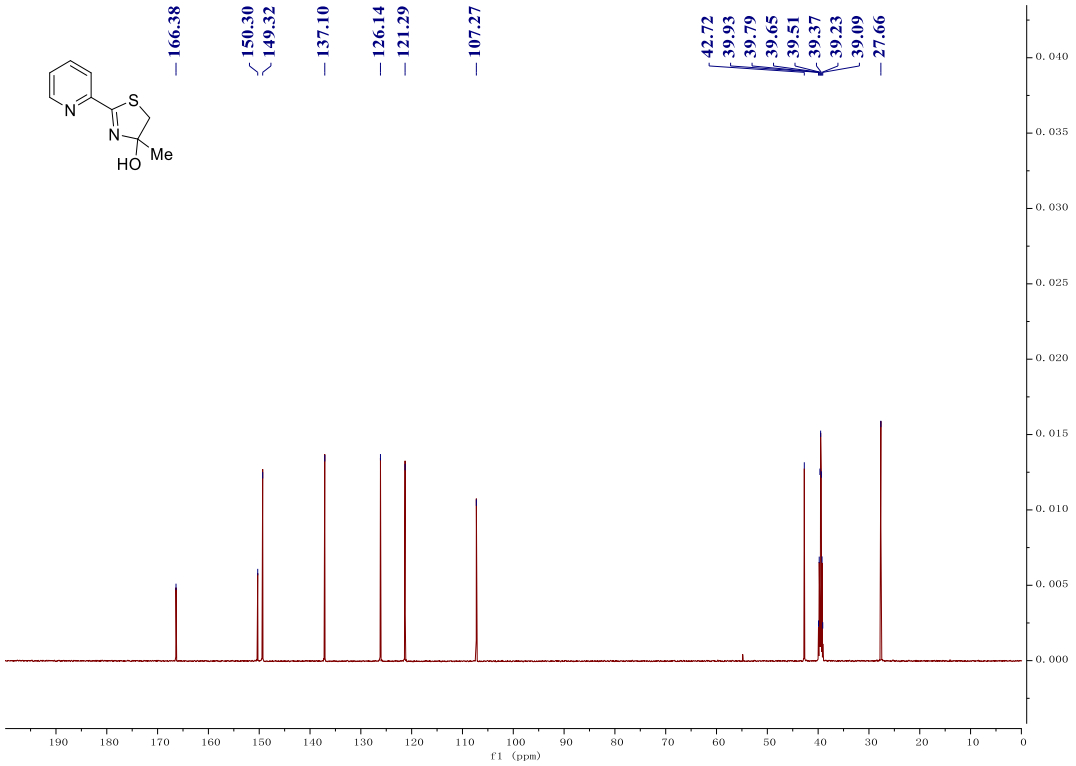
^{13}C NMR Spectrum of **5aa** (150 MHz, DMSO-D6)



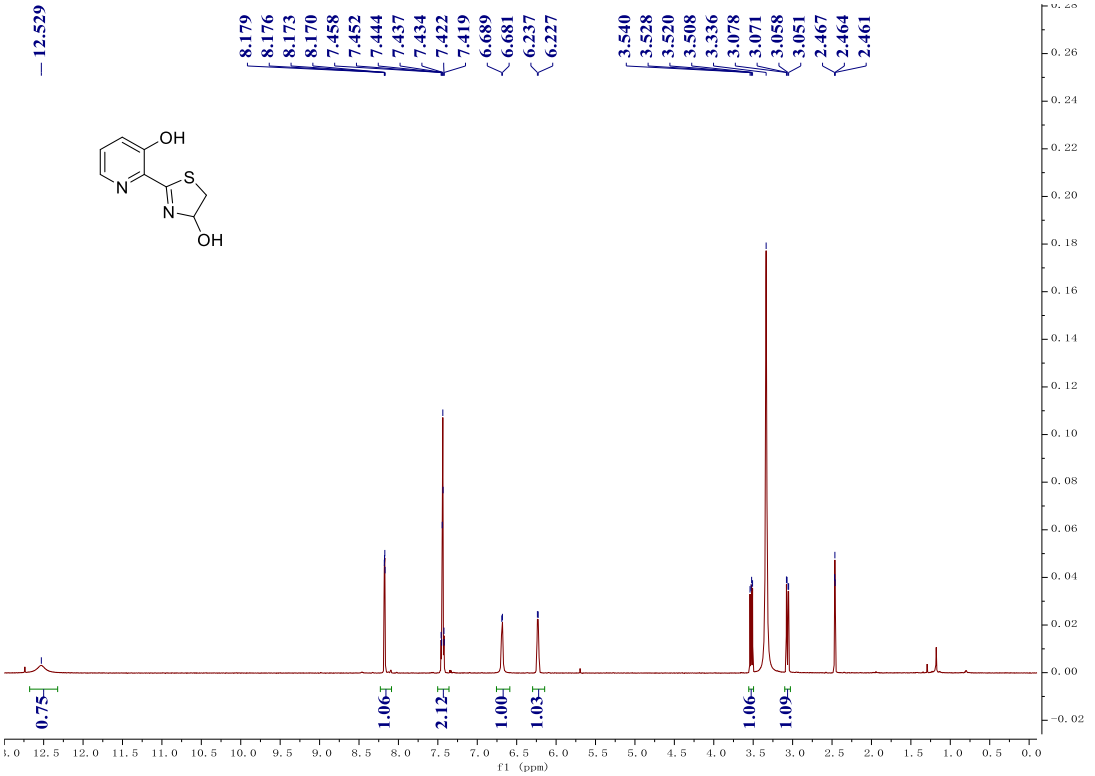
^{1}H NMR Spectrum of **5a'a** (600 MHz, DMSO-D6)



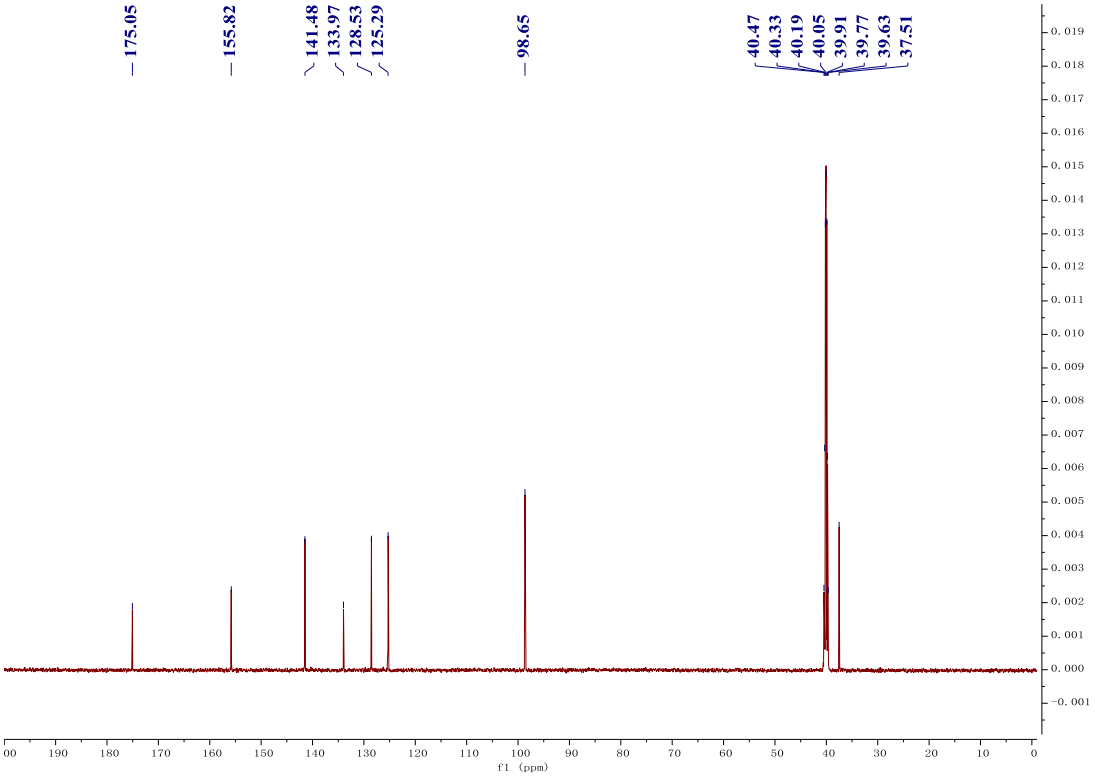
^{13}C NMR Spectrum of **5a'a** (150 MHz, DMSO-D6)



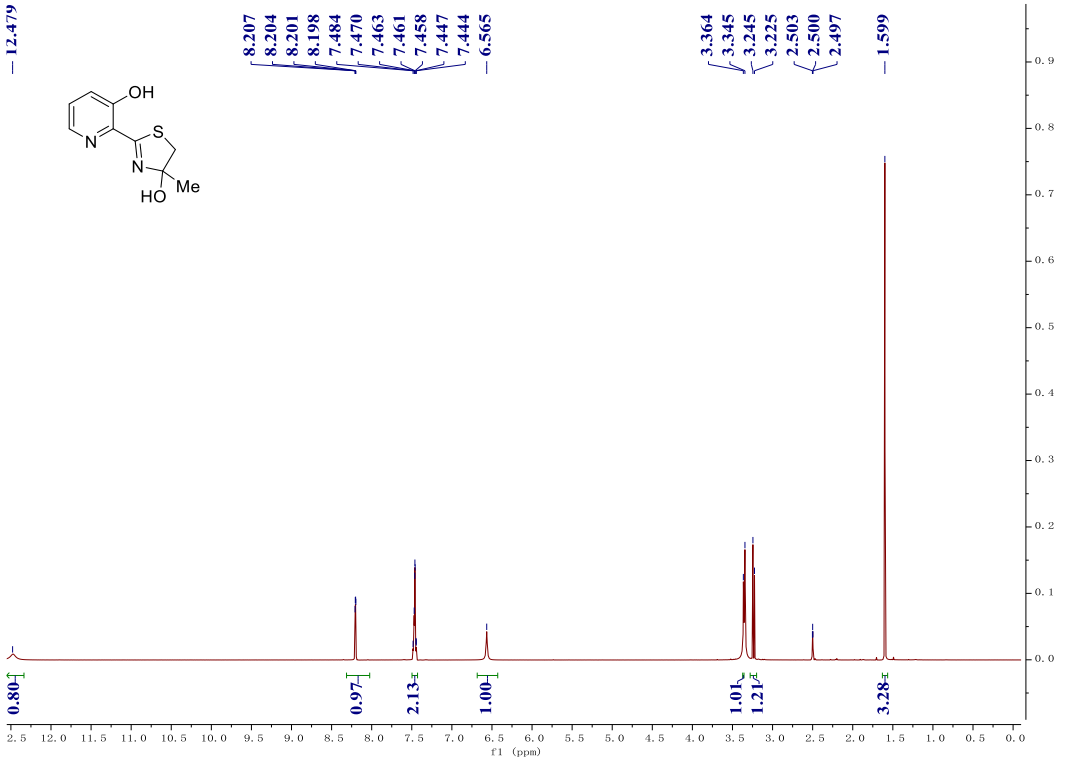
^{1}H NMR Spectrum of **5ab** (600 MHz, DMSO-*D6*)



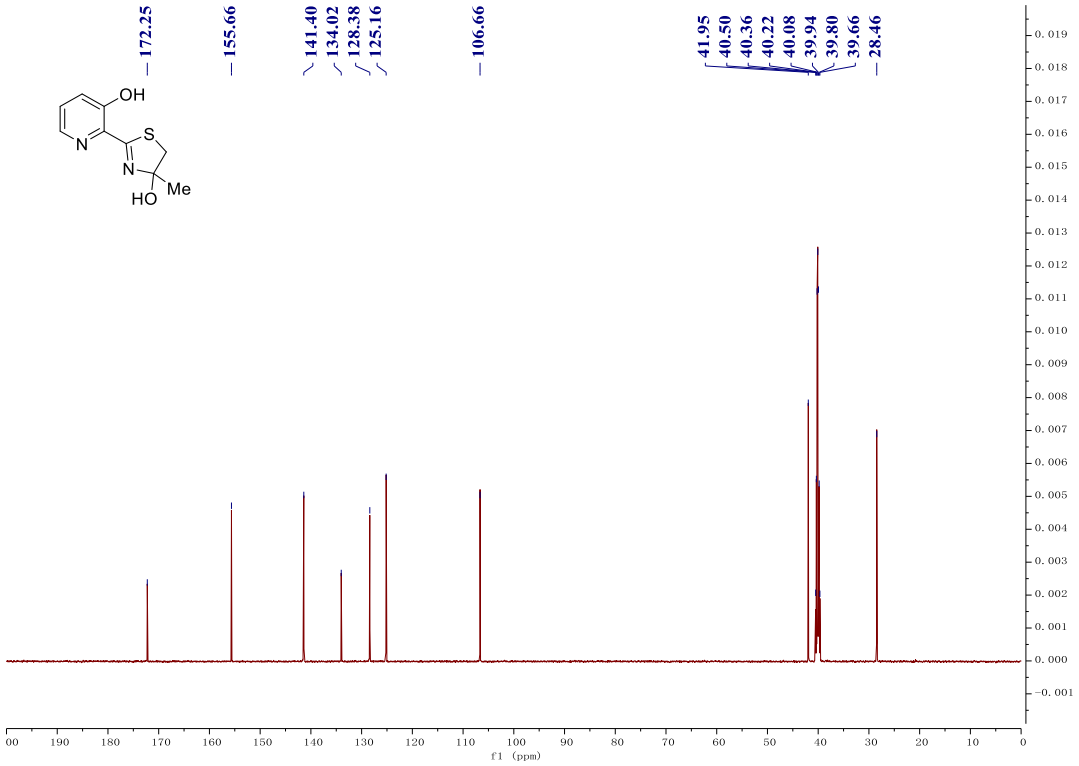
^{13}C NMR Spectrum of **5ab** (150 MHz, DMSO-*D6*)



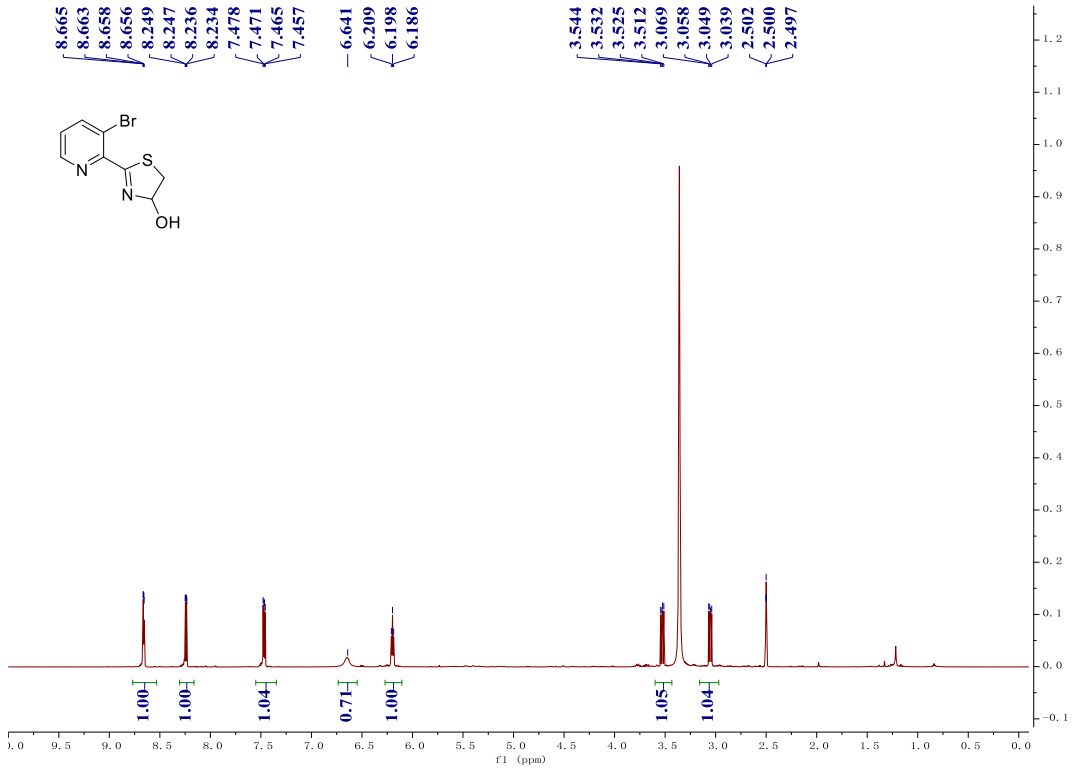
^{1}H NMR Spectrum of **5a'b** (600 MHz, DMSO-*D6*)



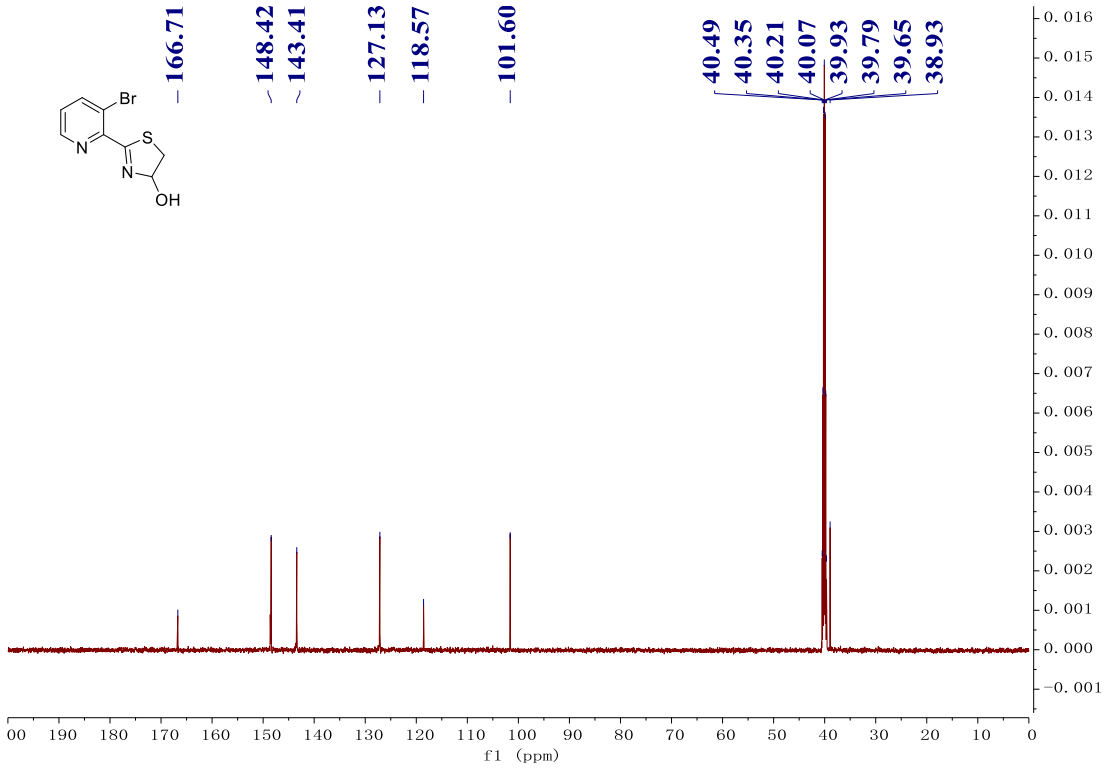
^{13}C NMR Spectrum of **5a'b** (150 MHz, DMSO-D6)



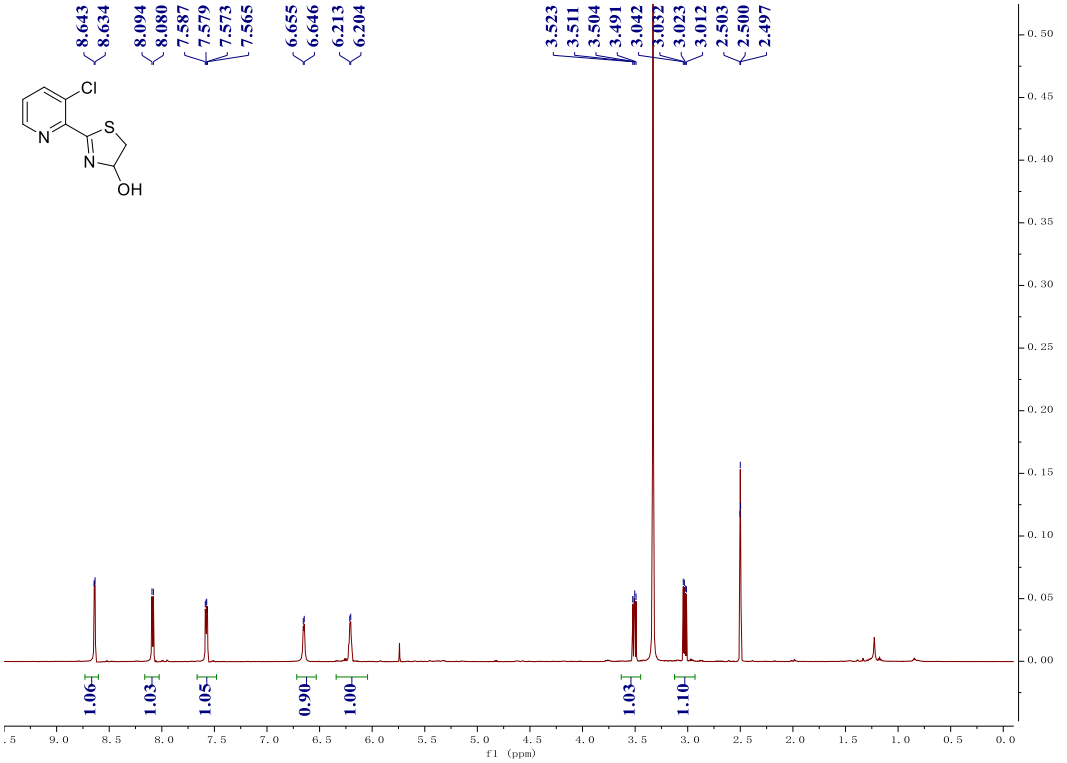
^{1}H NMR Spectrum of **5ac** (600 MHz, DMSO-D6)



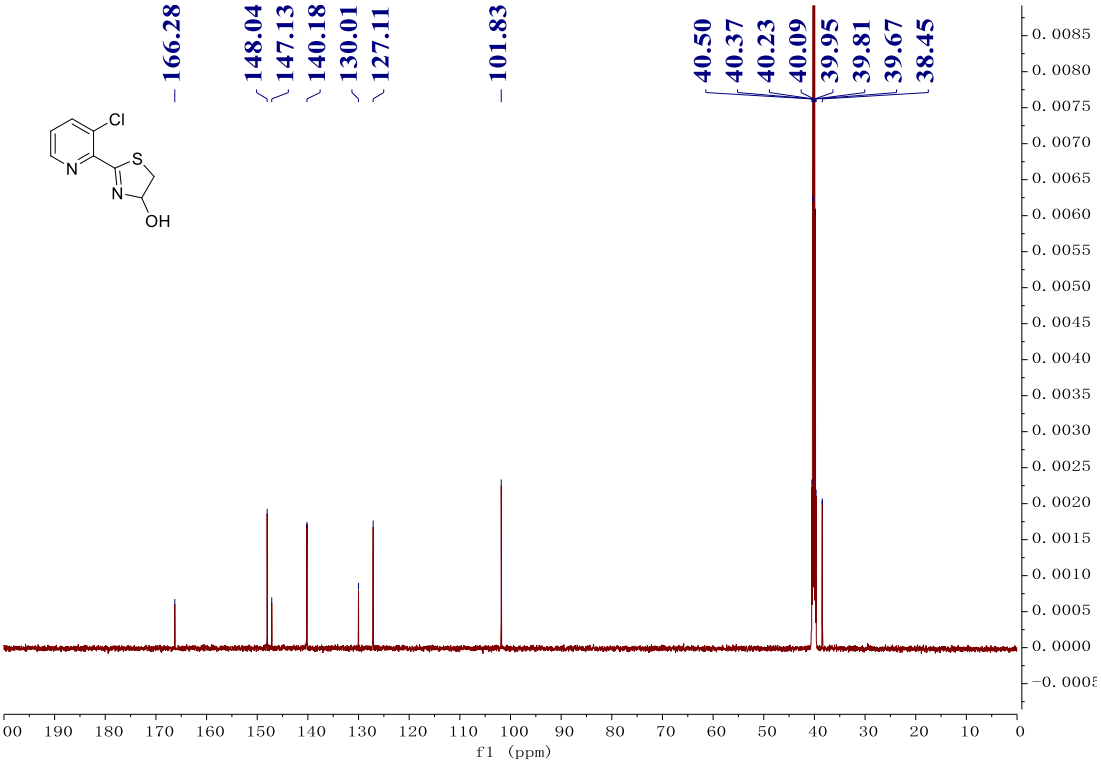
^{13}C NMR Spectrum of **5ac** (150 MHz, DMSO-D6)



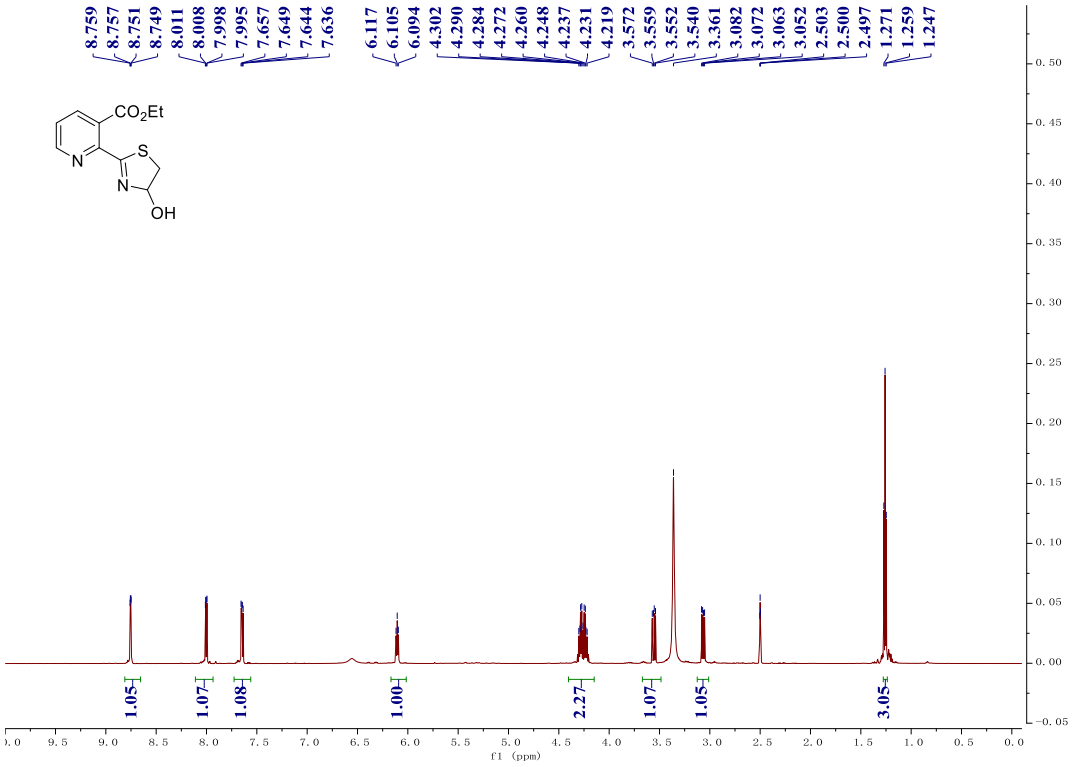
^{1}H NMR Spectrum of **5ad** (600 MHz, DMSO-D6)



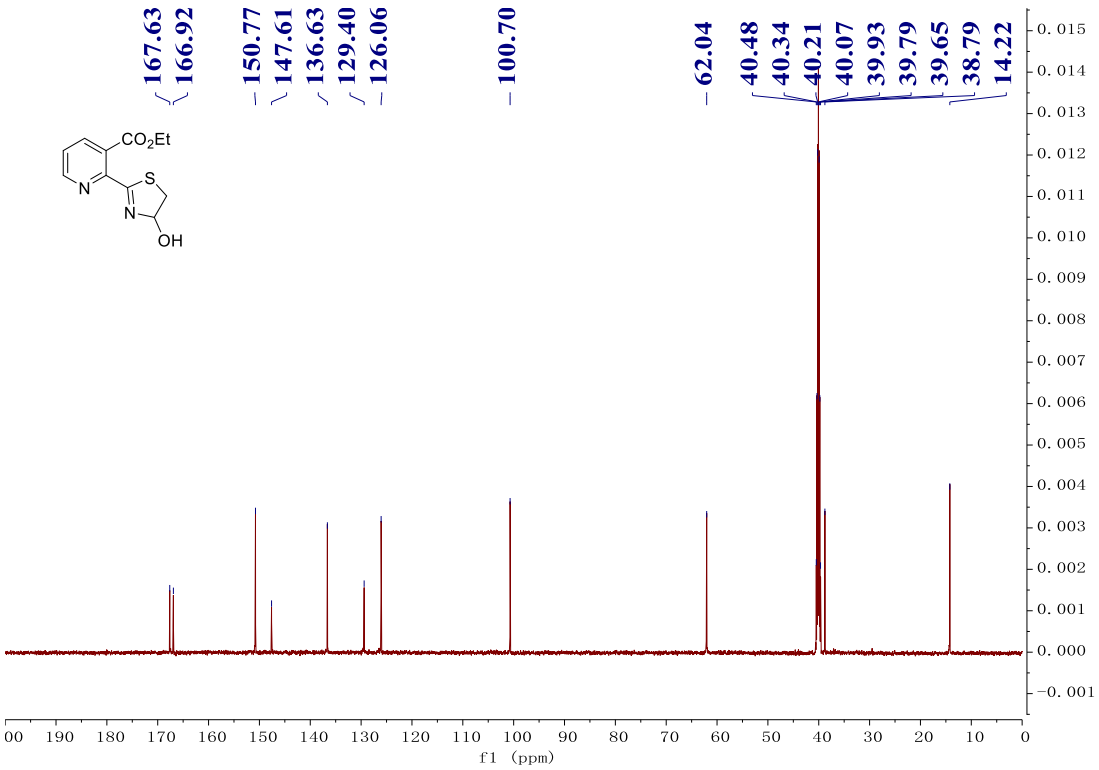
^{13}C NMR Spectrum of **5ad** (150 MHz, DMSO-D6)



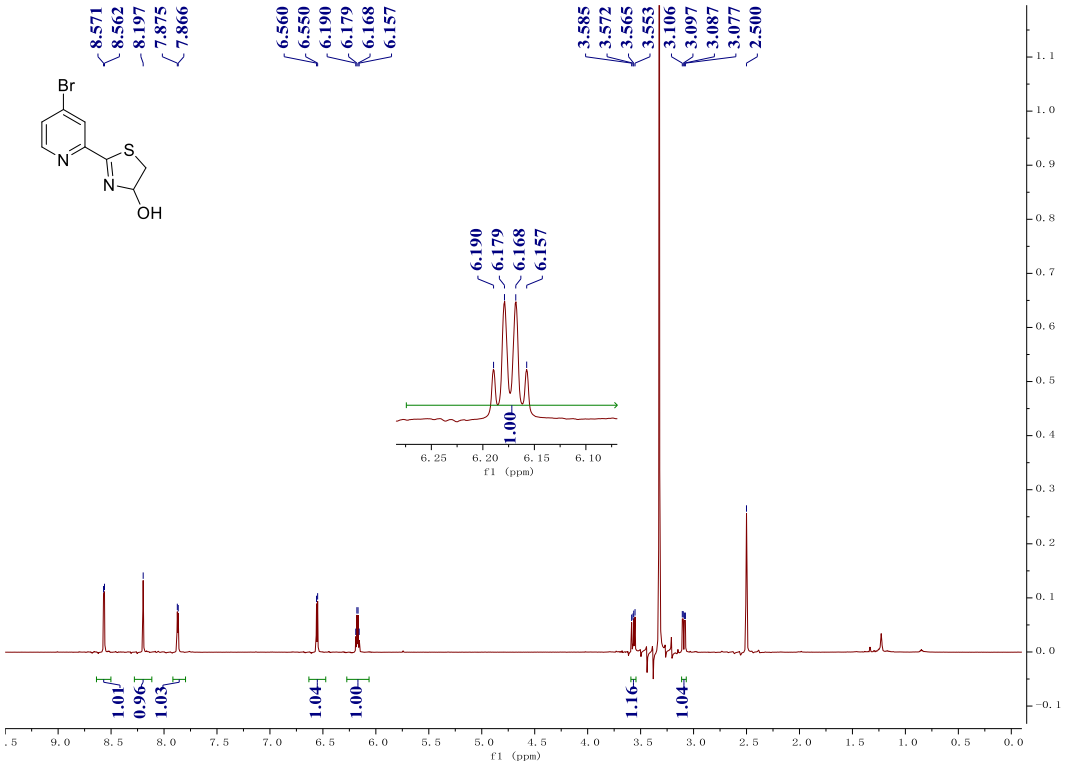
^{1}H NMR Spectrum of **5ae** (600 MHz, DMSO-D6)



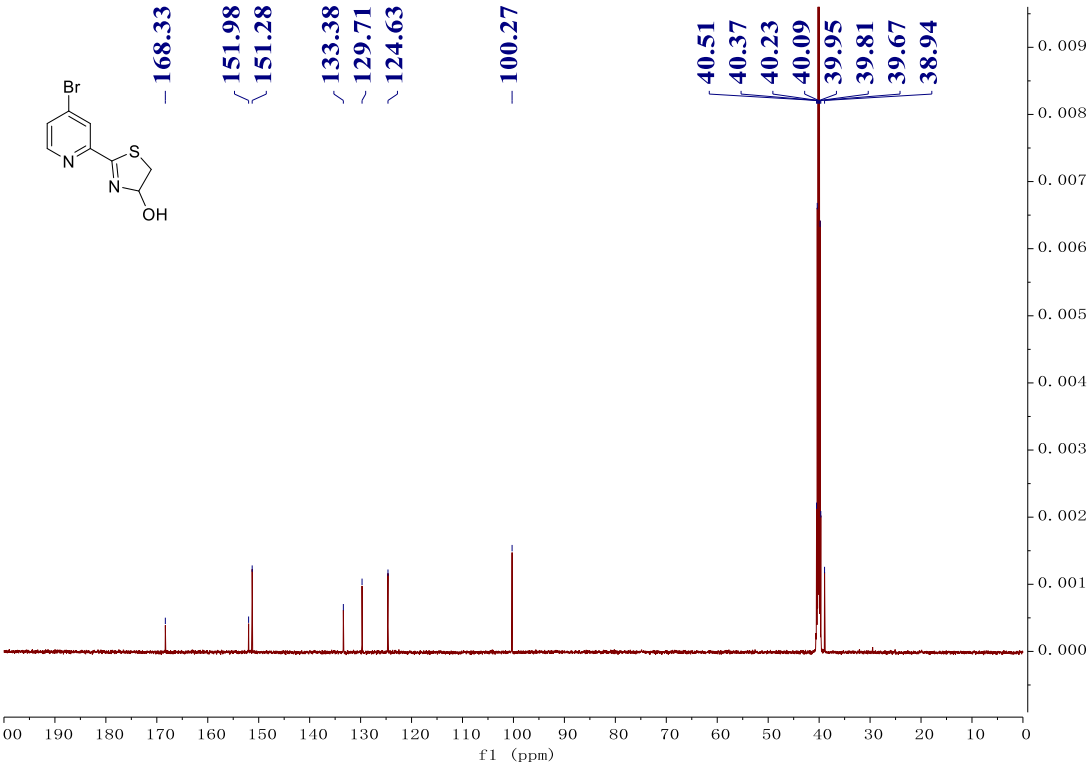
^{13}C NMR Spectrum of **5ae** (150 MHz, DMSO-D6)



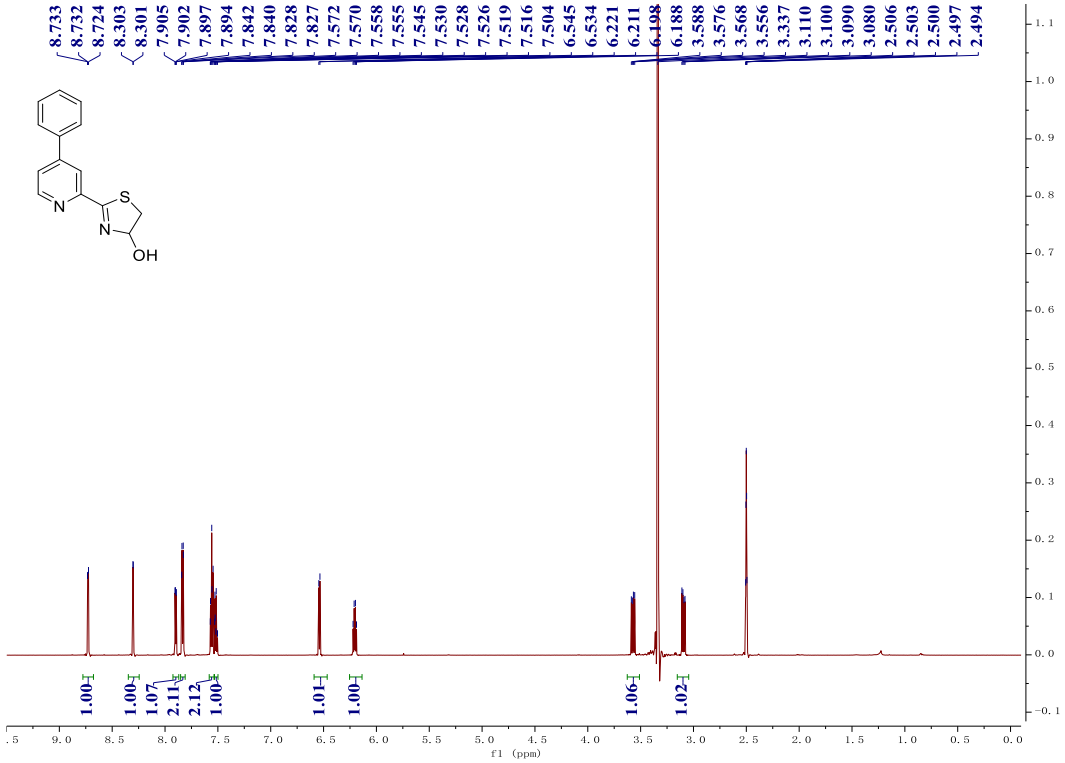
^{1}H NMR Spectrum of **5af** (600 MHz, DMSO-D6)



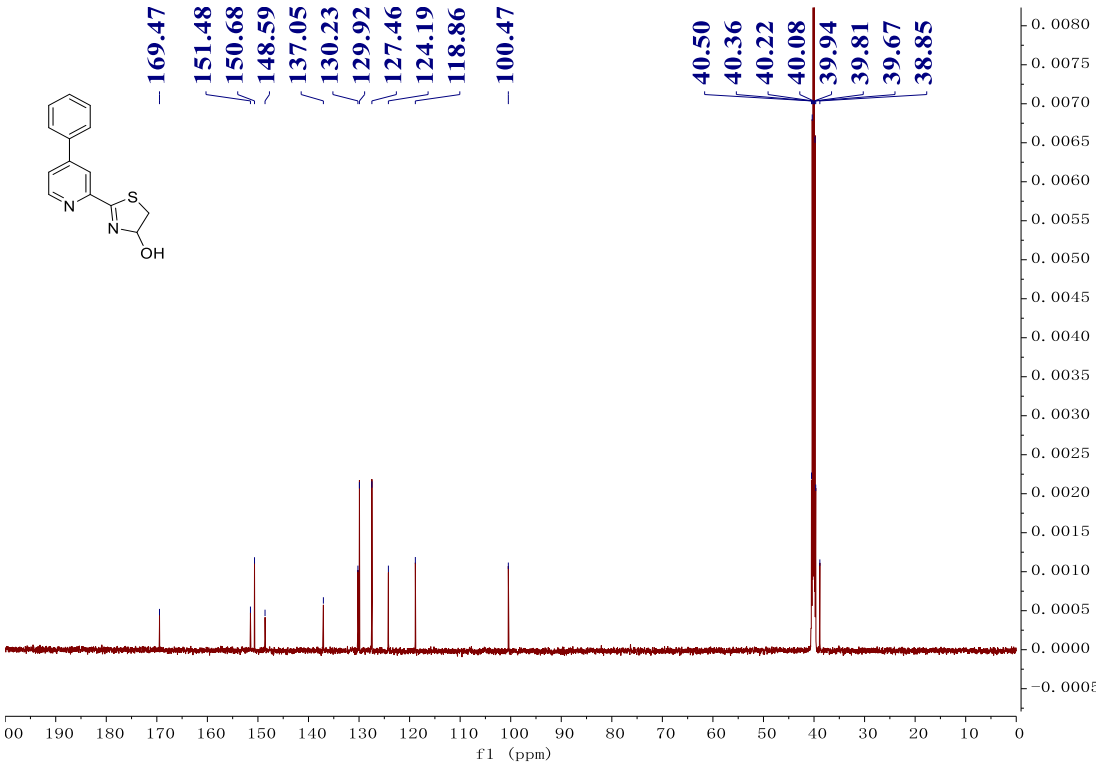
^{13}C NMR Spectrum of **5af** (150 MHz, DMSO-D6)



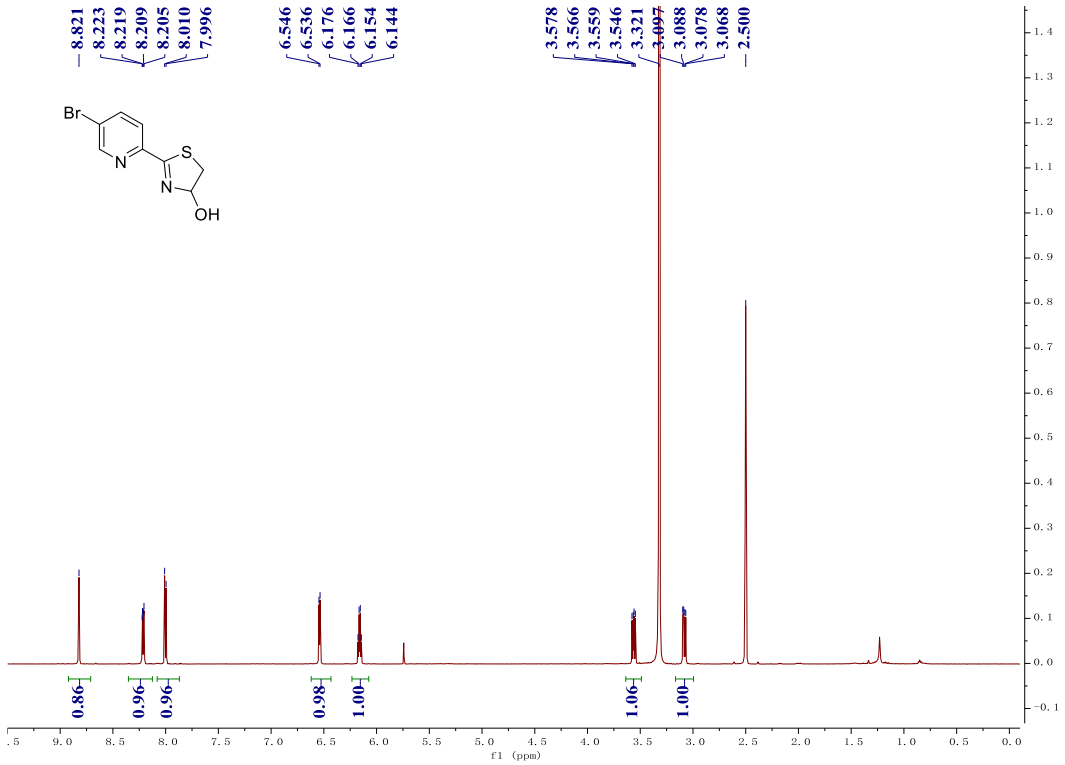
^{1}H NMR Spectrum of **5ag** (600 MHz, DMSO-D6)



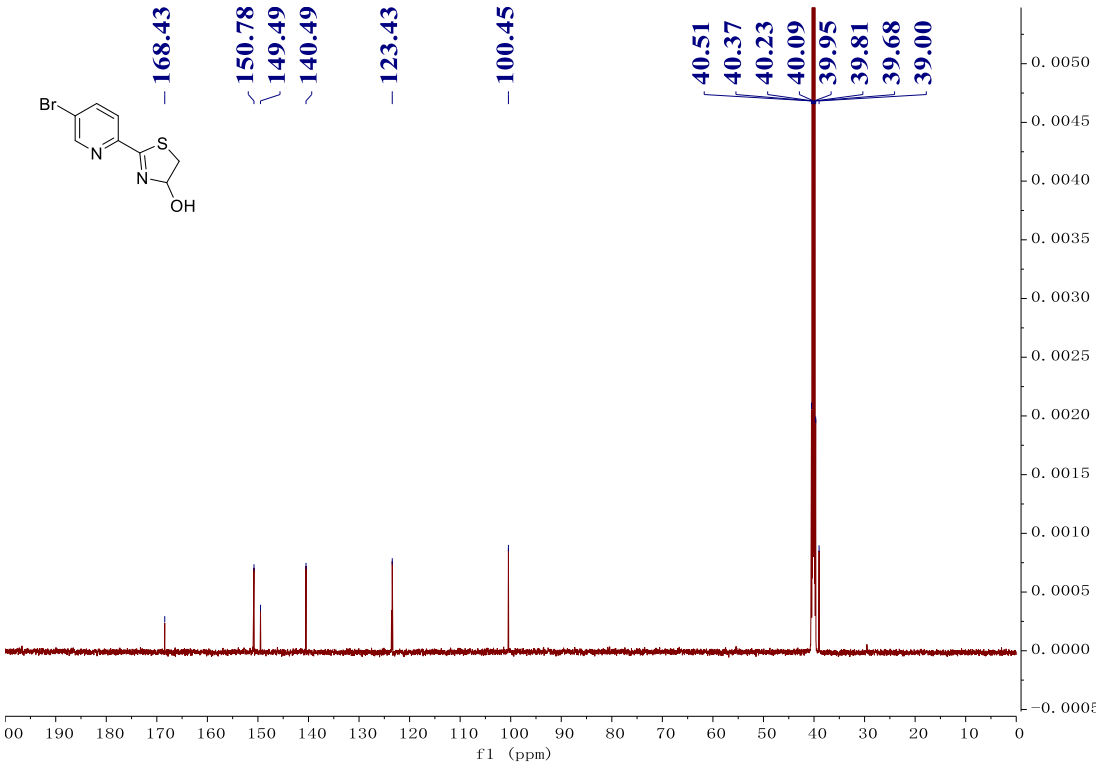
^{13}C NMR Spectrum of **5ag** (150 MHz, DMSO-D6)



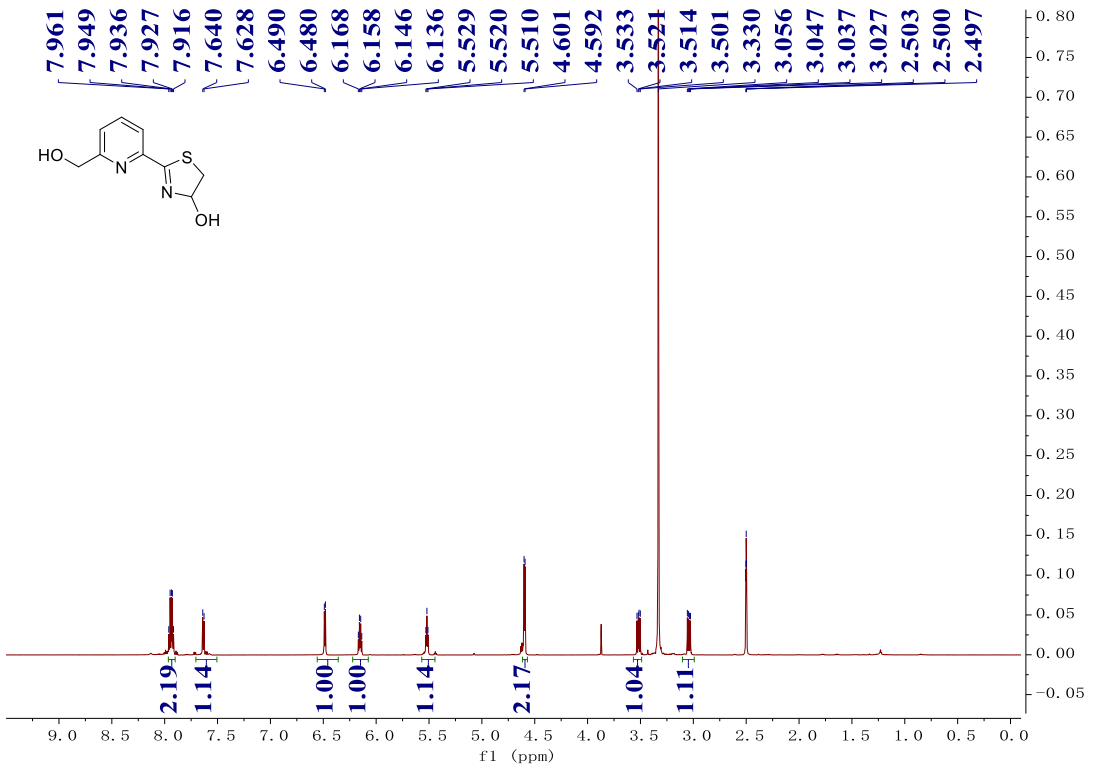
^{1}H NMR Spectrum of **5ah** (600 MHz, DMSO-D6)



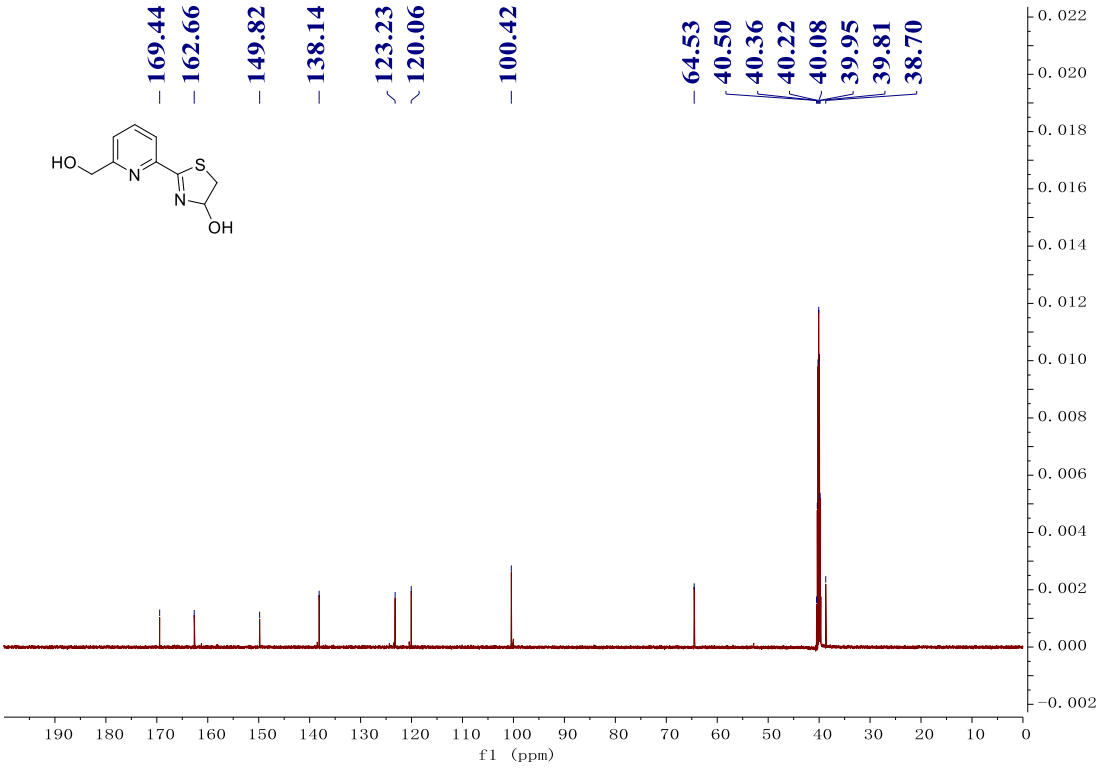
^{13}C NMR Spectrum of **5ah** (150 MHz, DMSO-D6)



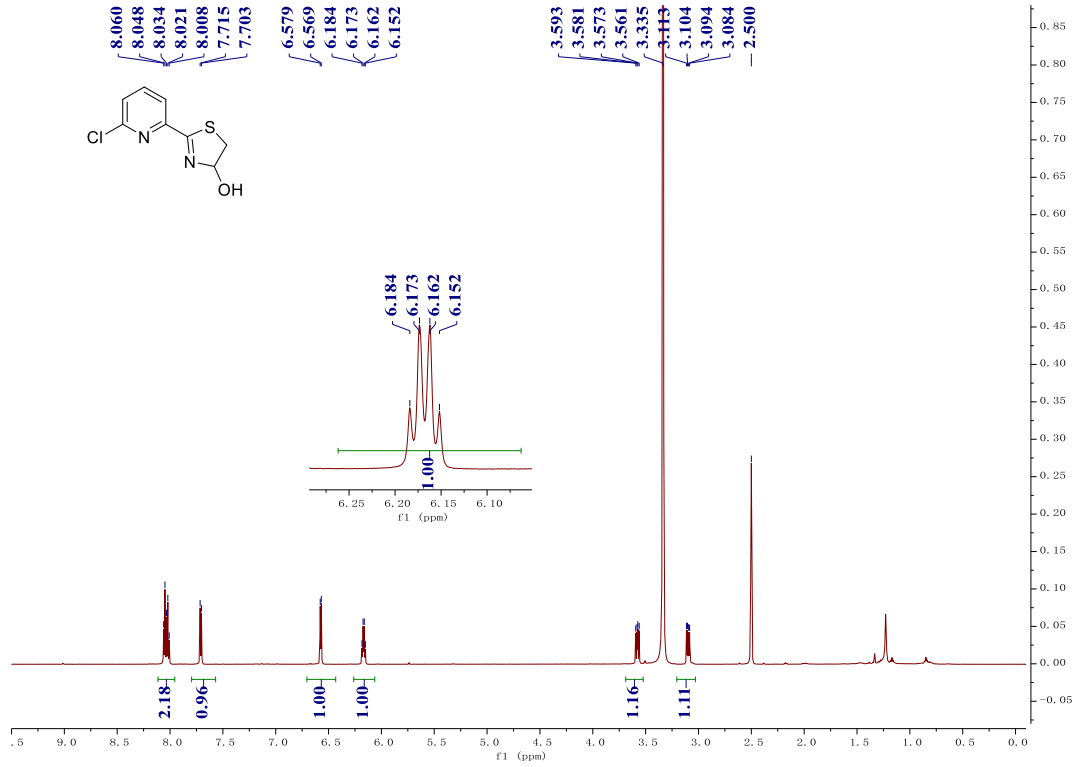
^{1}H NMR Spectrum of **5ai** (600 MHz, DMSO-D6)



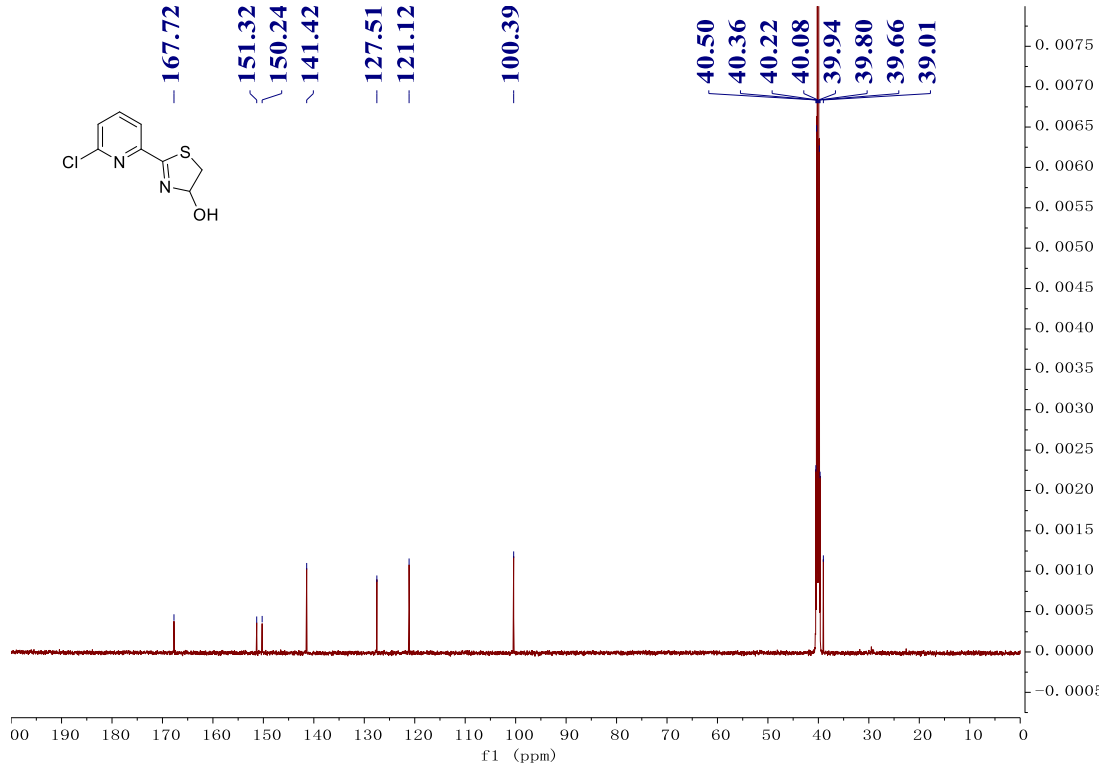
^{13}C NMR Spectrum of **5ai** (150 MHz, DMSO-D6)



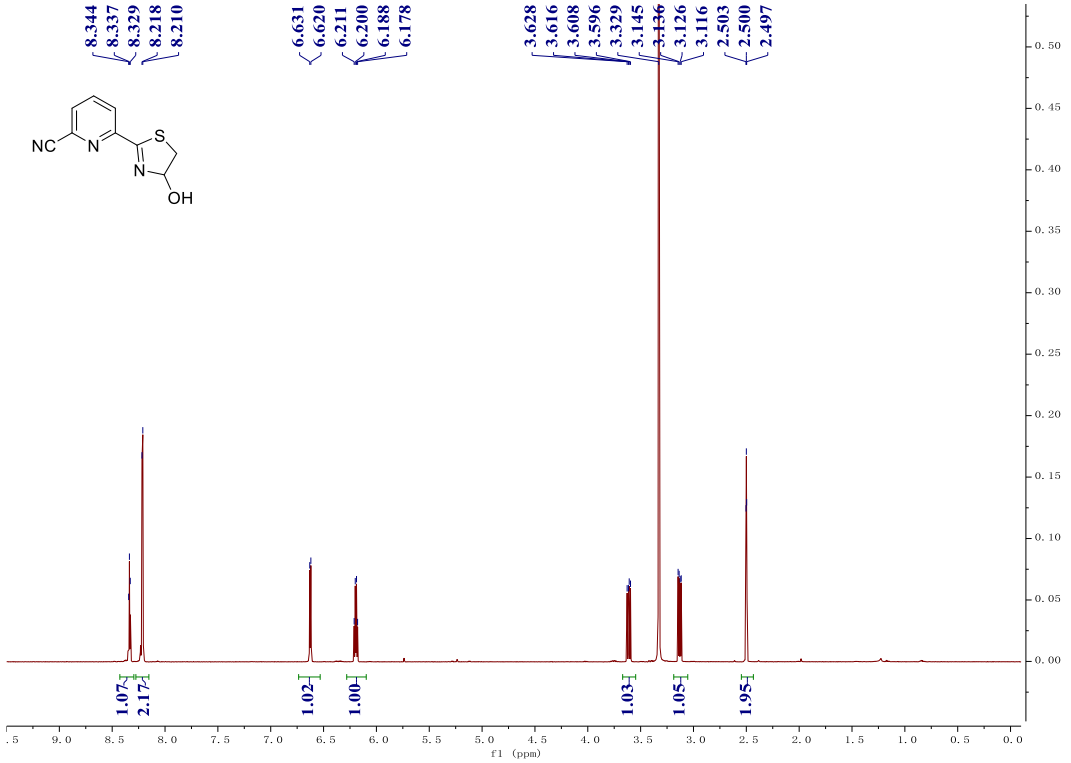
^{1}H NMR Spectrum of **5aj** (600 MHz, DMSO-D6)



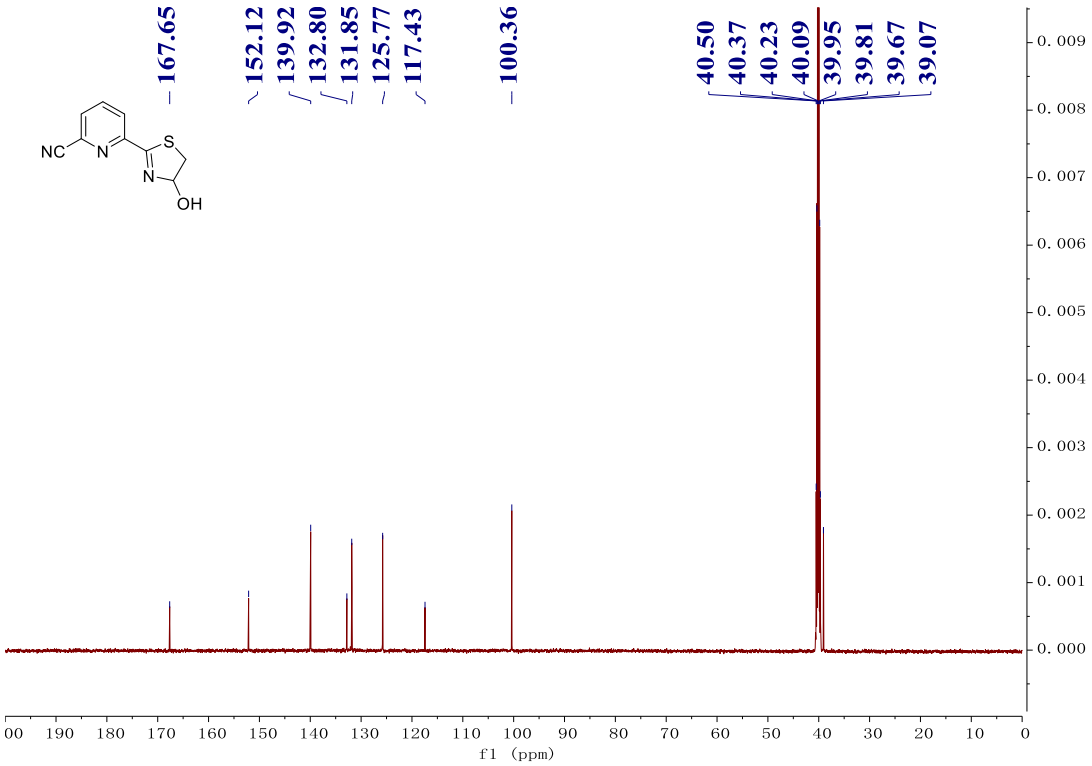
^{13}C NMR Spectrum of **5aj** (150 MHz, DMSO-D6)



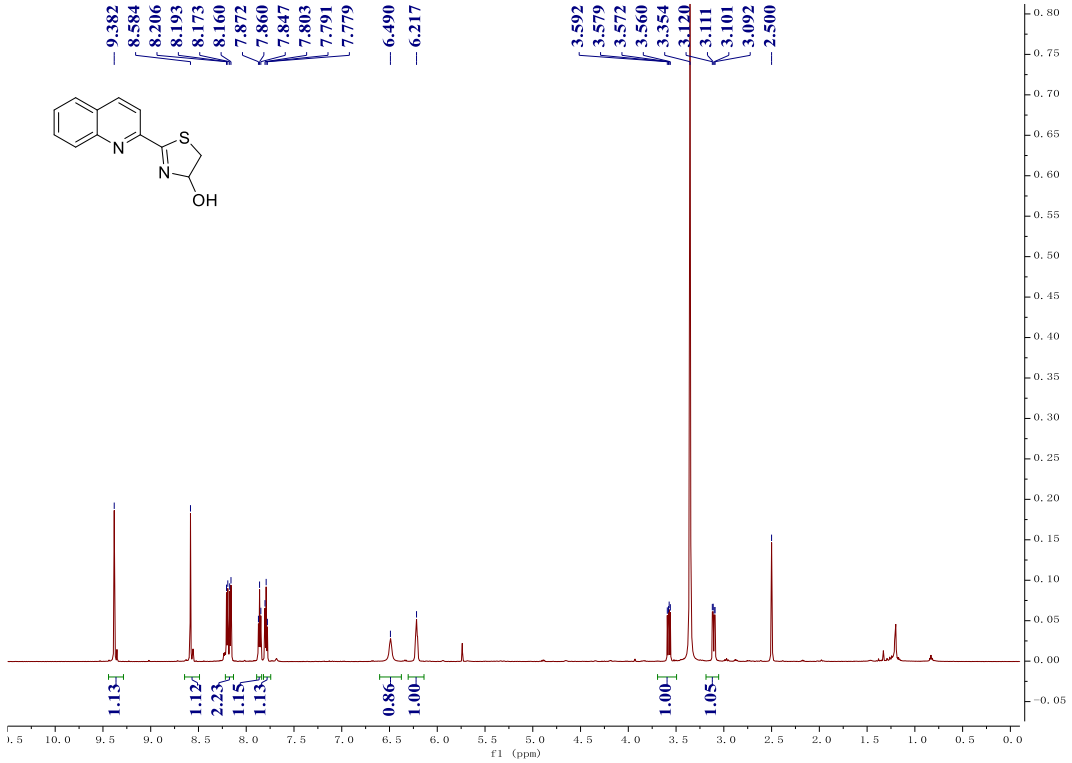
^{1}H NMR Spectrum of **5ak** (600 MHz, DMSO-D6)



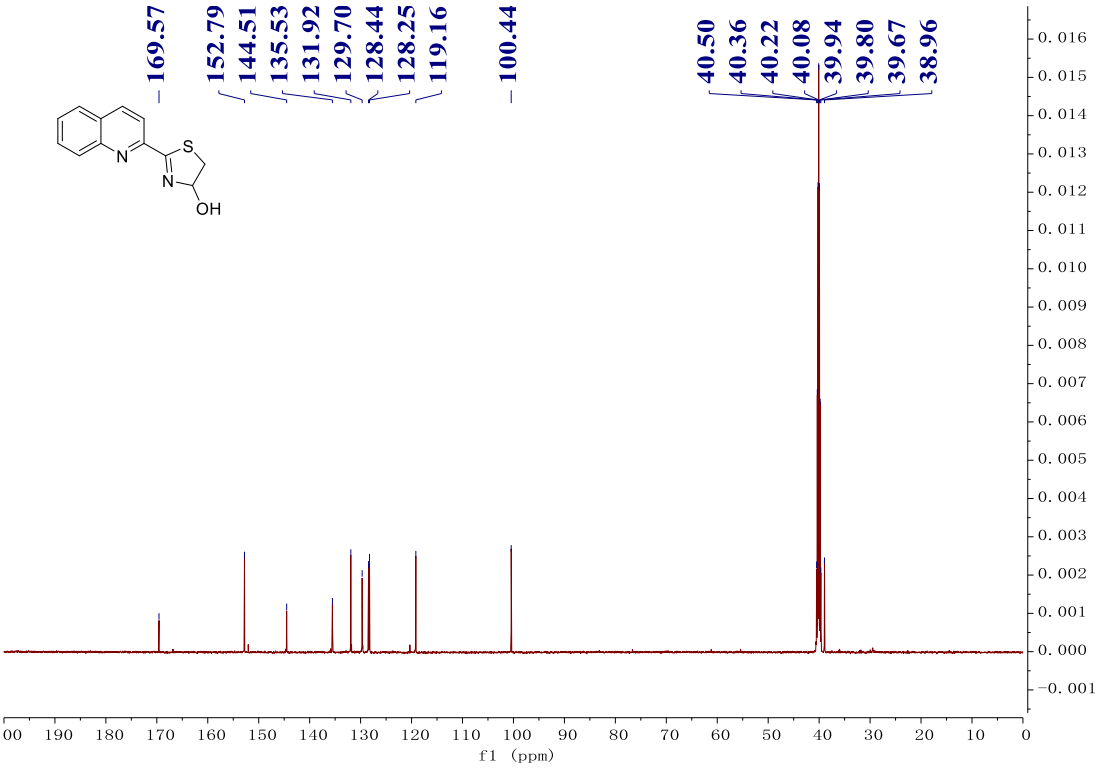
^{13}C NMR Spectrum of **5ak** (150 MHz, DMSO-D6)



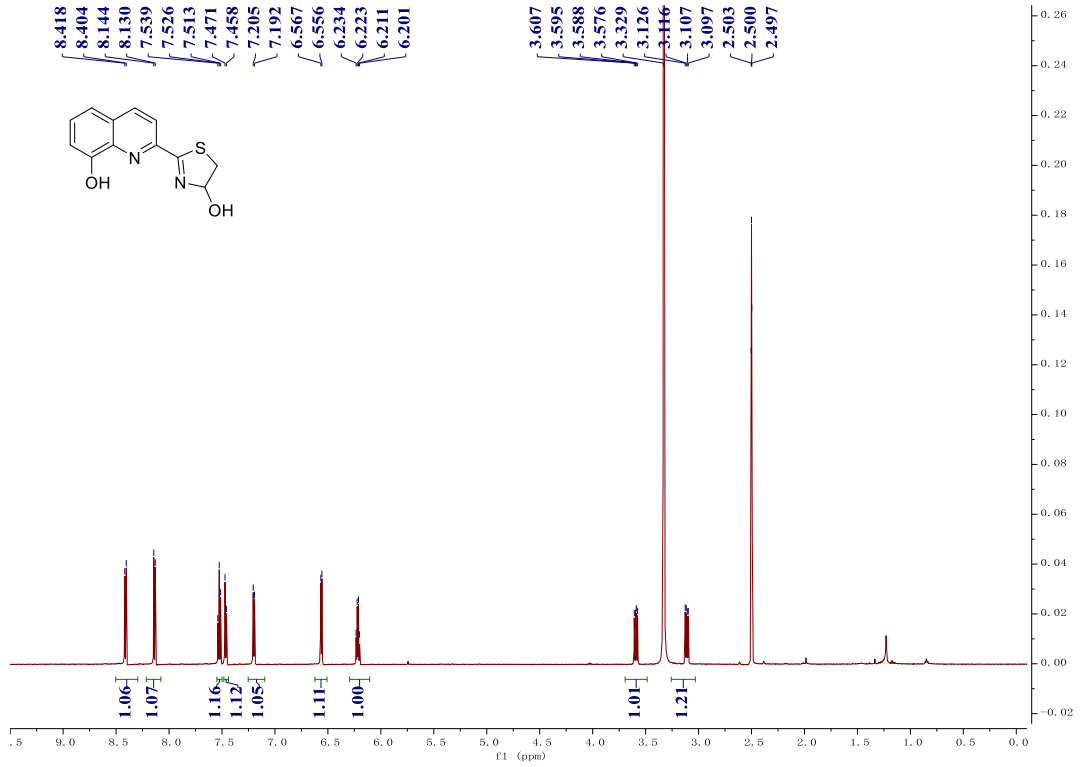
^{1}H NMR Spectrum of **5al** (600 MHz, DMSO-D6)



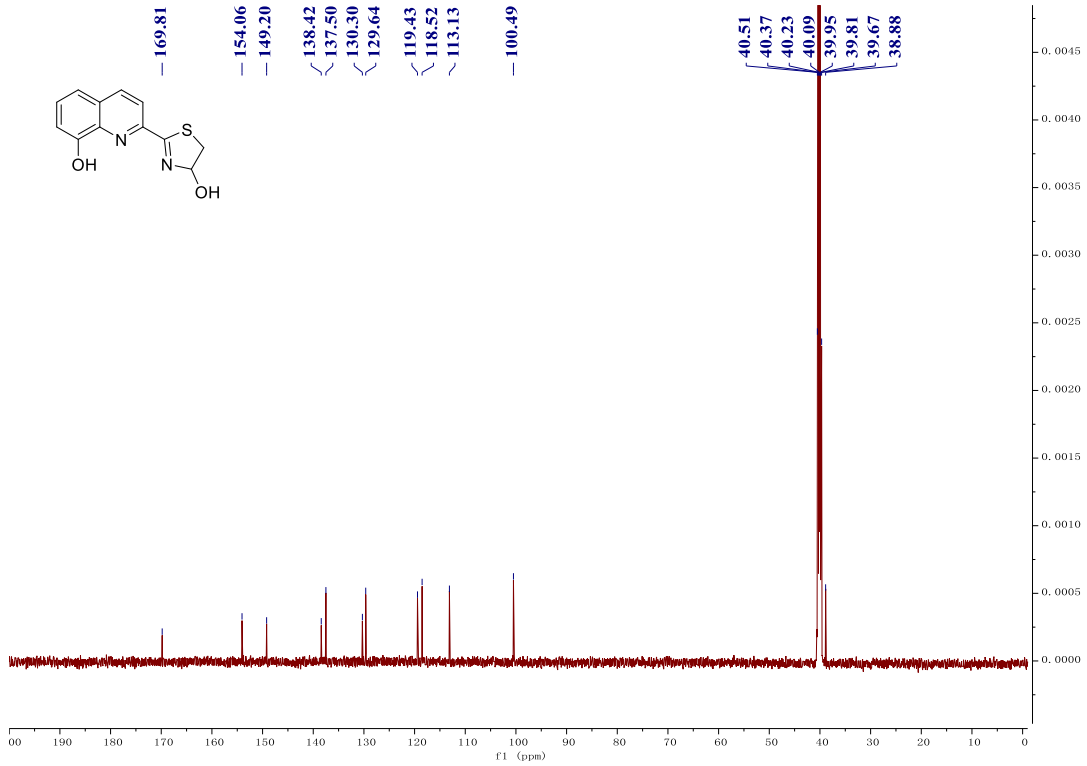
^{13}C NMR Spectrum of **5al** (150 MHz, DMSO-D6)



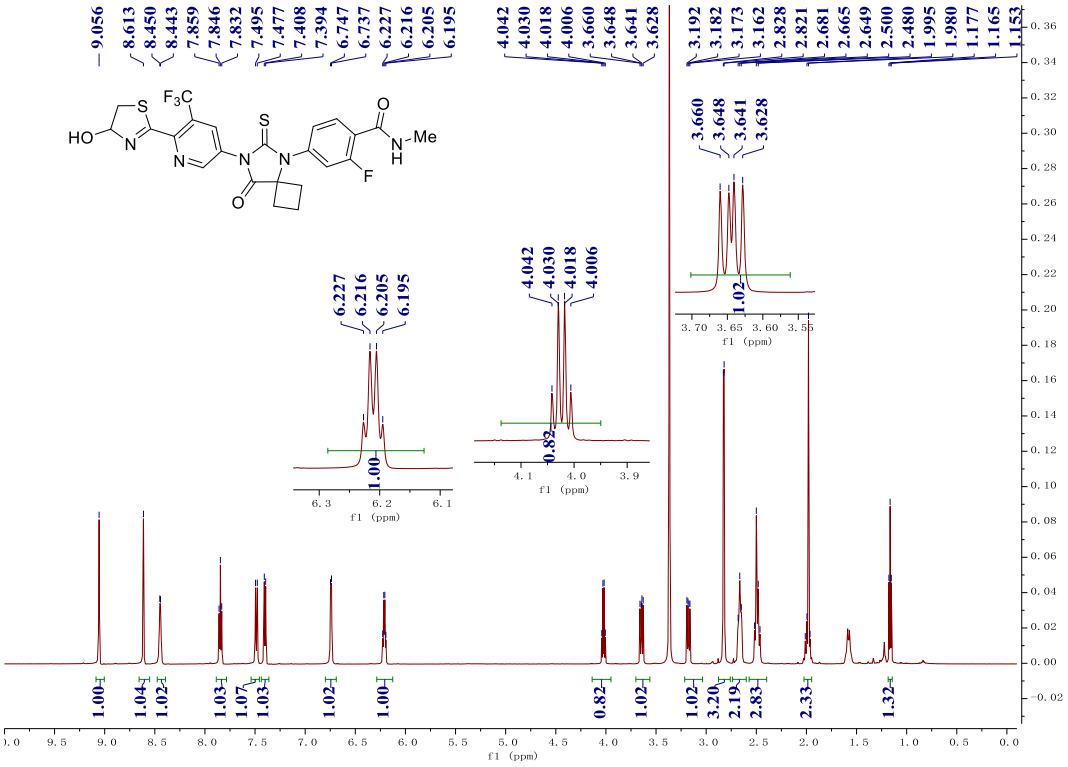
^{1}H NMR Spectrum of **5am** (600 MHz, DMSO-D6)



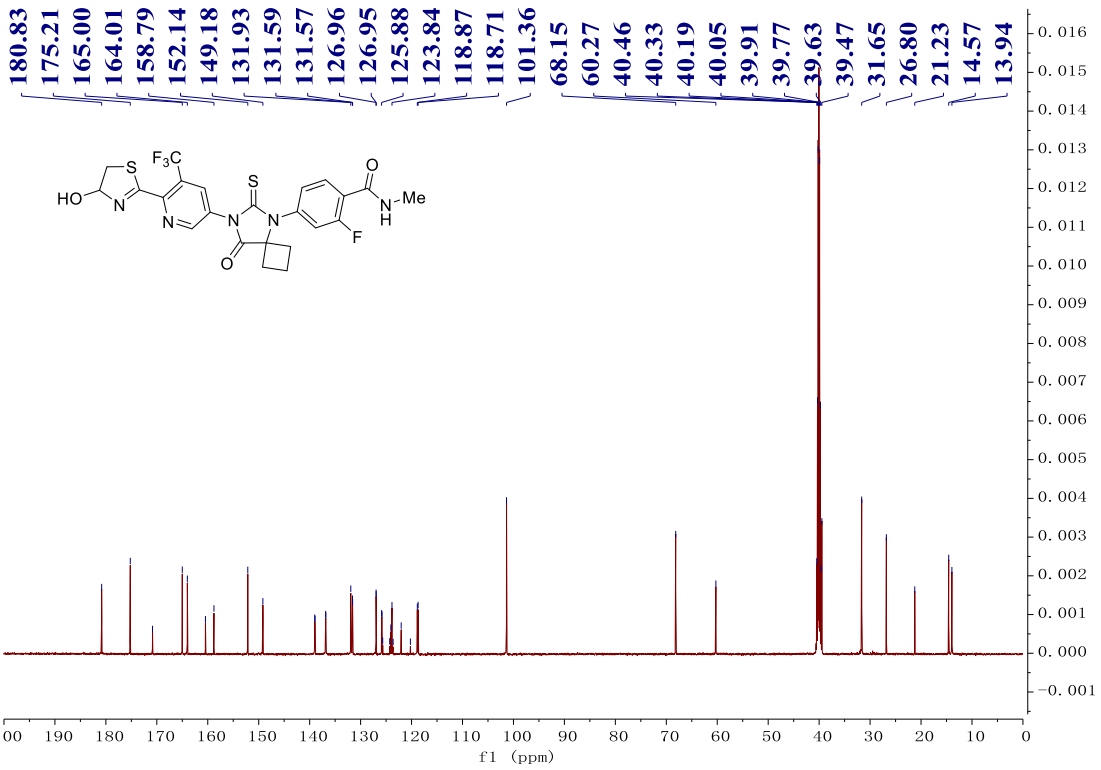
^{13}C NMR Spectrum of **5am** (150 MHz, DMSO-D6)



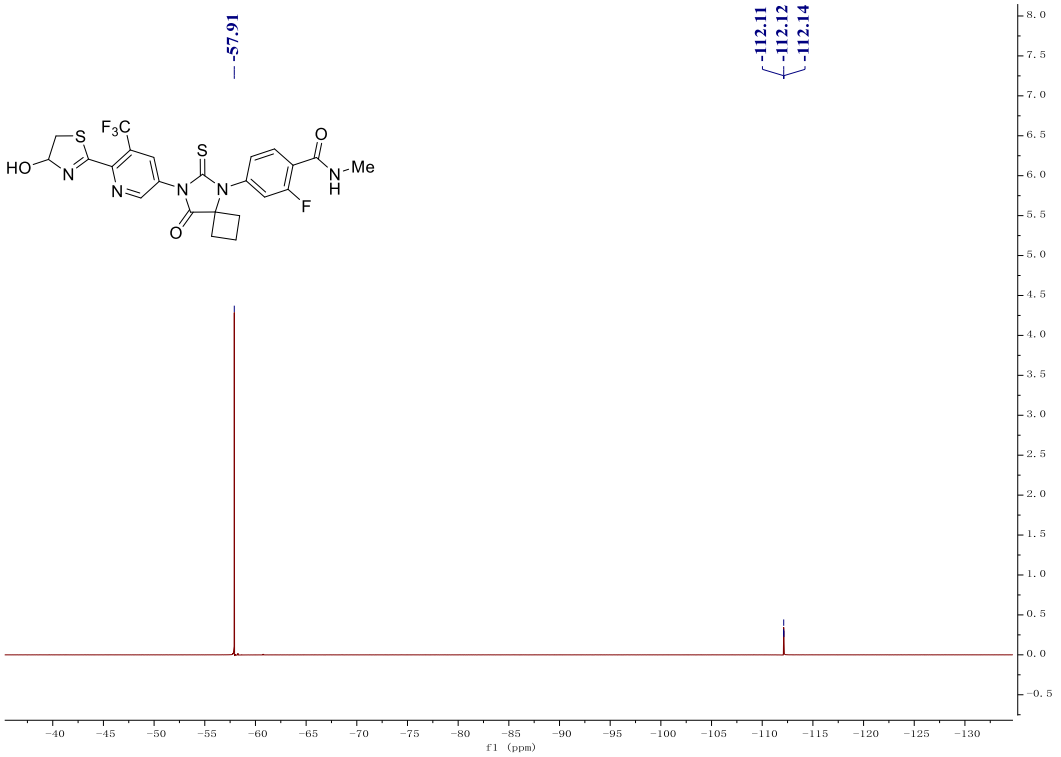
^{1}H NMR Spectrum of **5an** (600 MHz, DMSO-D6)



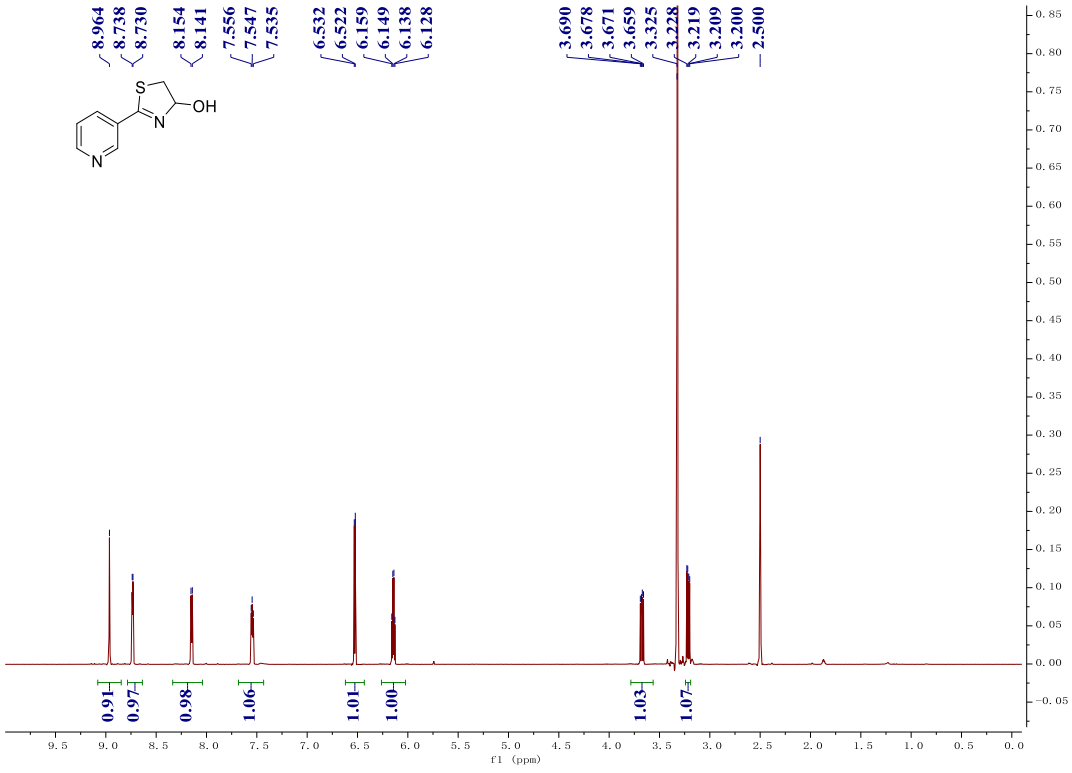
^{13}C NMR Spectrum of **5an** (150 MHz, DMSO-D6)



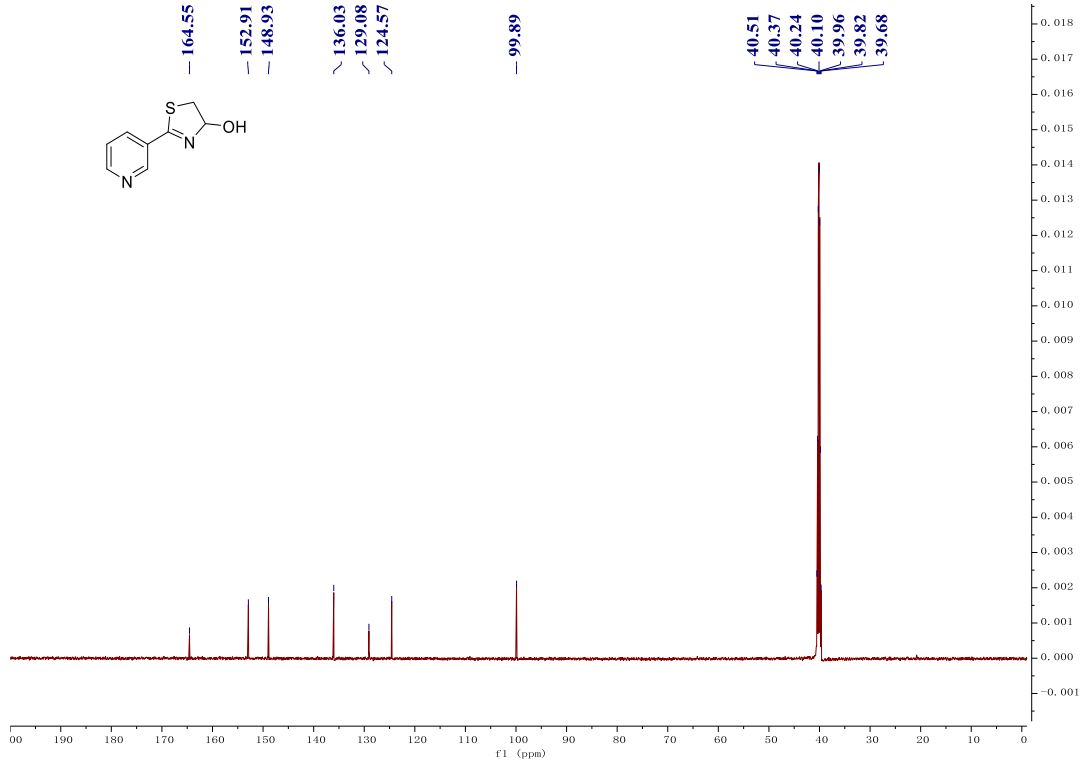
^{19}F NMR Spectrum of **5an** (565 MHz, DMSO-D_6)



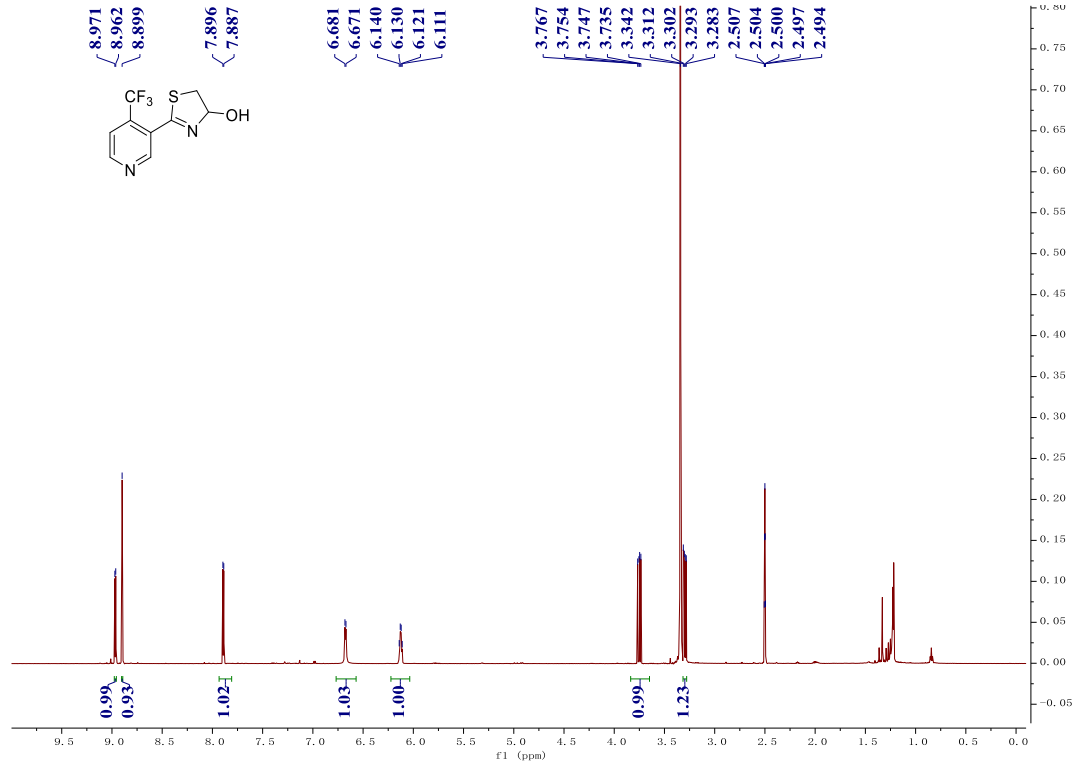
^{1}H NMR Spectrum of **6aa** (600 MHz, DMSO-D6)



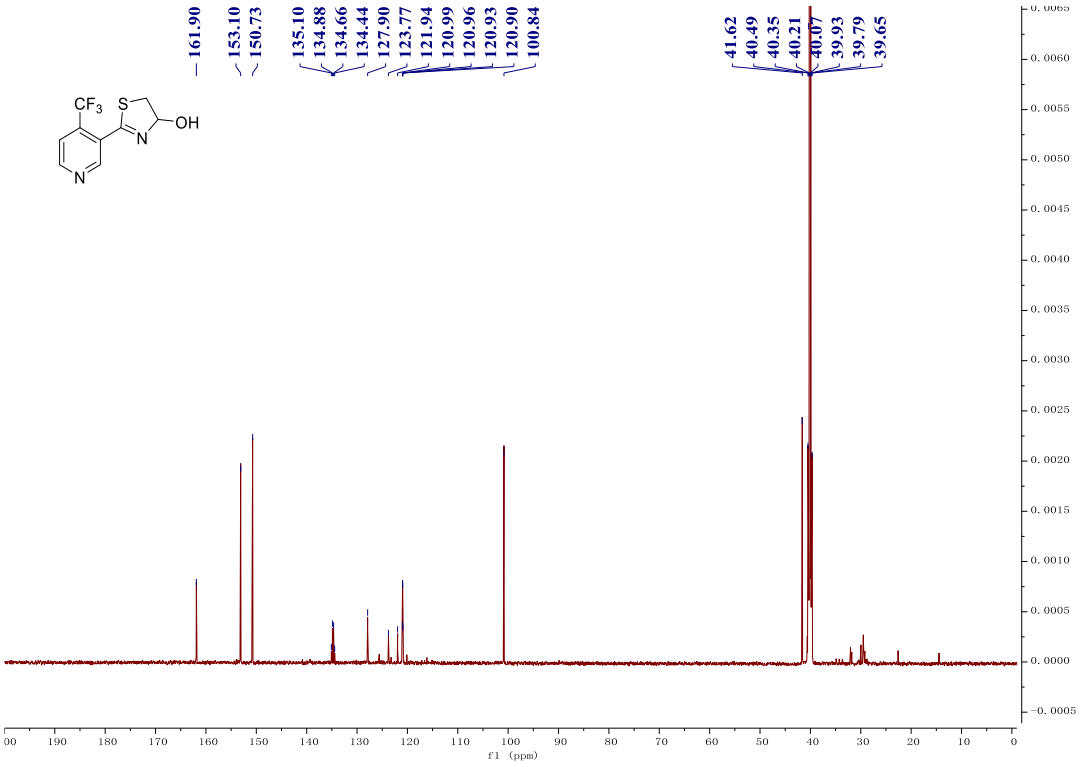
^{13}C NMR Spectrum of **6aa** (150 MHz, DMSO-D6)



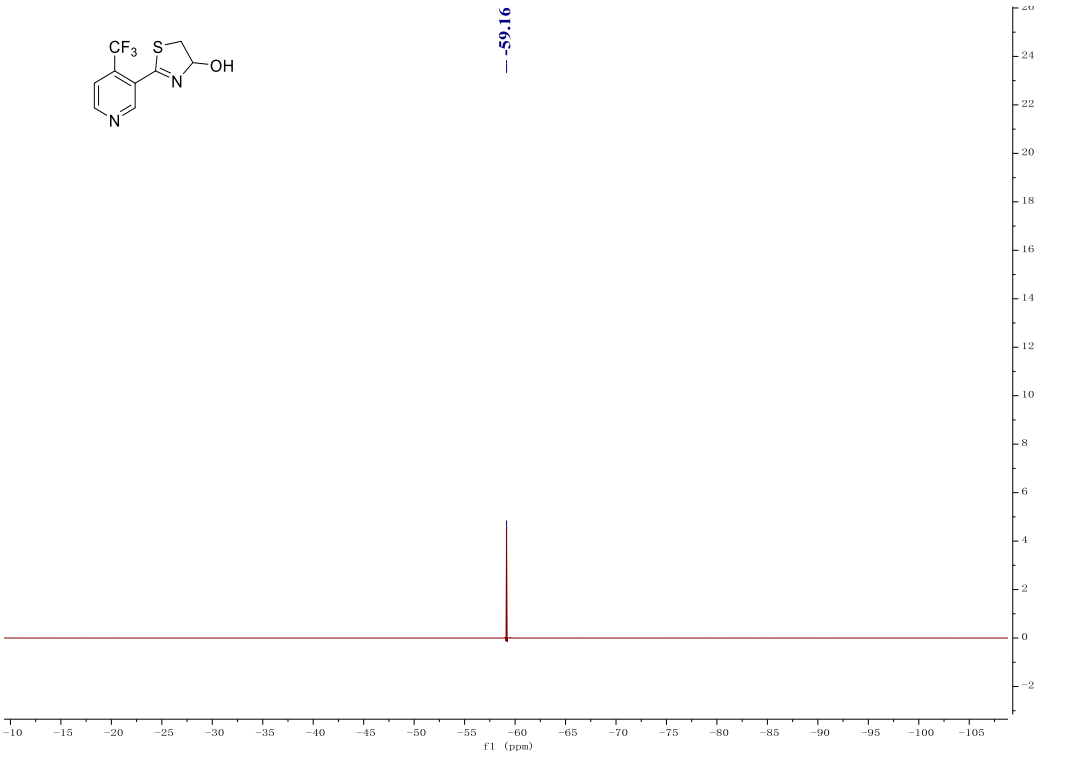
^{1}H NMR Spectrum of **6ab** (600 MHz, DMSO-D6)



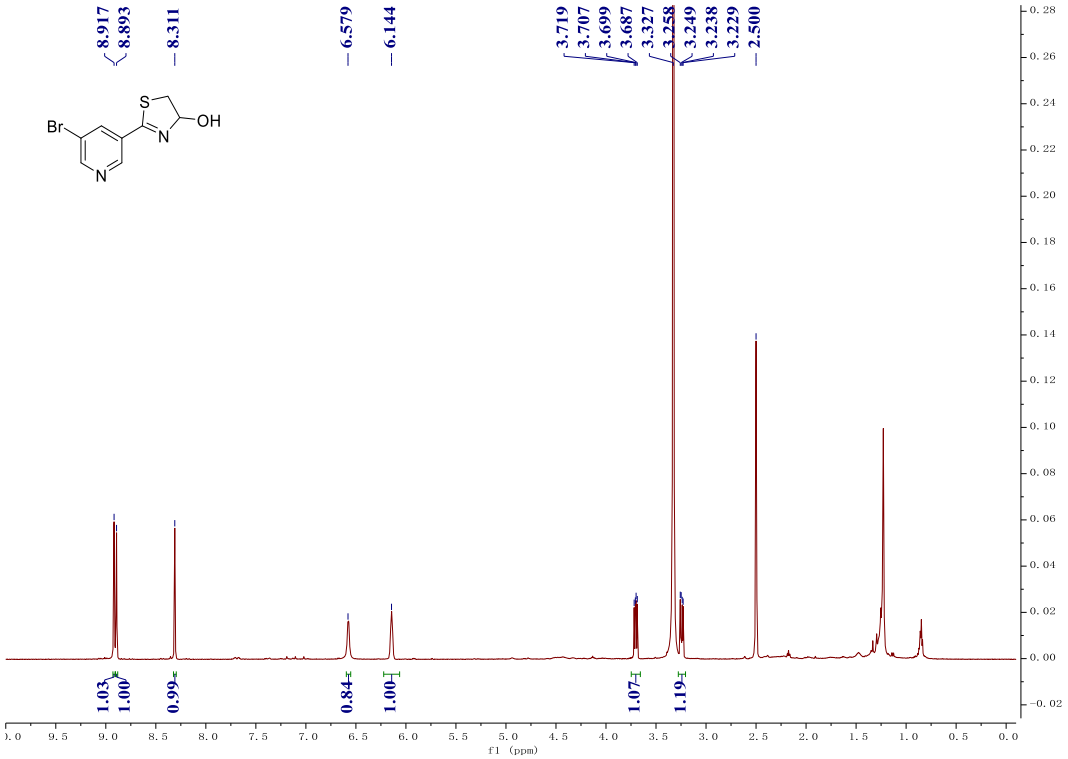
^{13}C NMR Spectrum of **6ab** (150 MHz, DMSO-D6)



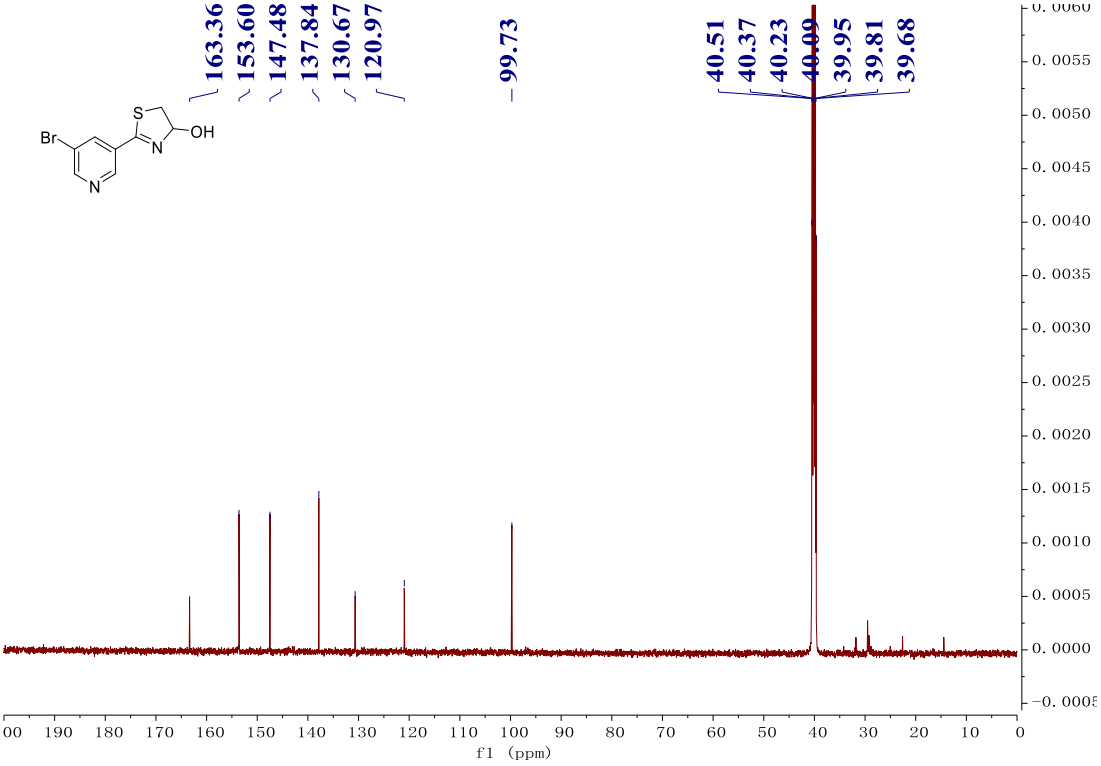
^{19}F NMR Spectrum of **6ab** (565 MHz, DMSO-D_6)



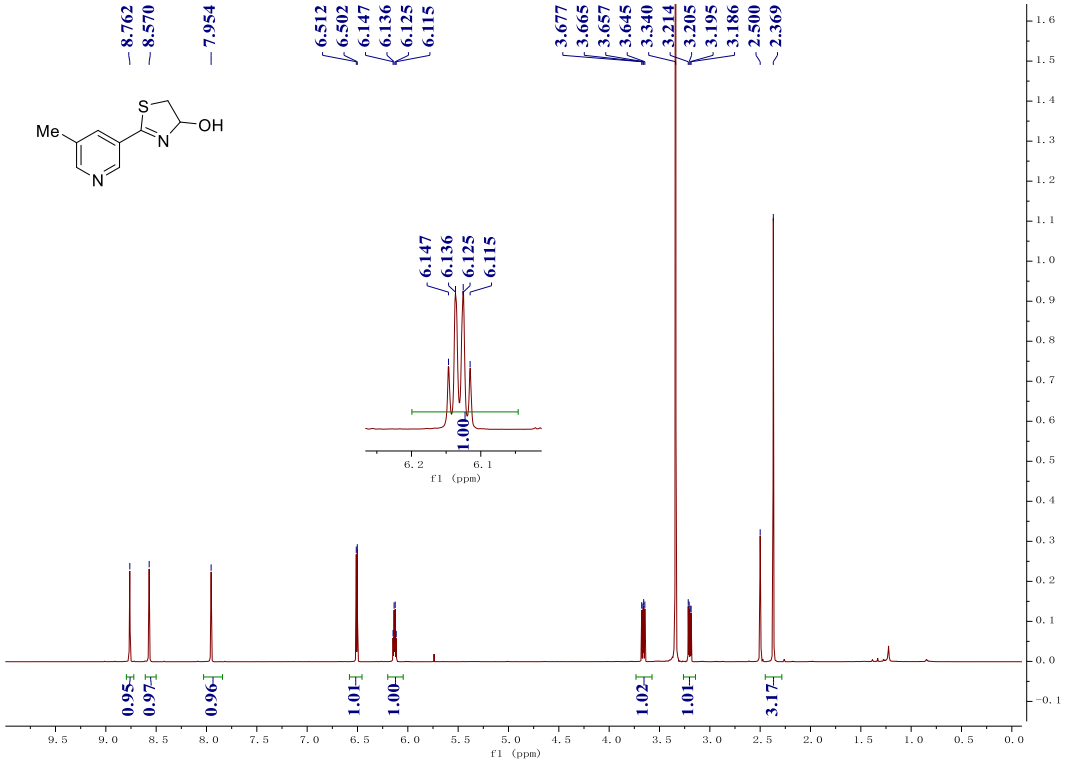
^{1}H NMR Spectrum of **6ac** (600 MHz, DMSO-D6)



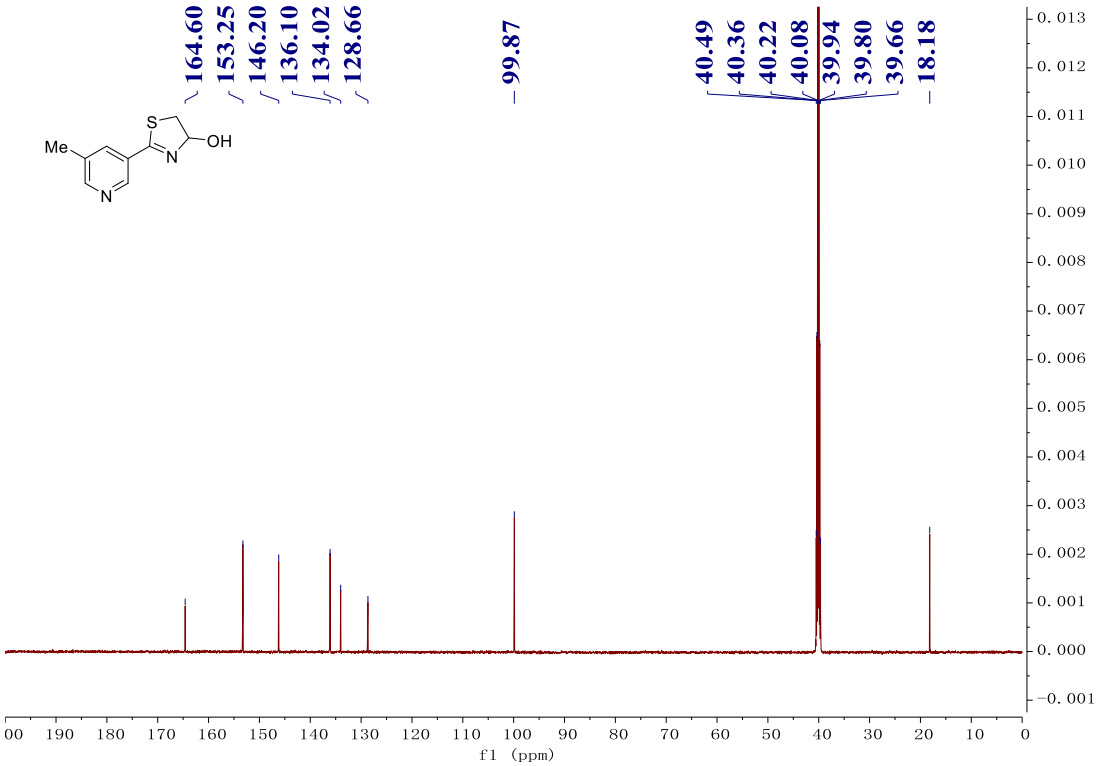
^{13}C NMR Spectrum of **6ac** (150 MHz, DMSO-D6)



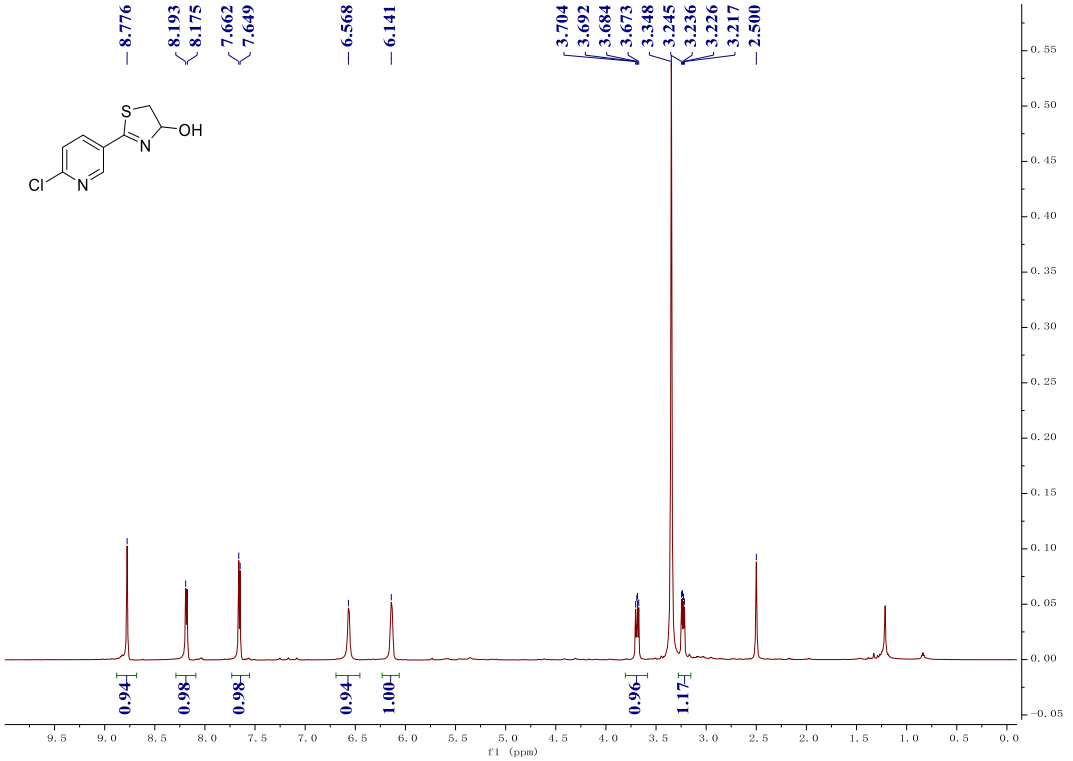
^{1}H NMR Spectrum of **6ad** (600 MHz, DMSO-D6)



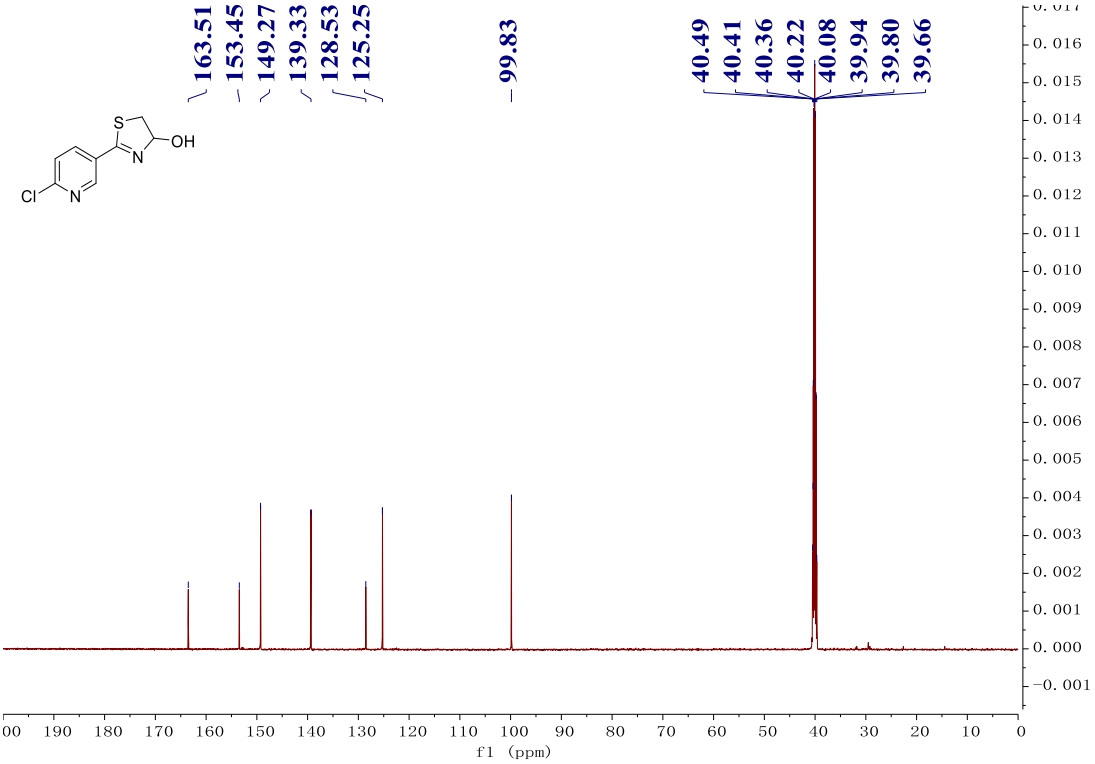
^{13}C NMR Spectrum of **6ad** (150 MHz, DMSO-D6)



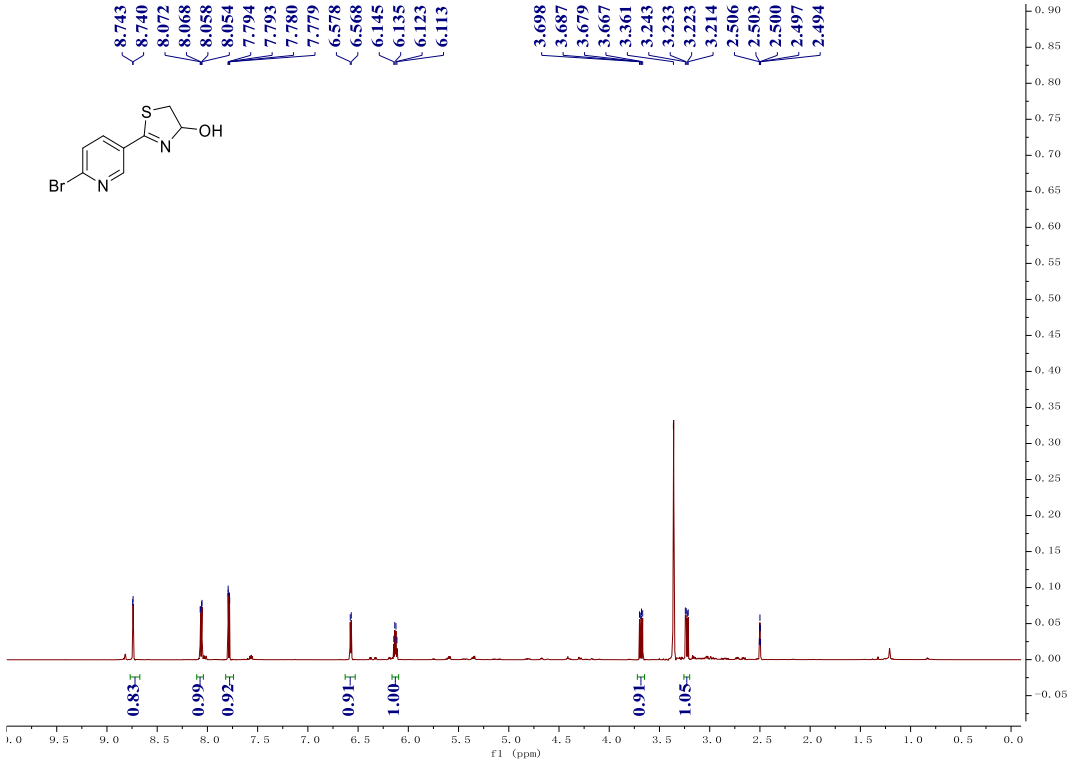
^{1}H NMR Spectrum of **6ae** (600 MHz, DMSO-D6)



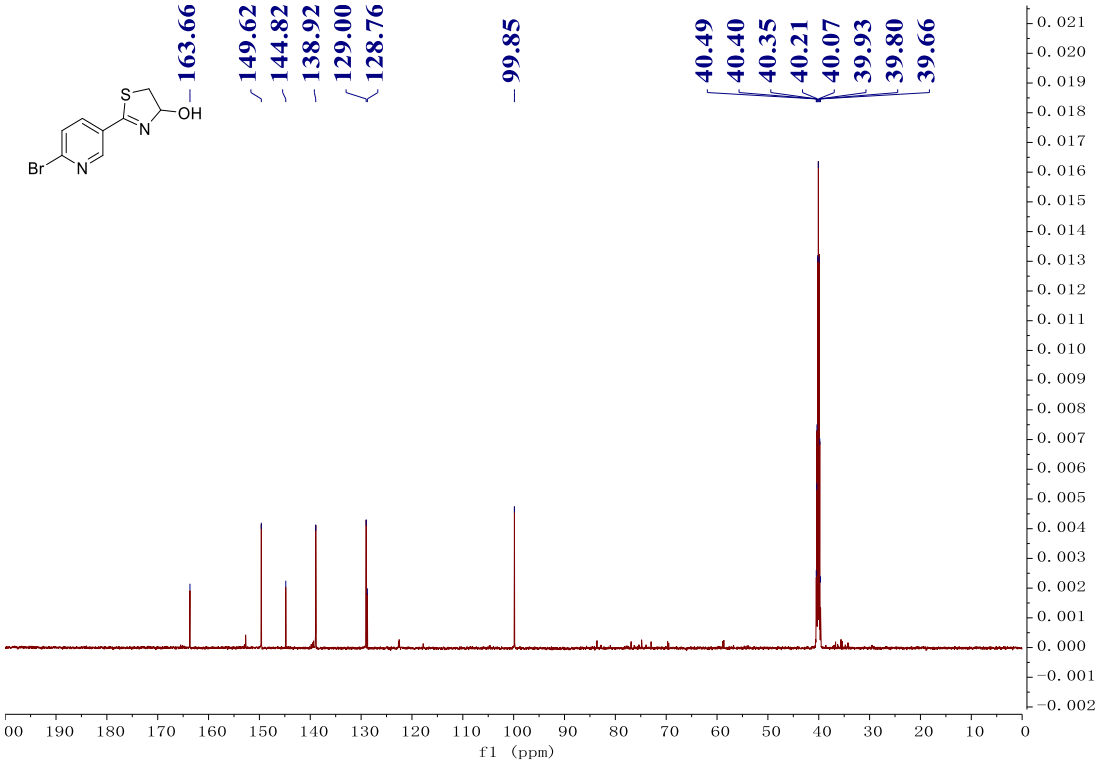
^{13}C NMR Spectrum of **6ae** (150 MHz, DMSO-D6)



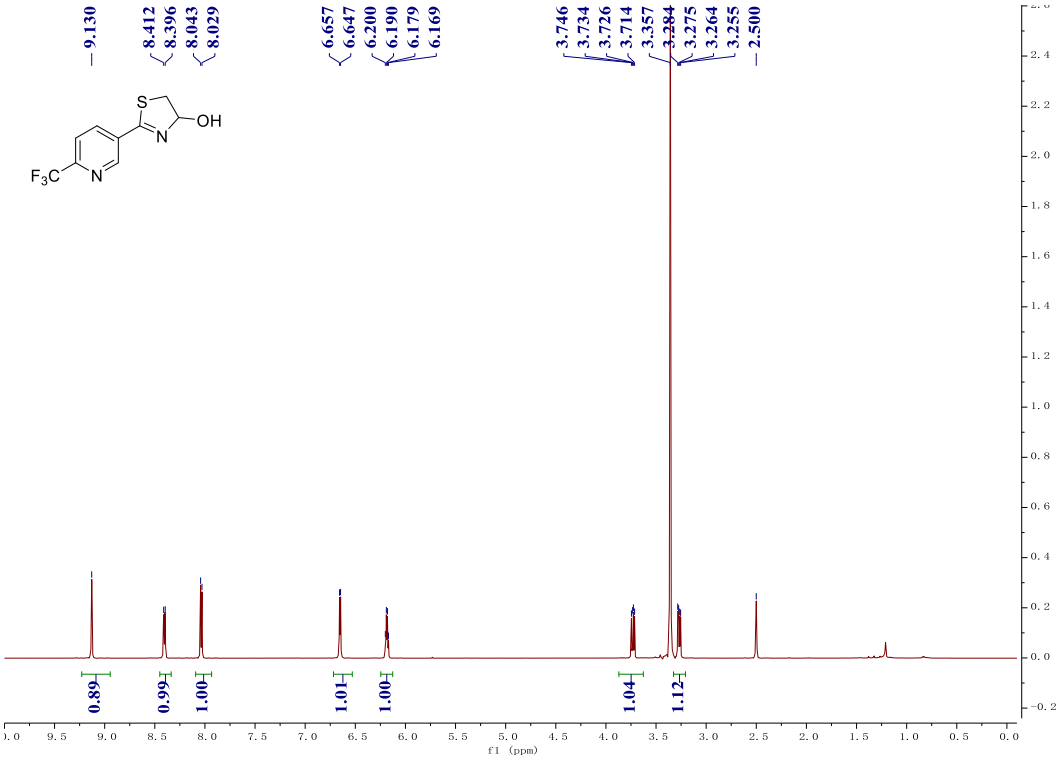
^{1}H NMR Spectrum of **6af** (600 MHz, DMSO-D6)



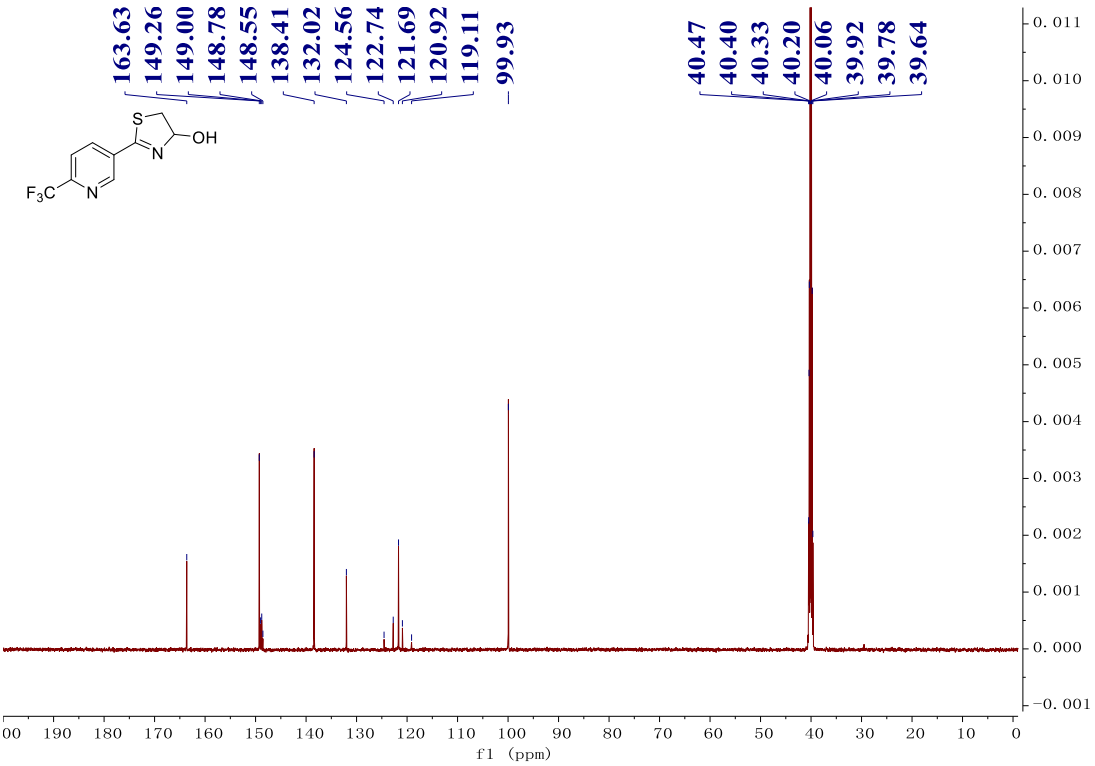
^{13}C NMR Spectrum of **6af** (150 MHz, DMSO-D6)



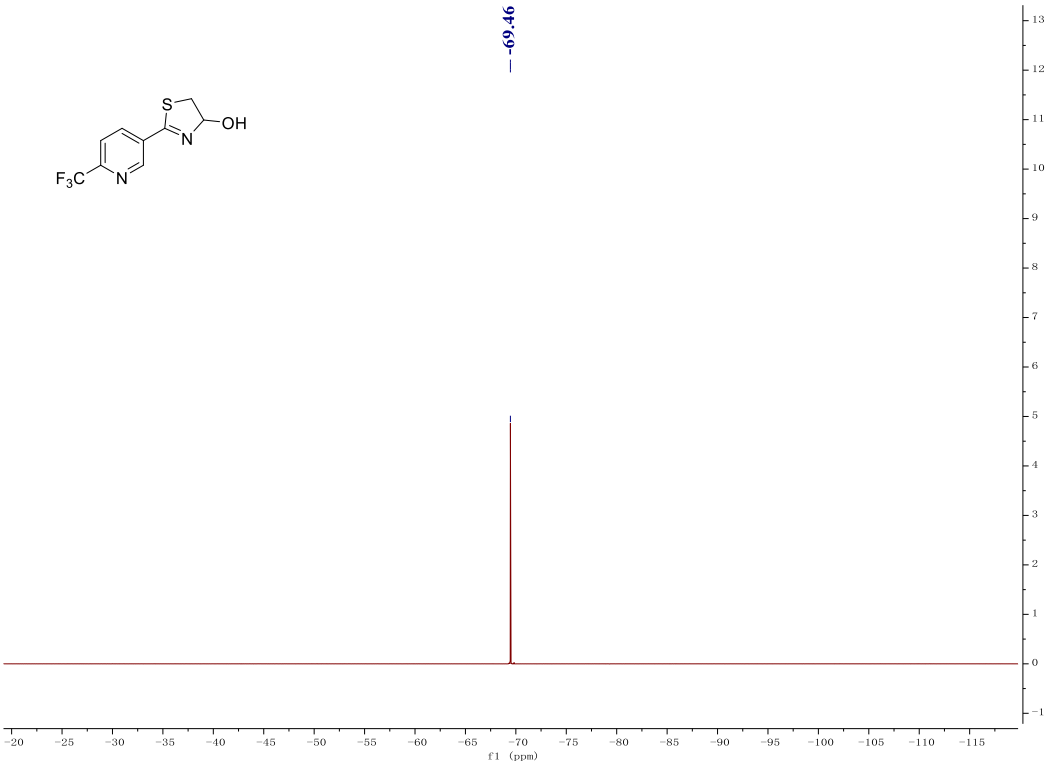
^{1}H NMR Spectrum of **6ag** (600 MHz, DMSO-D6)



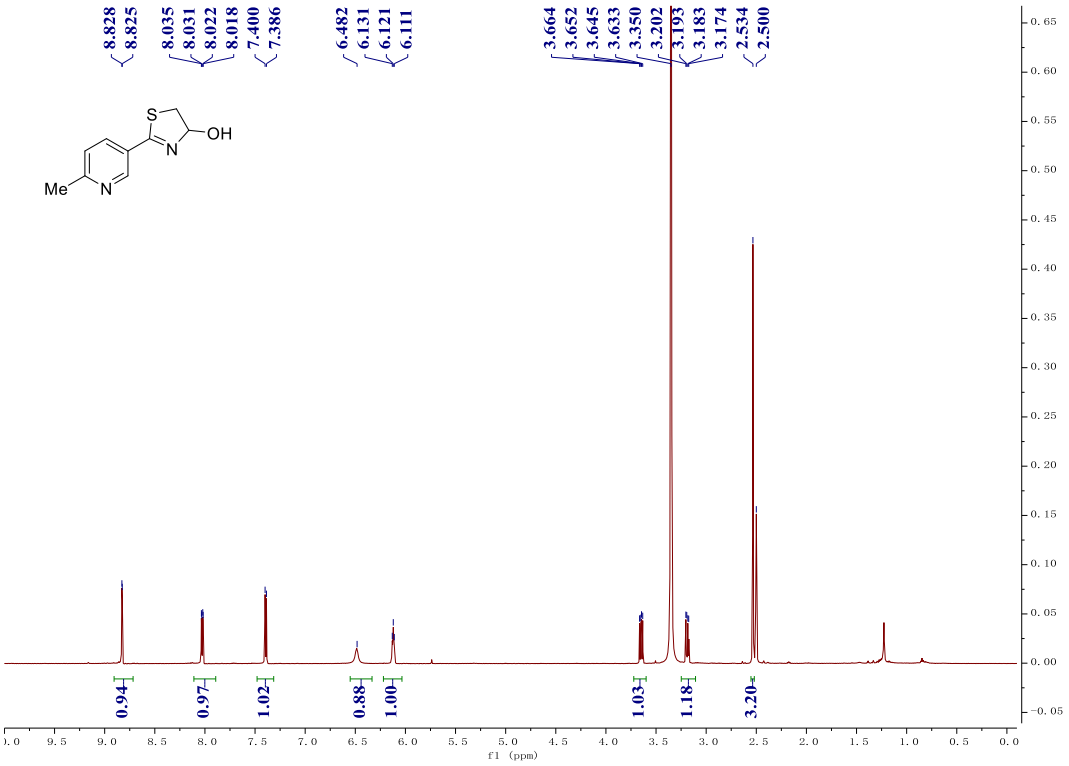
^{13}C NMR Spectrum of **6ag** (150 MHz, DMSO-D6)



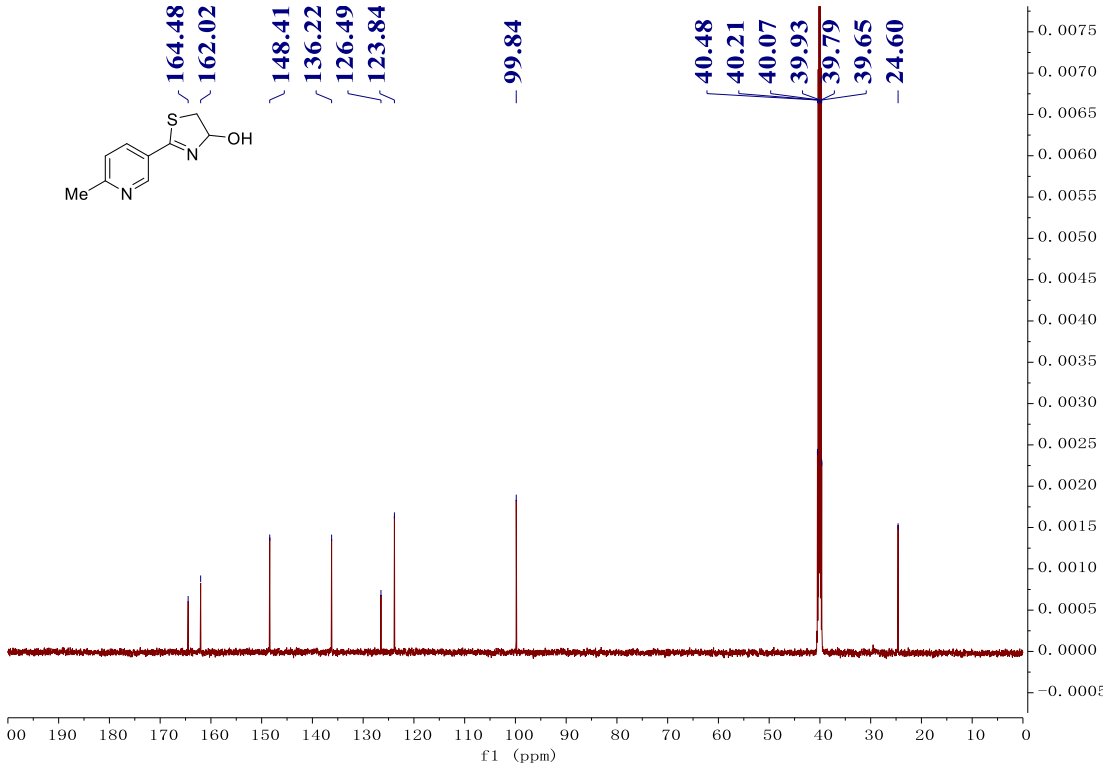
^{19}F NMR Spectrum of **6ag** (565 MHz, DMSO-D_6)



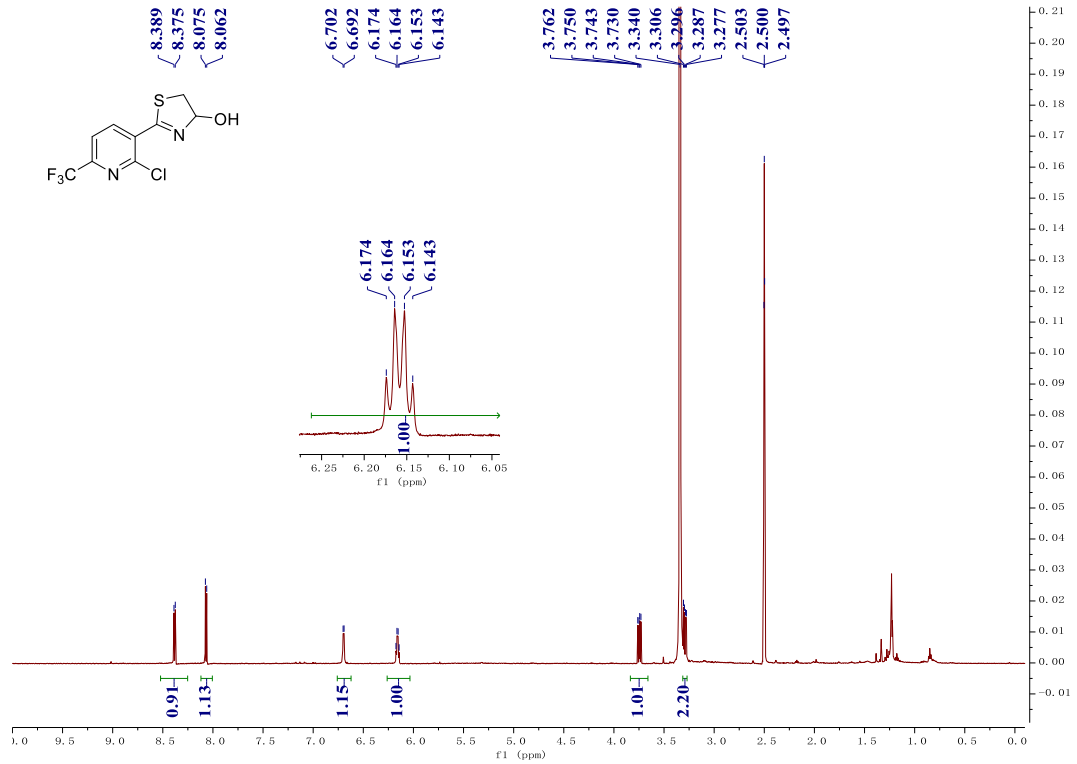
^{1}H NMR Spectrum of **6ah** (600 MHz, DMSO-D6)



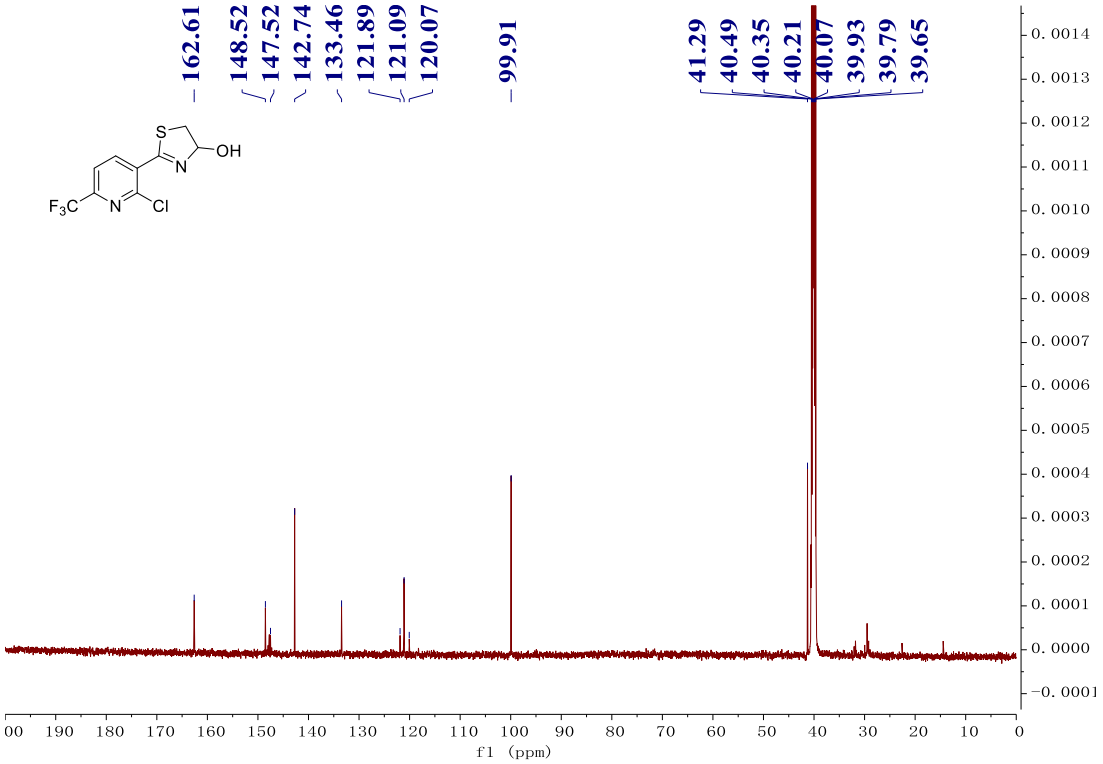
^{13}C NMR Spectrum of **6ah** (150 MHz, DMSO-D6)



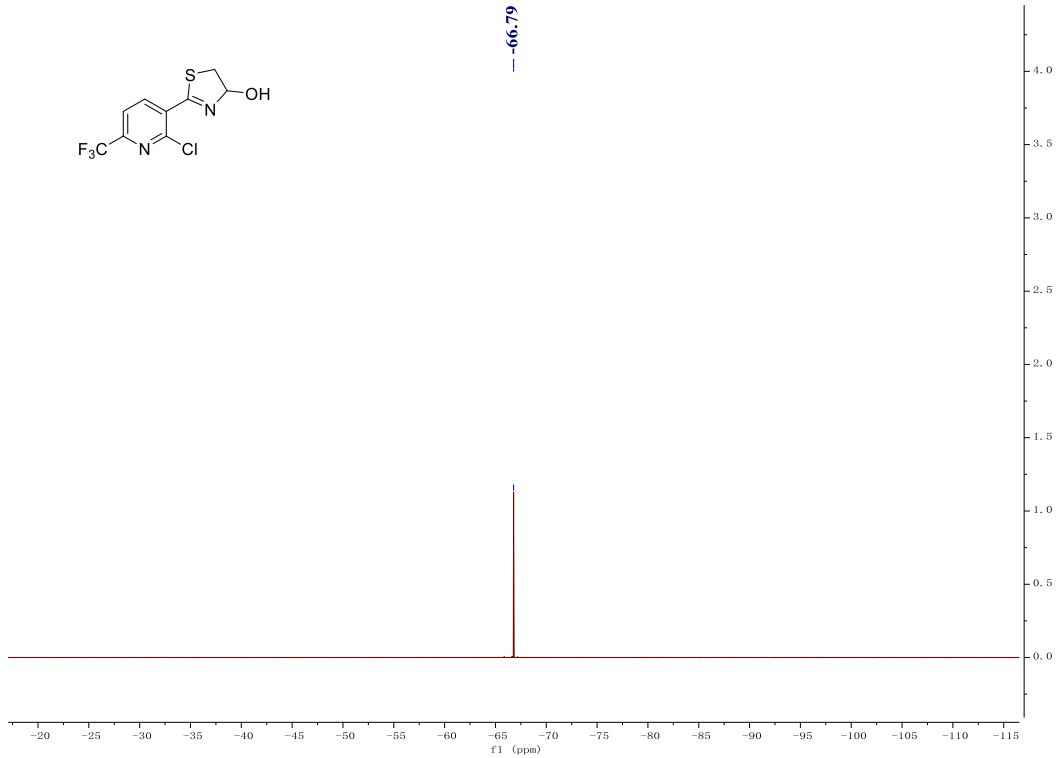
^{1}H NMR Spectrum of **6ai** (600 MHz, DMSO-D6)



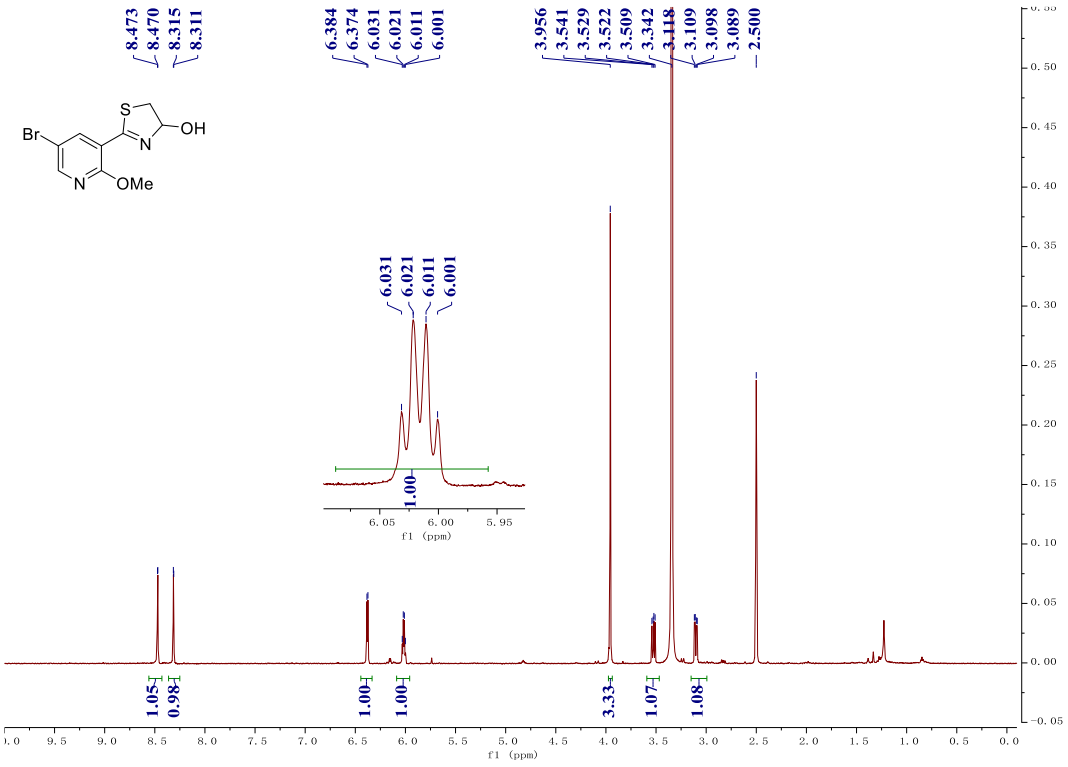
^{13}C NMR Spectrum of **6ai** (150 MHz, DMSO-D6)



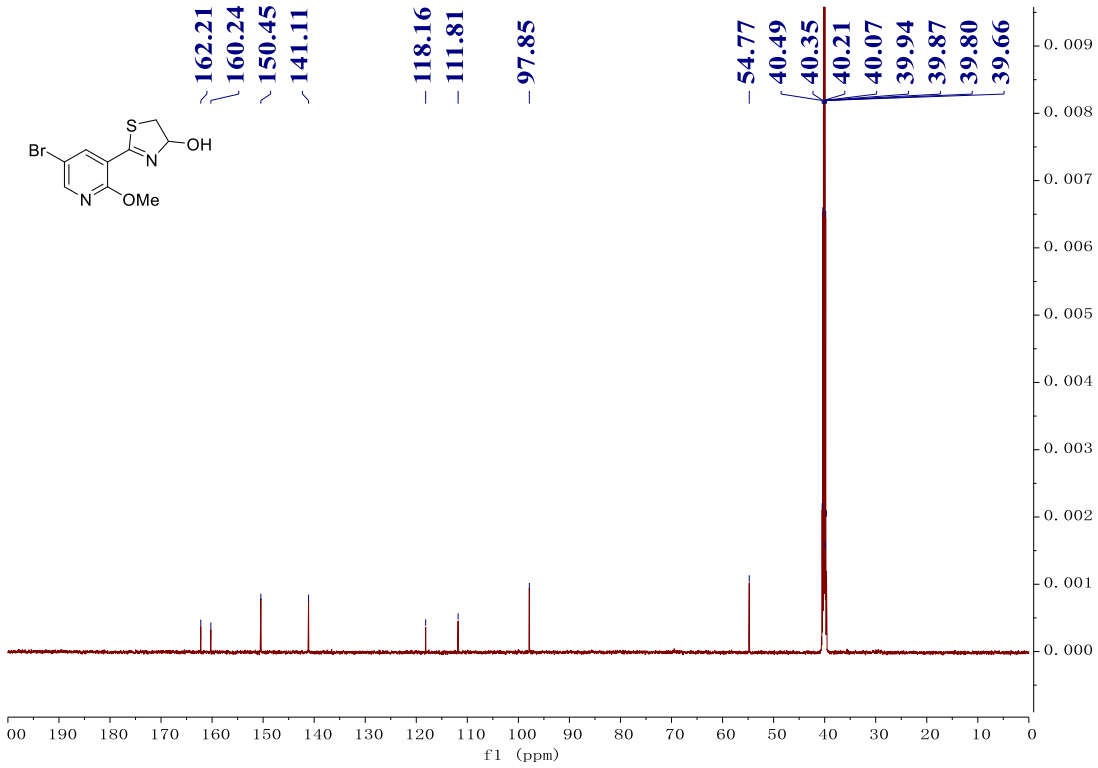
^{19}F NMR Spectrum of **6ai** (565 MHz, DMSO-D_6)



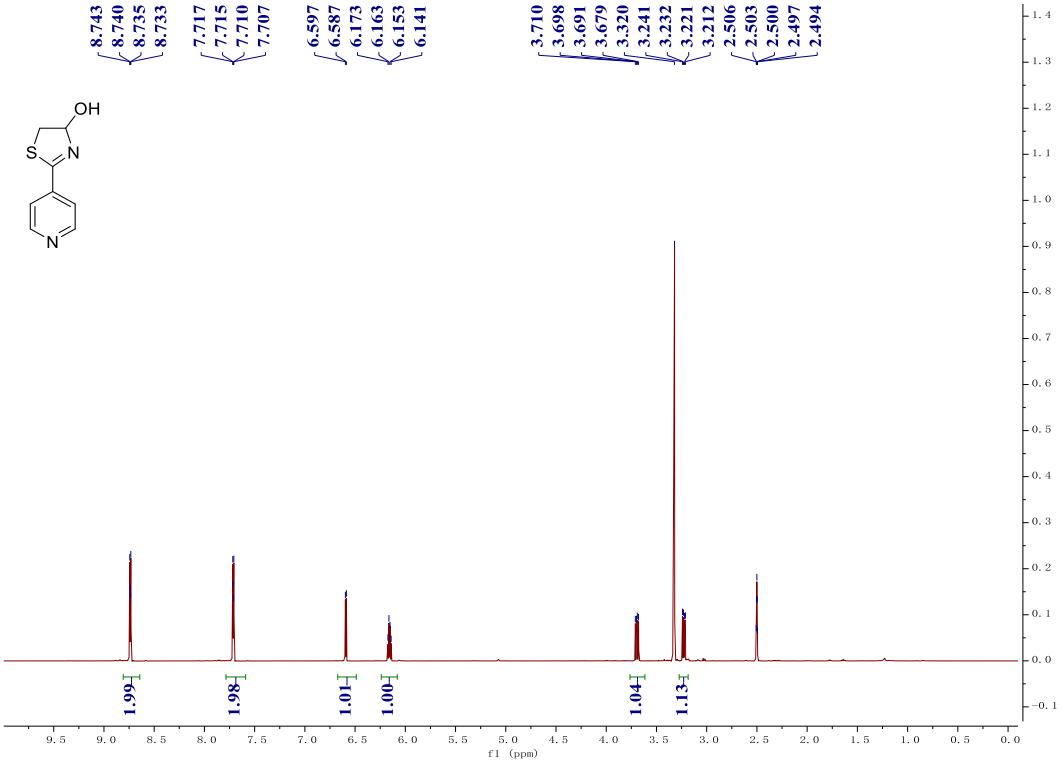
^{1}H NMR Spectrum of **6aj** (600 MHz, DMSO-D6)



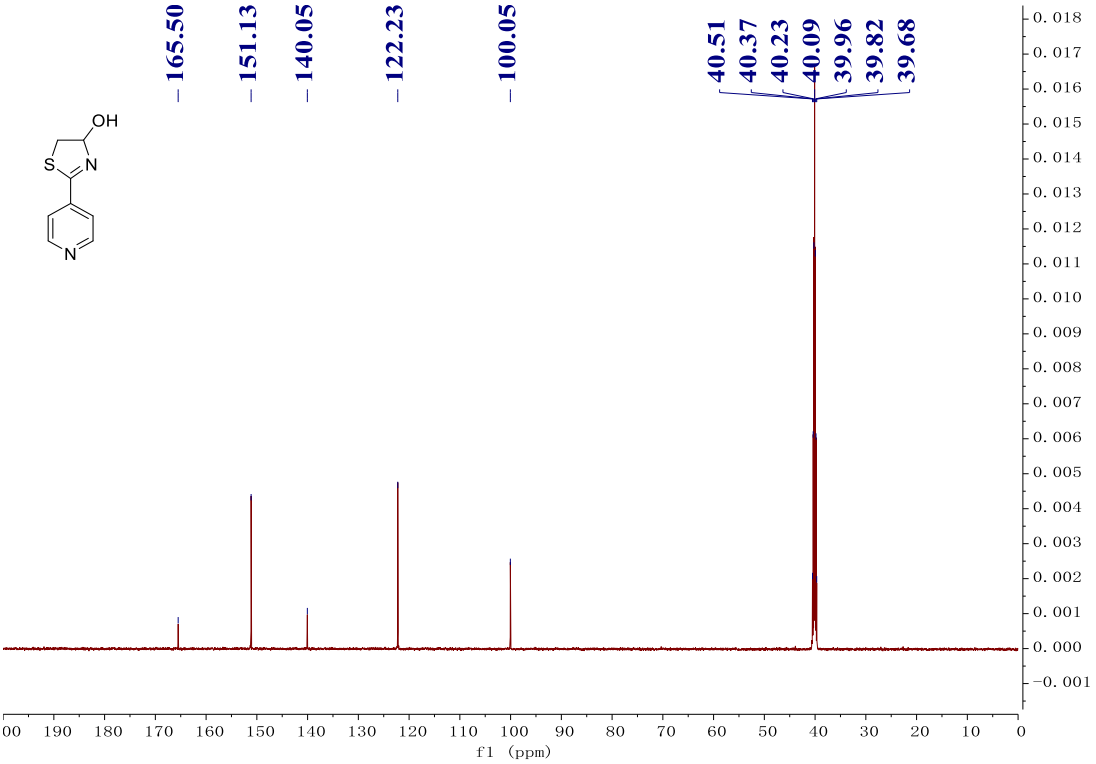
^{13}C NMR Spectrum of **6aj** (150 MHz, DMSO-D6)



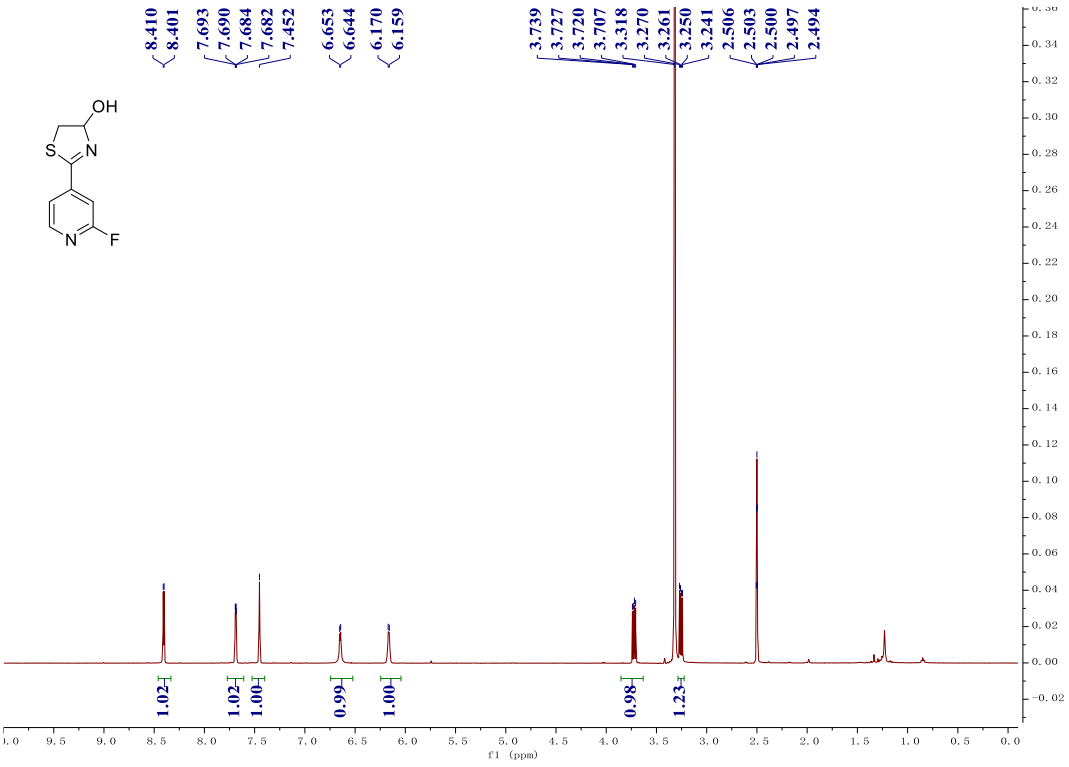
^{1}H NMR Spectrum of **7aa** (600 MHz, DMSO-D6)



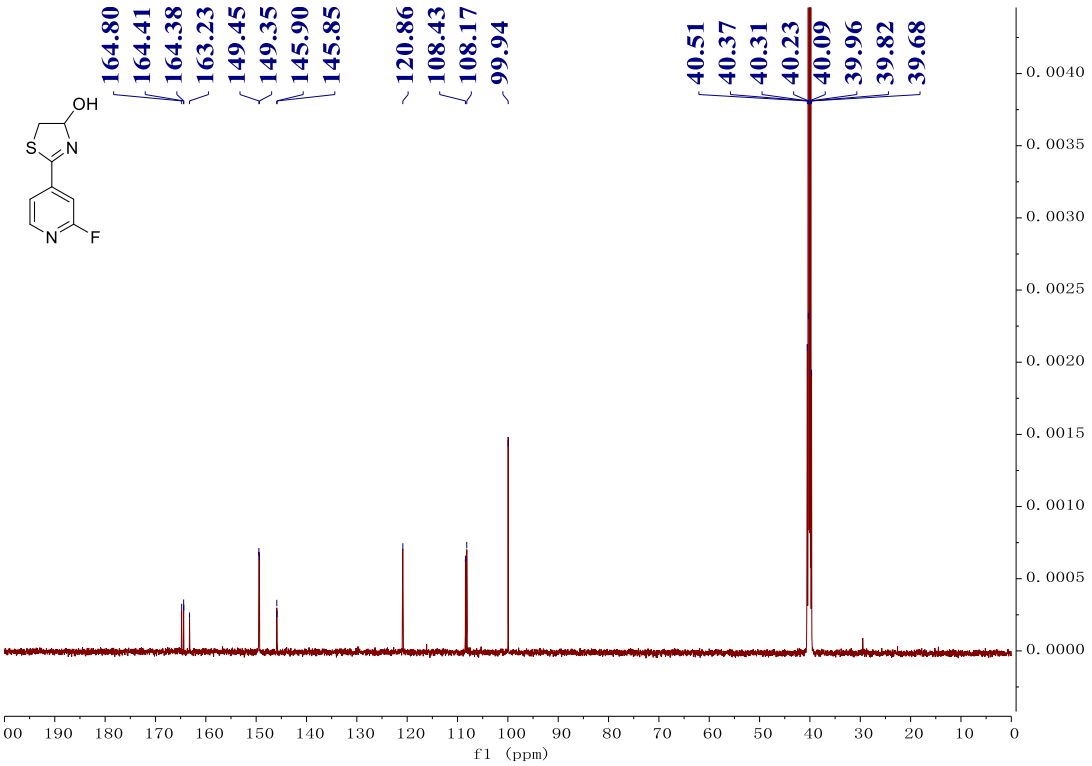
^{13}C NMR Spectrum of **7aa** (150 MHz, DMSO-D6)



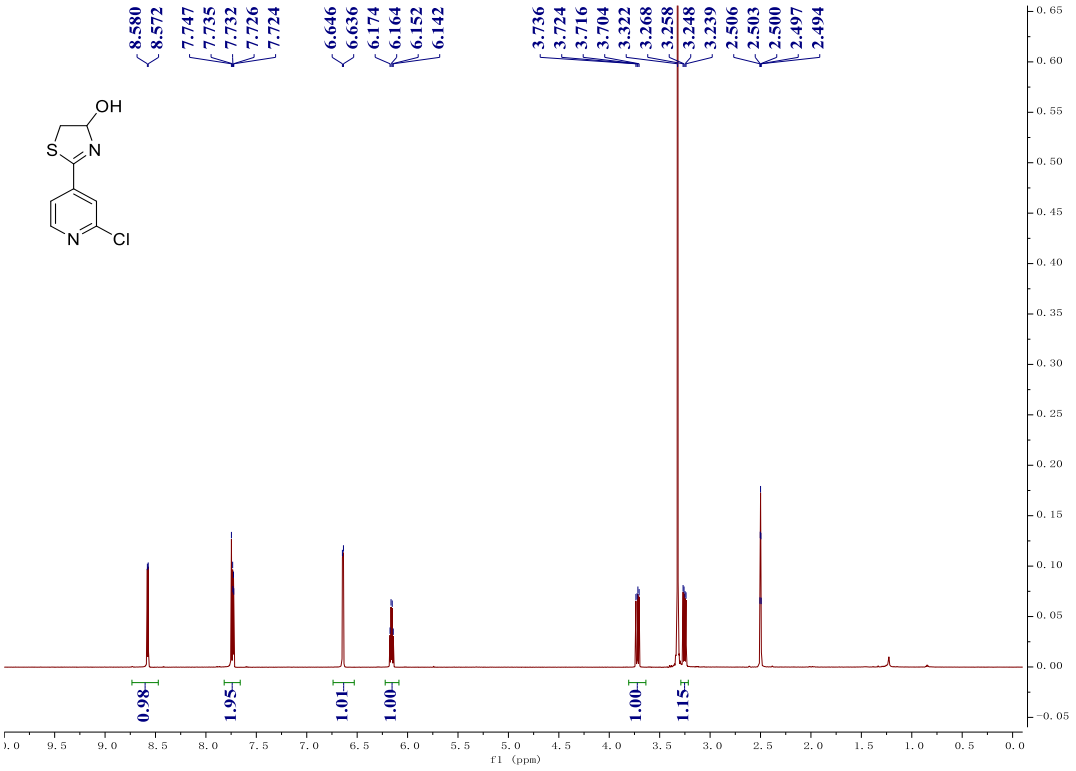
^{1}H NMR Spectrum of **7ab** (600 MHz, DMSO-D6)



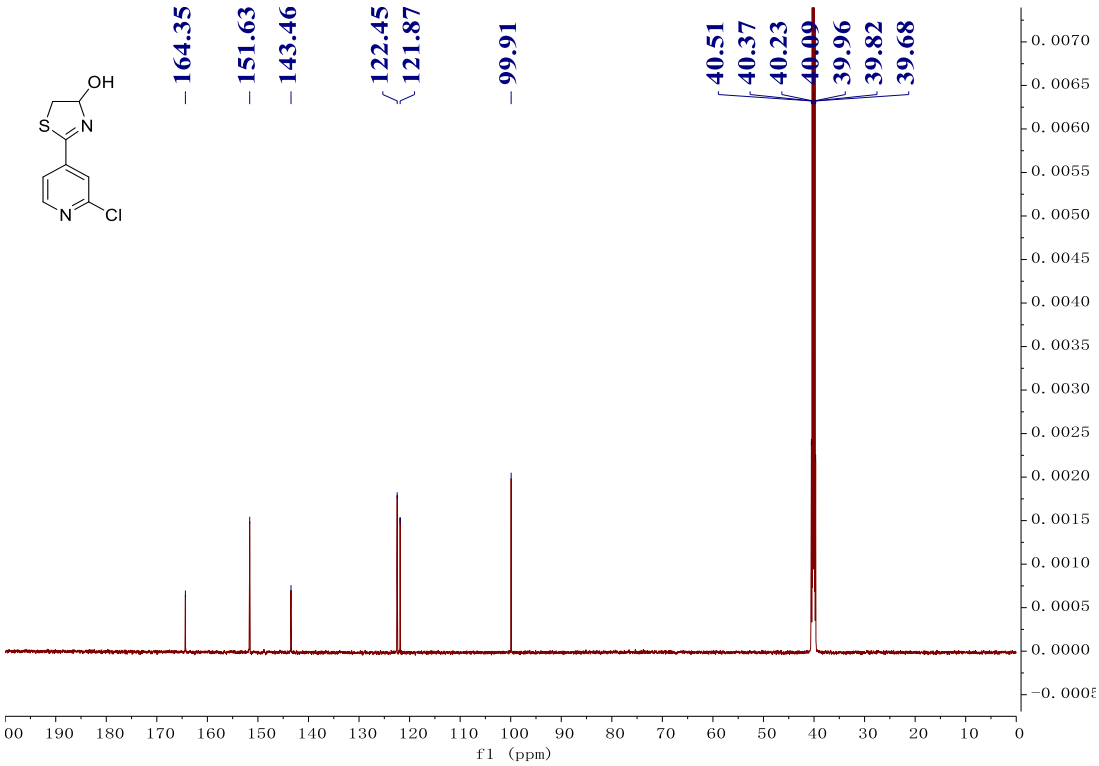
^{13}C NMR Spectrum of **7ab** (150 MHz, DMSO-D6)



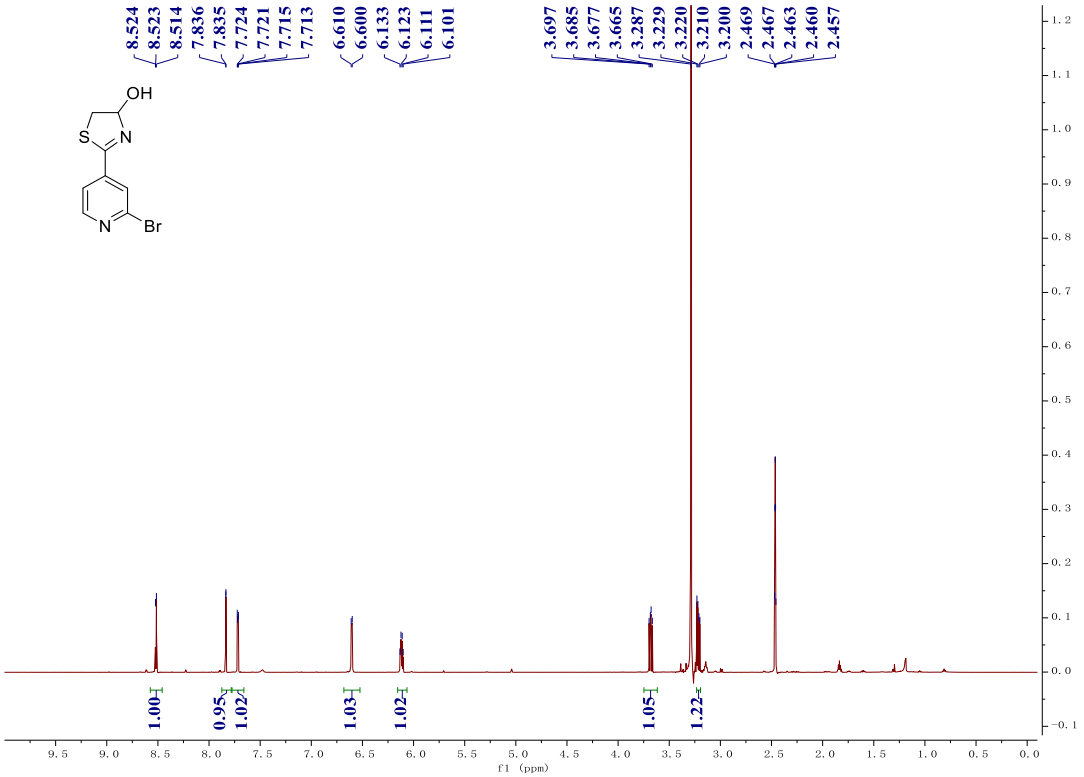
^{1}H NMR Spectrum of **7ac** (600 MHz, DMSO-D6)



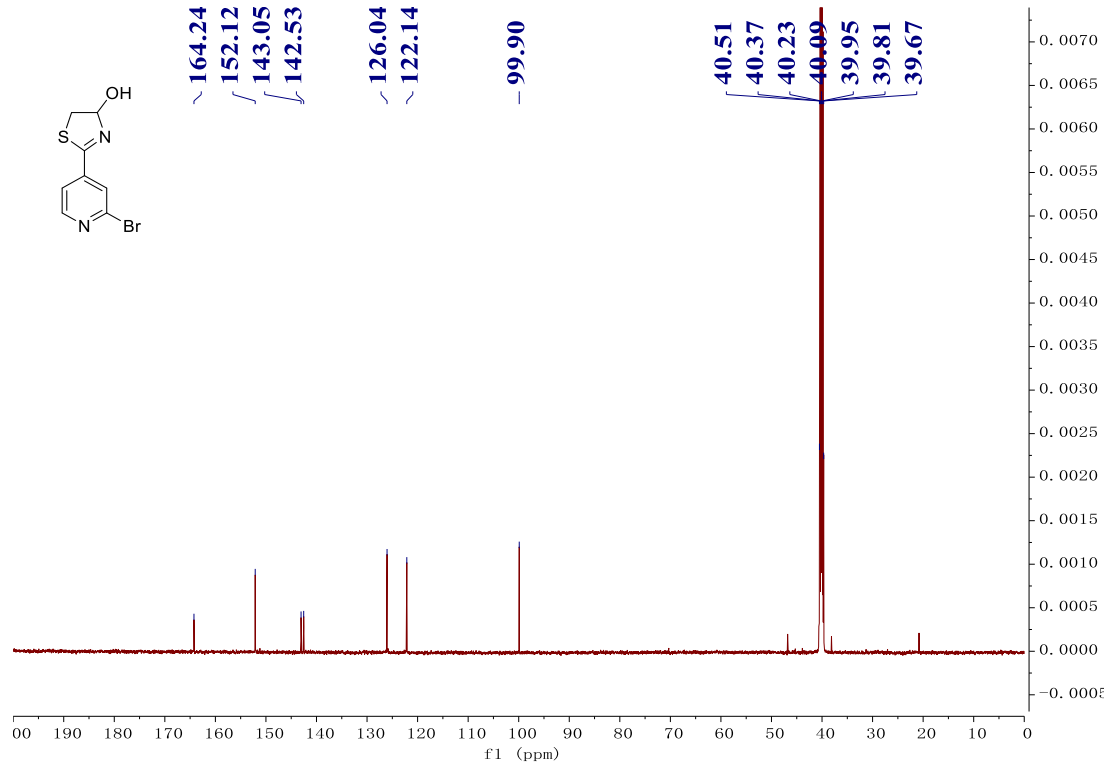
^{13}C NMR Spectrum of **7ac** (150 MHz, DMSO-D6)



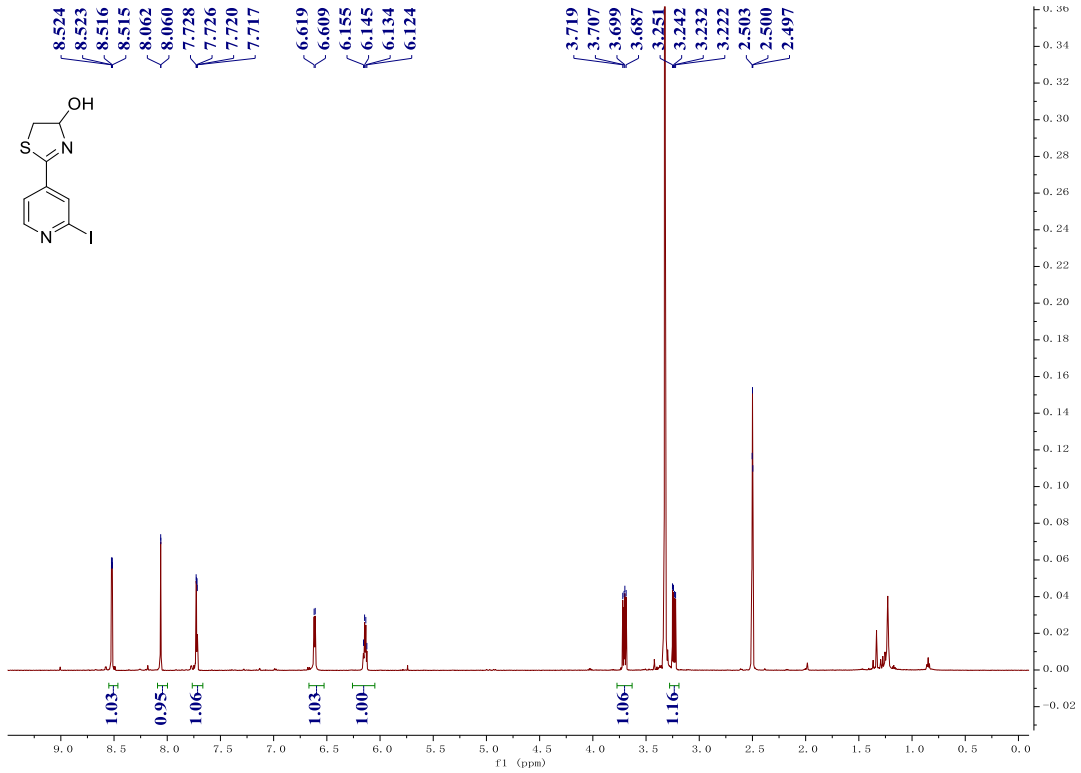
^{1}H NMR Spectrum of **7ad** (600 MHz, DMSO-D6)



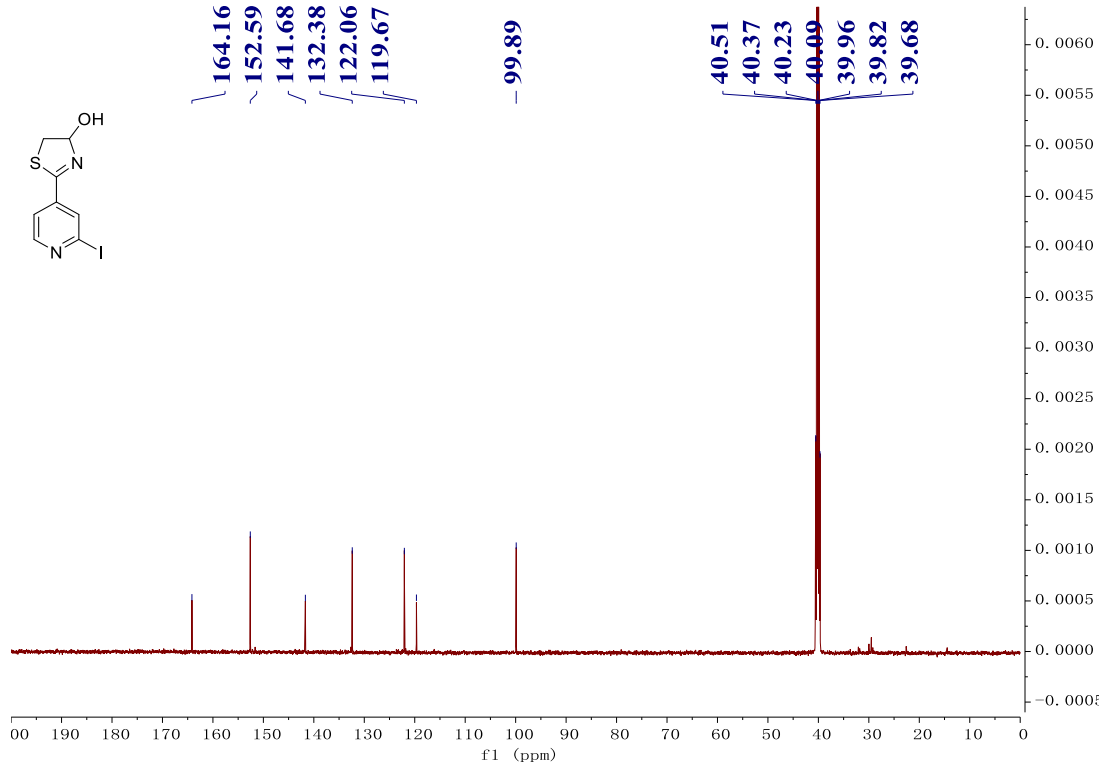
^{13}C NMR Spectrum of **7ad** (150 MHz, DMSO-D6)



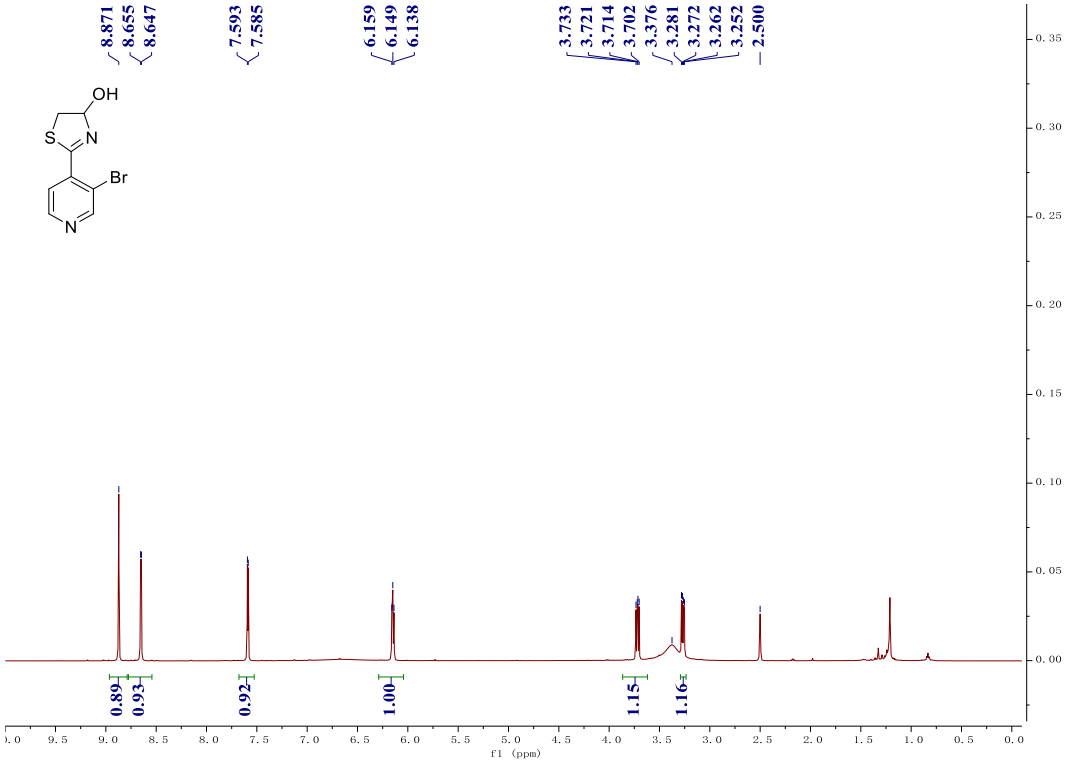
^{1}H NMR Spectrum of **7ae** (600 MHz, DMSO-D6)



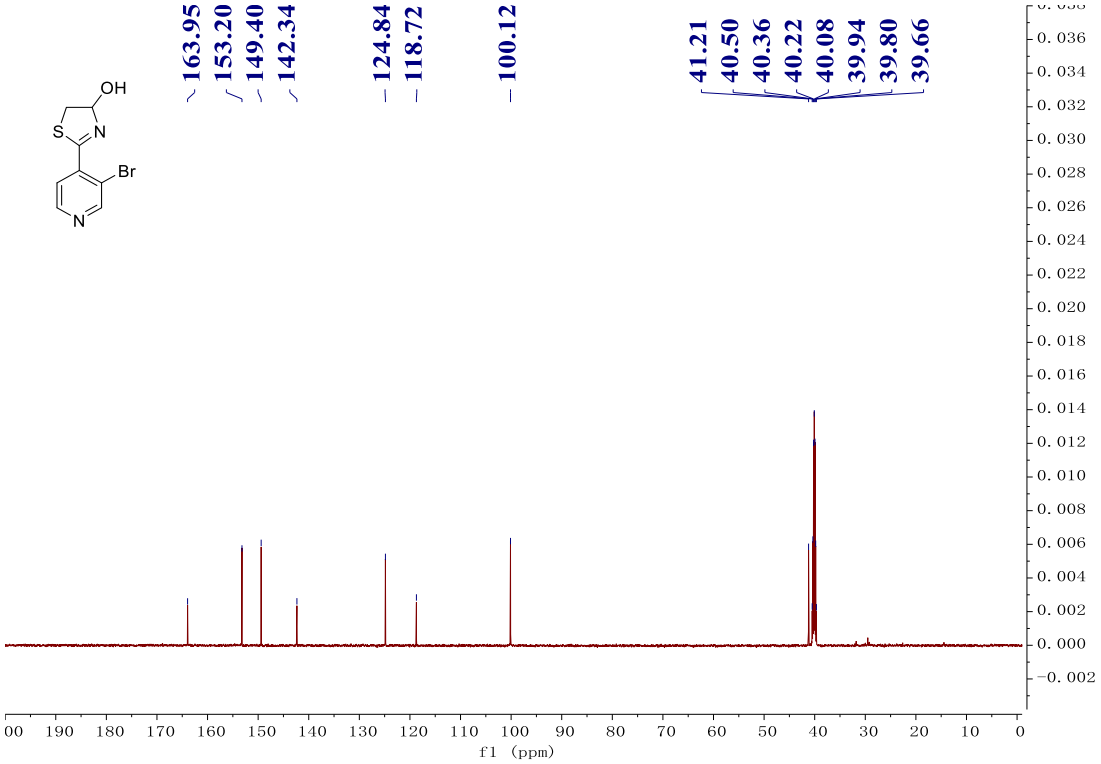
^{13}C NMR Spectrum of **7ae** (150 MHz, DMSO-D6)



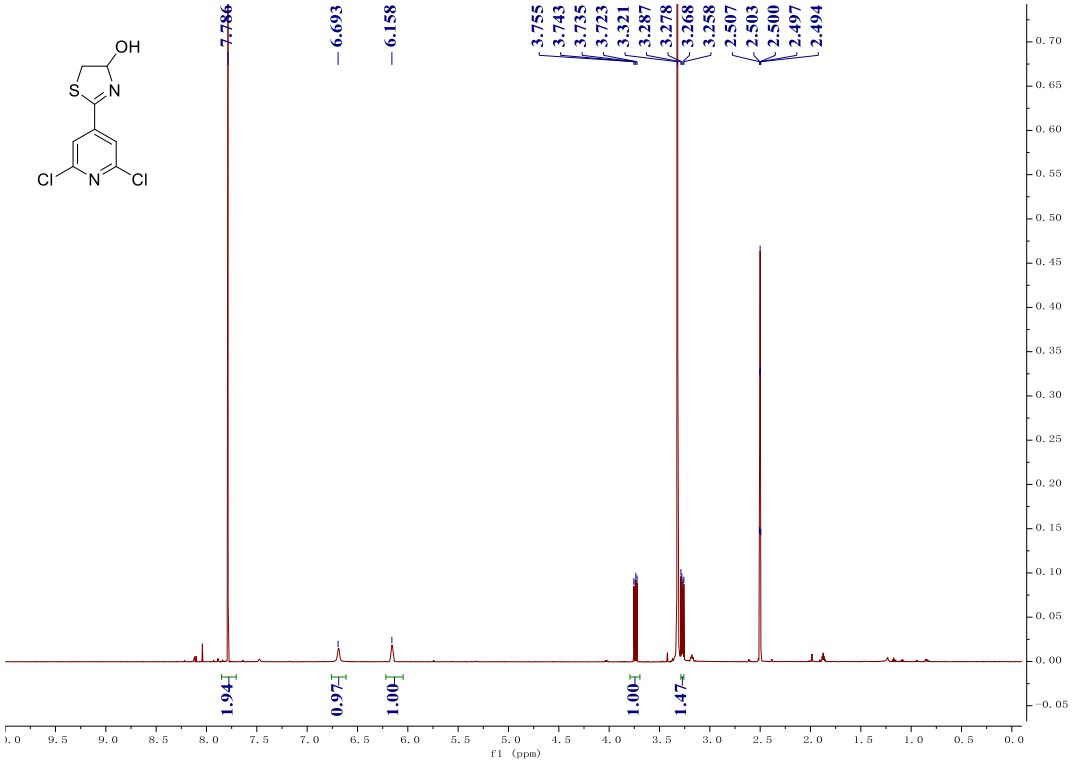
^{1}H NMR Spectrum of **7af** (600 MHz, DMSO-D6)



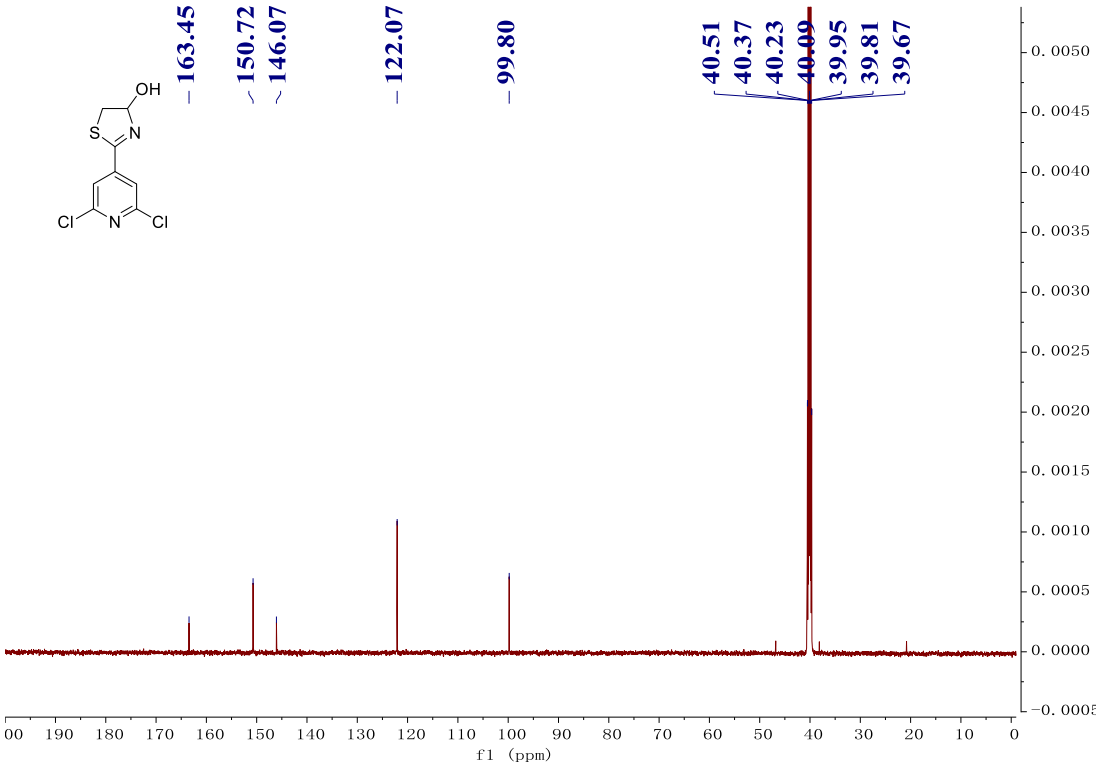
^{13}C NMR Spectrum of **7af** (150 MHz, DMSO-D6)



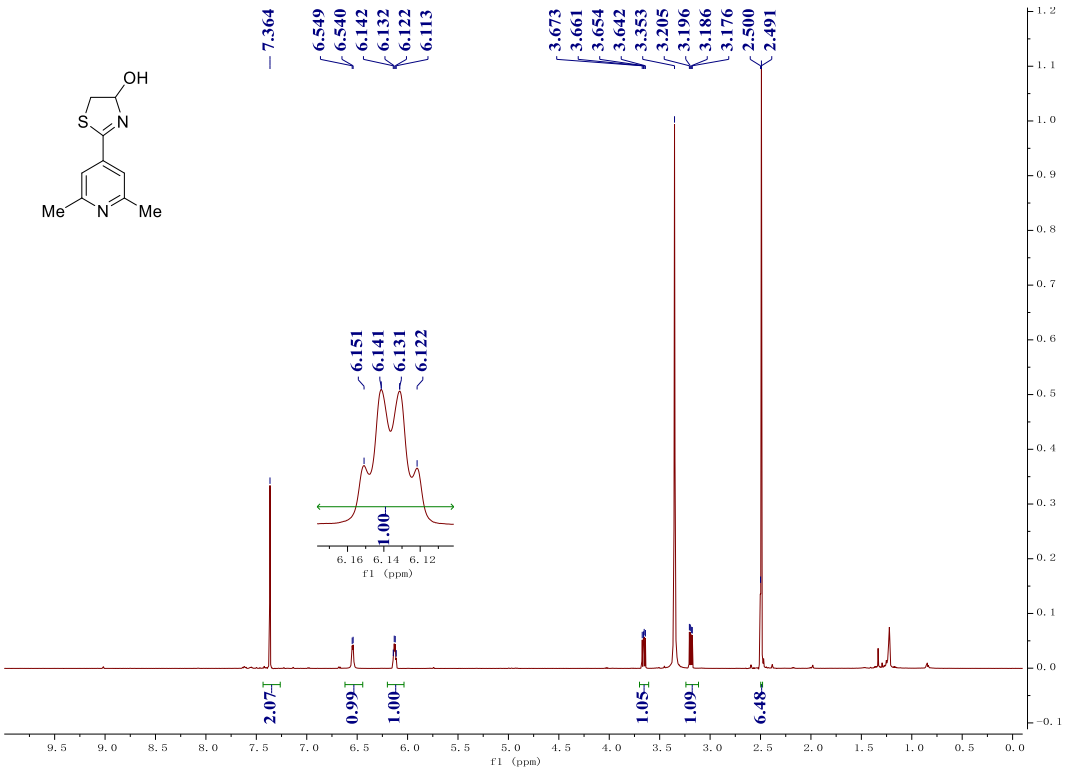
^{1}H NMR Spectrum of **7ag** (600 MHz, DMSO-D6)



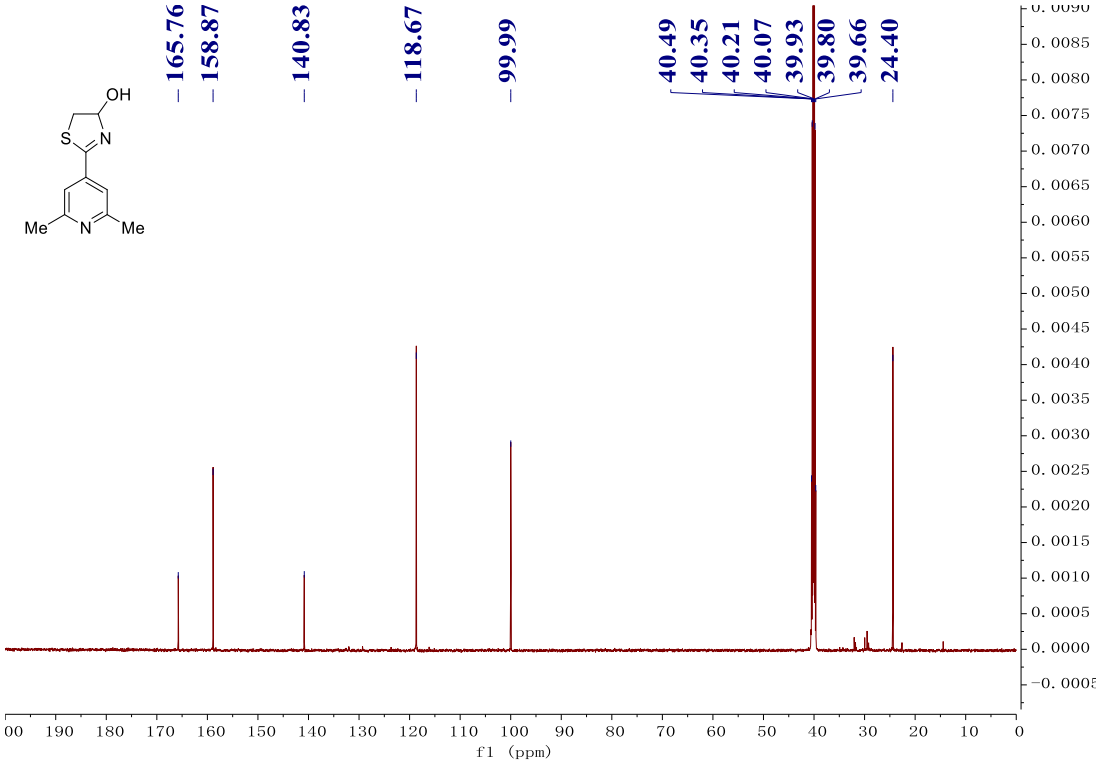
^{13}C NMR Spectrum of **7ag** (150 MHz, DMSO-D6)



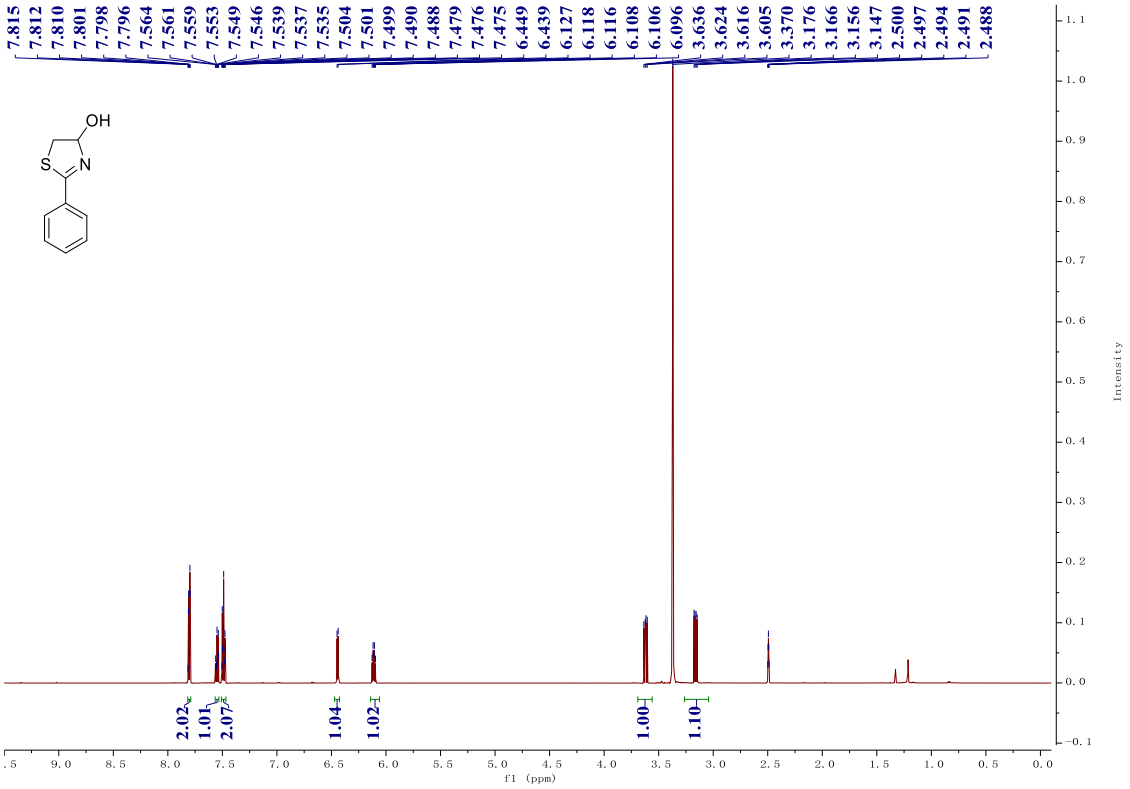
^{1}H NMR Spectrum of **7ah** (600 MHz, DMSO-D6)



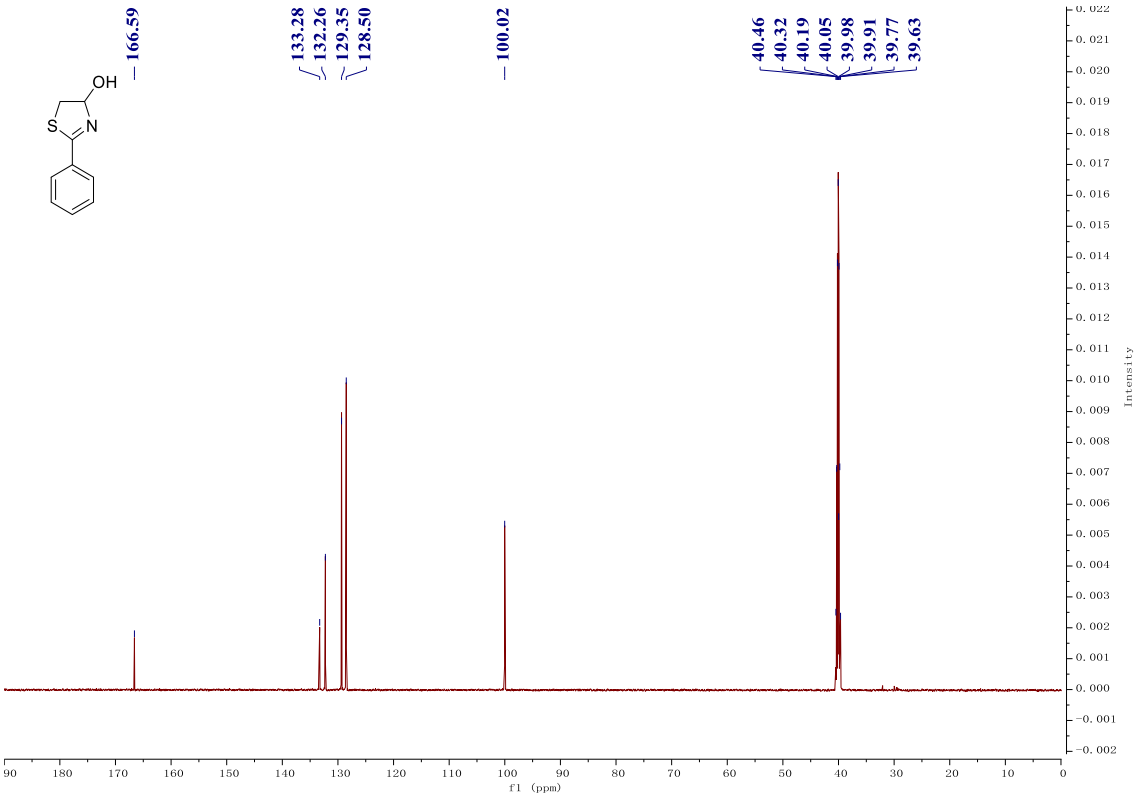
^{13}C NMR Spectrum of **7ah** (150 MHz, DMSO-D6)



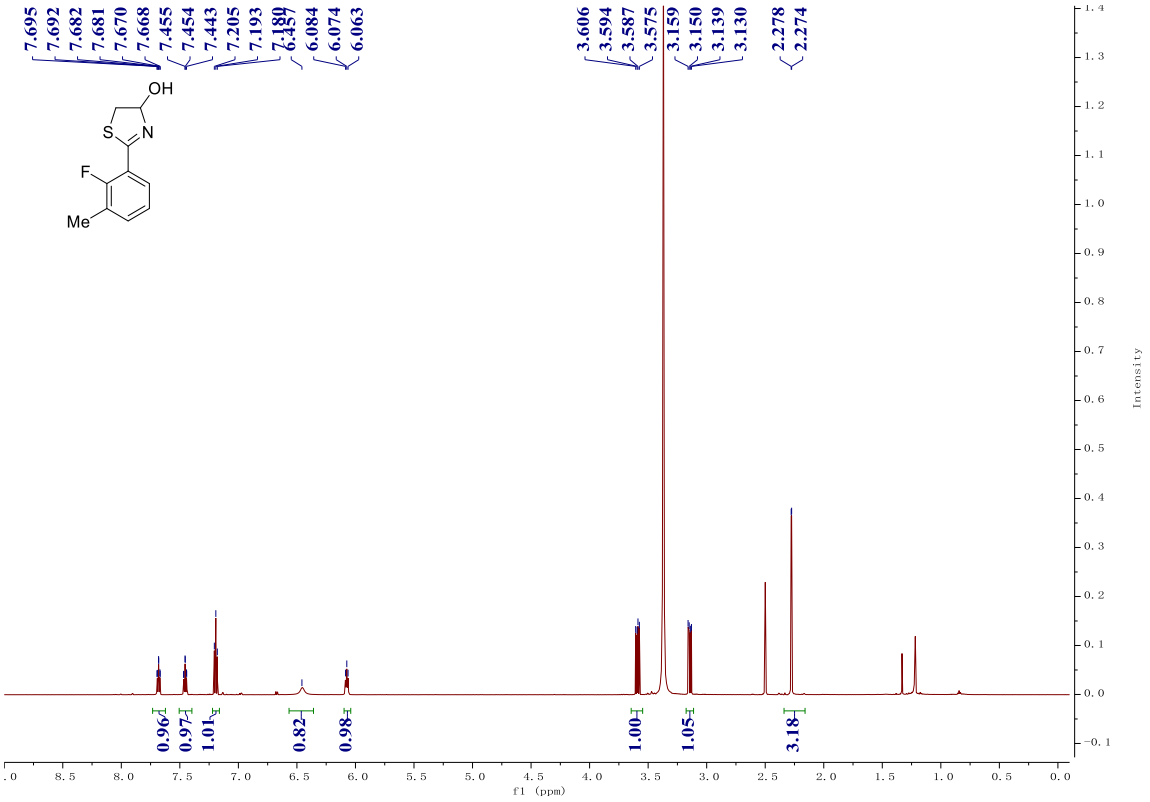
^{1}H NMR Spectrum of **7ai** (600 MHz, DMSO-D6)



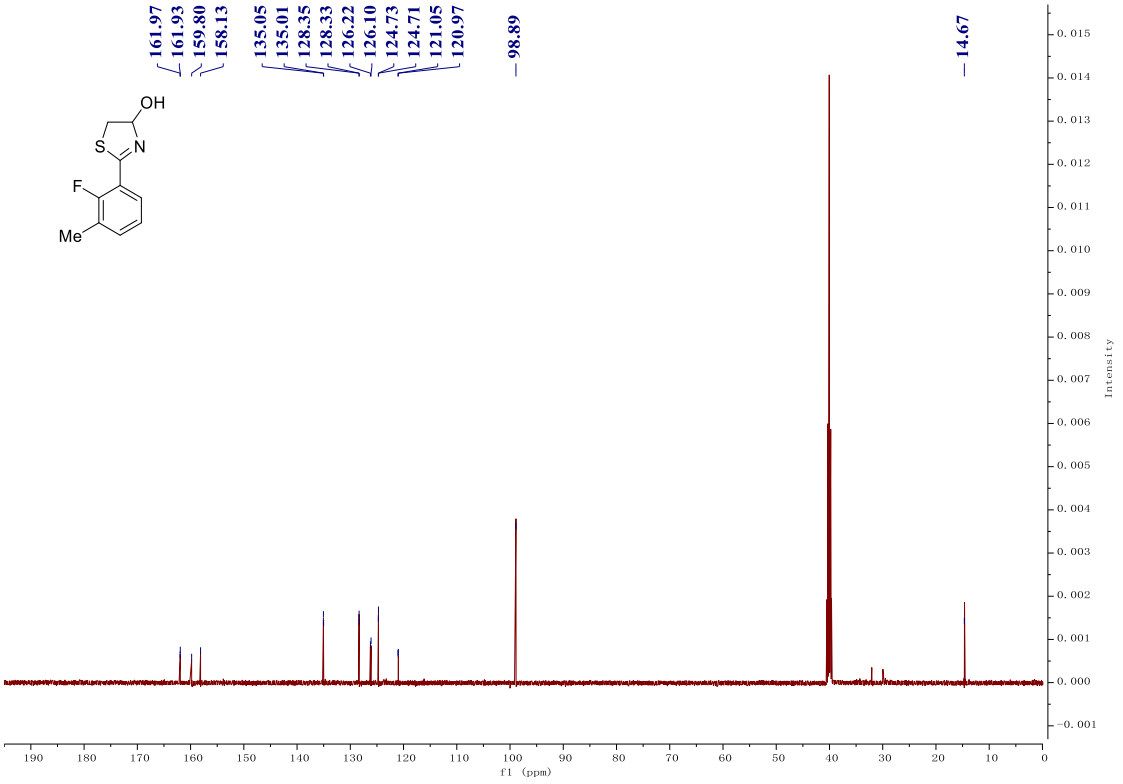
^{13}C NMR Spectrum of **7ai** (150 MHz, DMSO-D6)



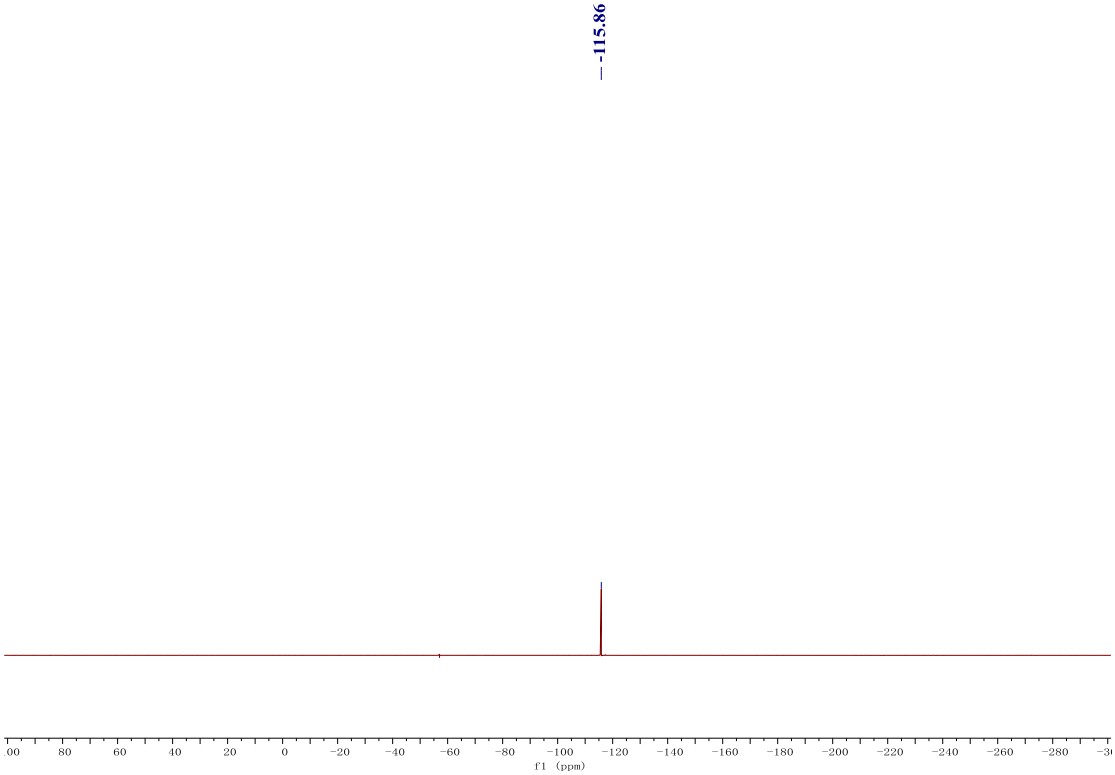
^{1}H NMR Spectrum of **7aj** (600 MHz, DMSO-D6)



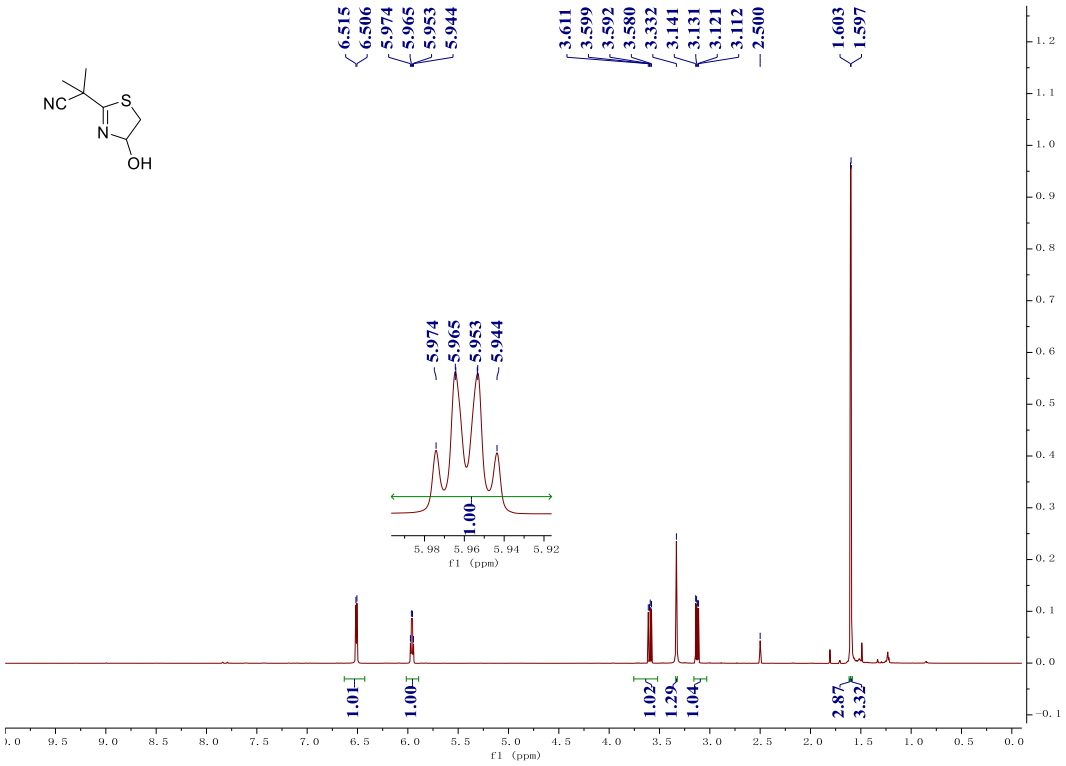
^{13}C NMR Spectrum of **7aj** (150 MHz, DMSO-D6)



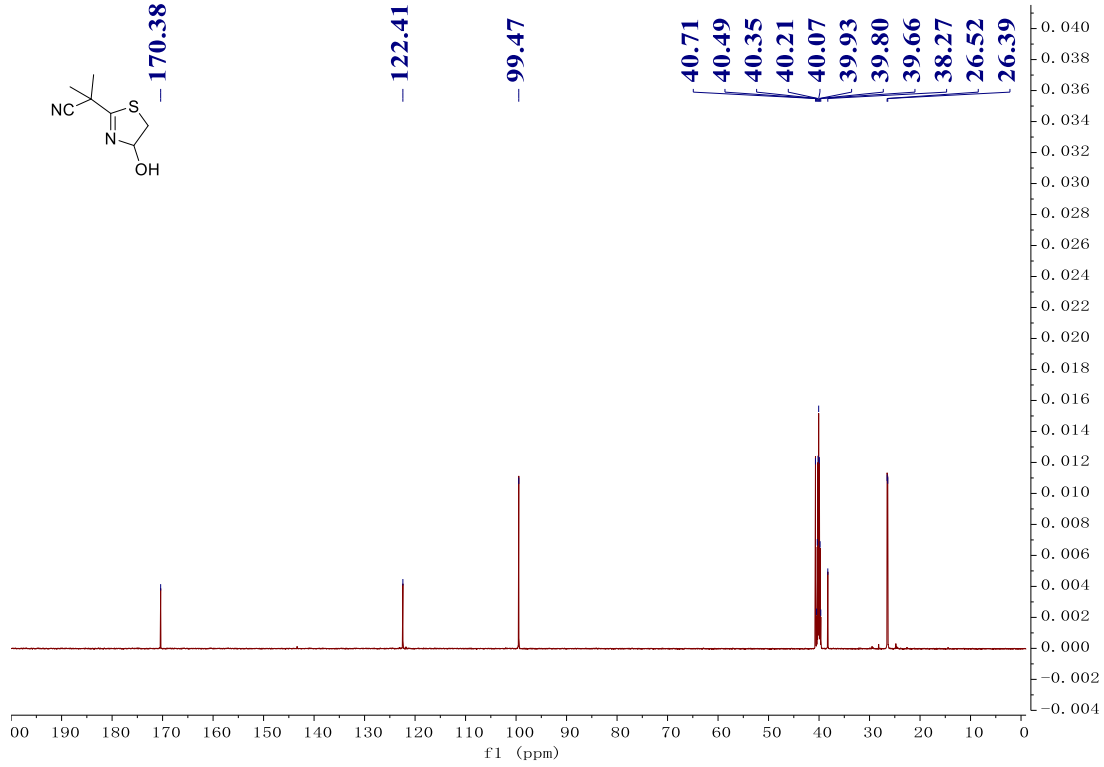
^{19}F NMR Spectrum of **7aj** (565 MHz, DMSO-D_6)



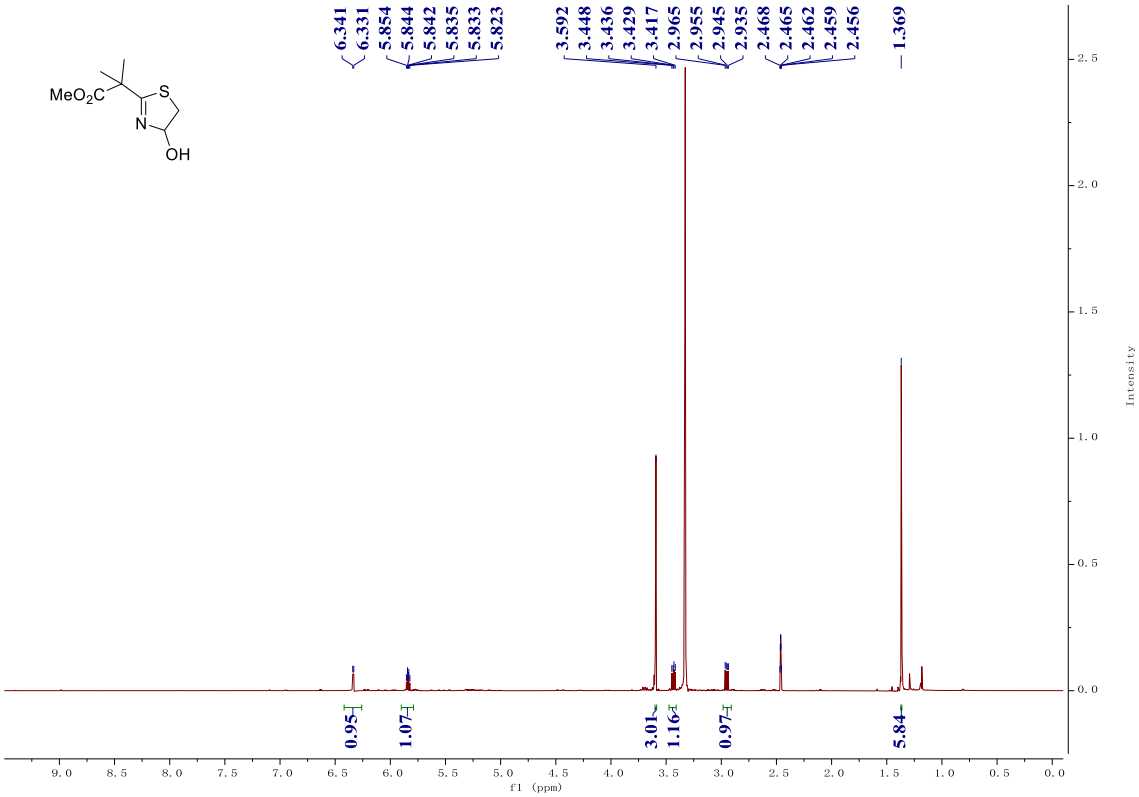
^{1}H NMR Spectrum of **7ak** (600 MHz, DMSO-D6)



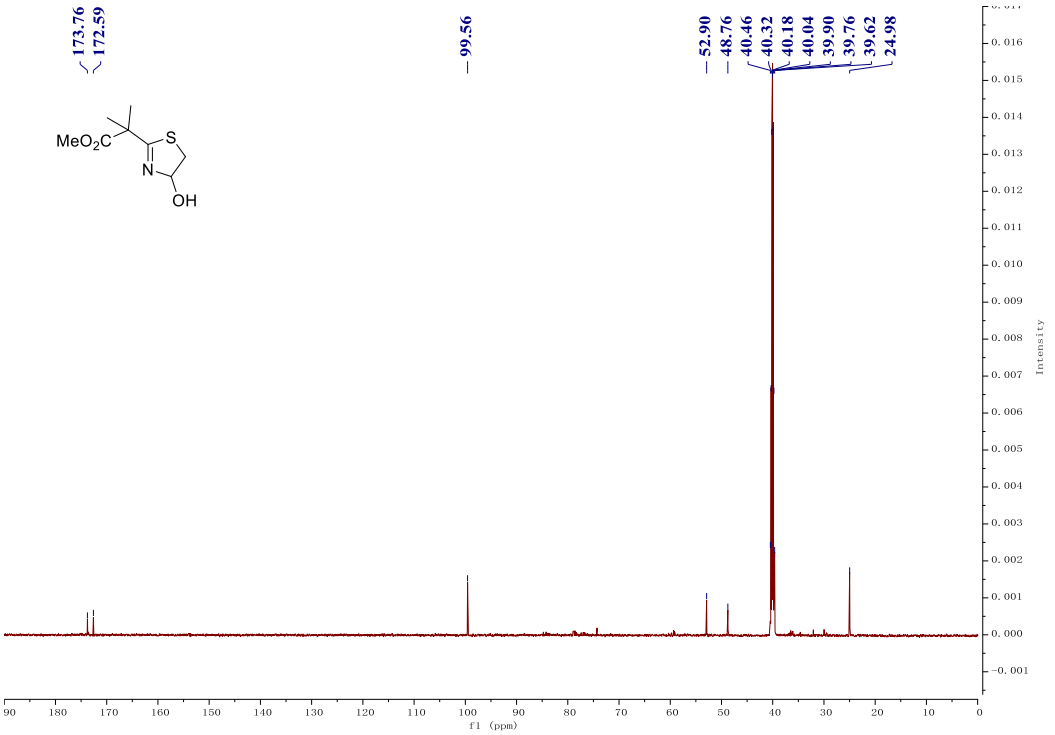
^{13}C NMR Spectrum of **7ak** (150 MHz, DMSO-D6)



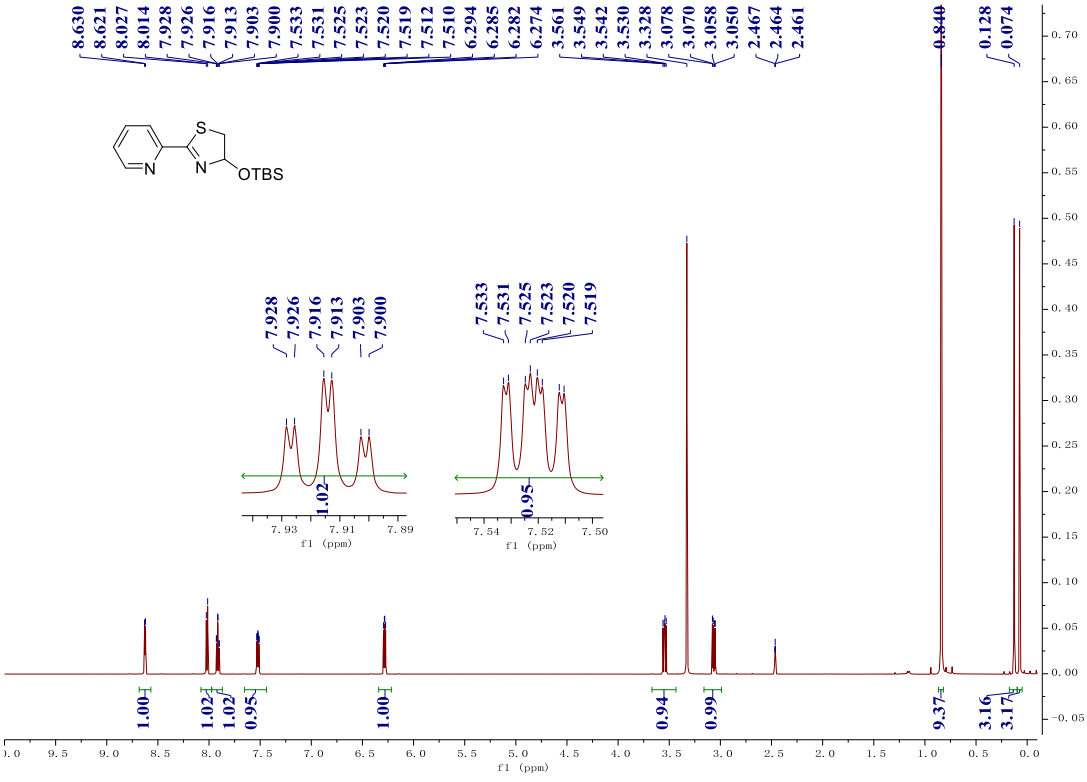
^{1}H NMR Spectrum of **7al** (600 MHz, DMSO-D6)



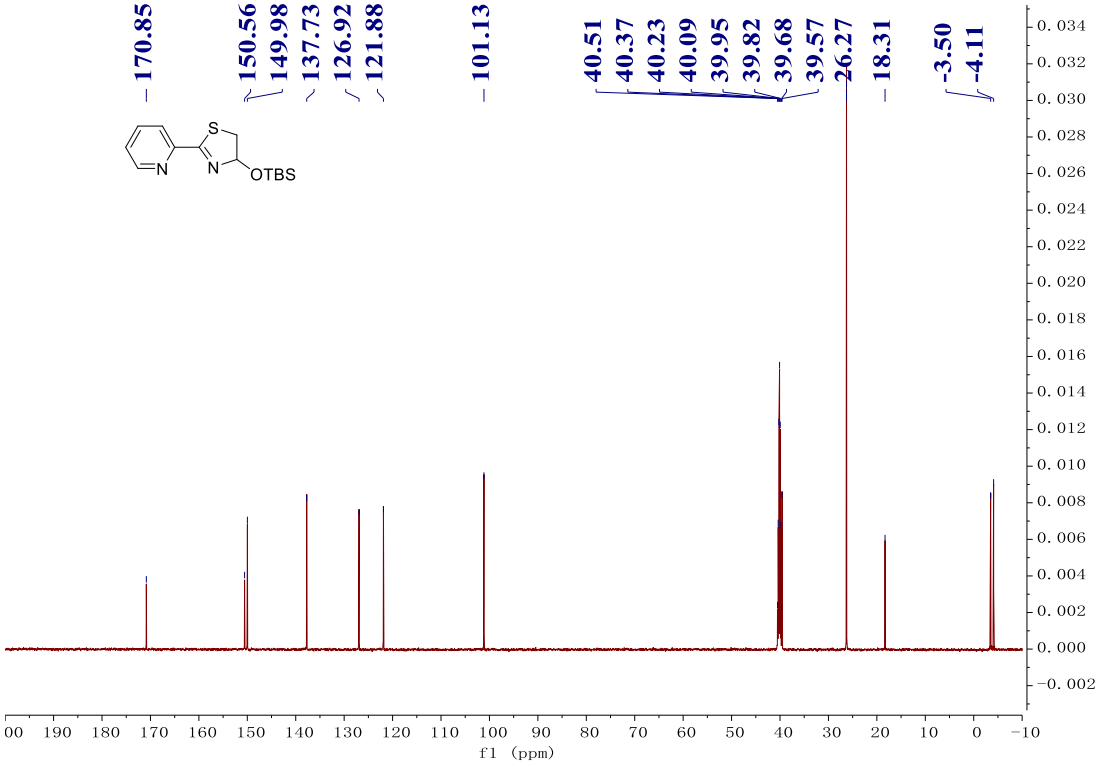
^{13}C NMR Spectrum of **7ak** (150 MHz, DMSO-D6)



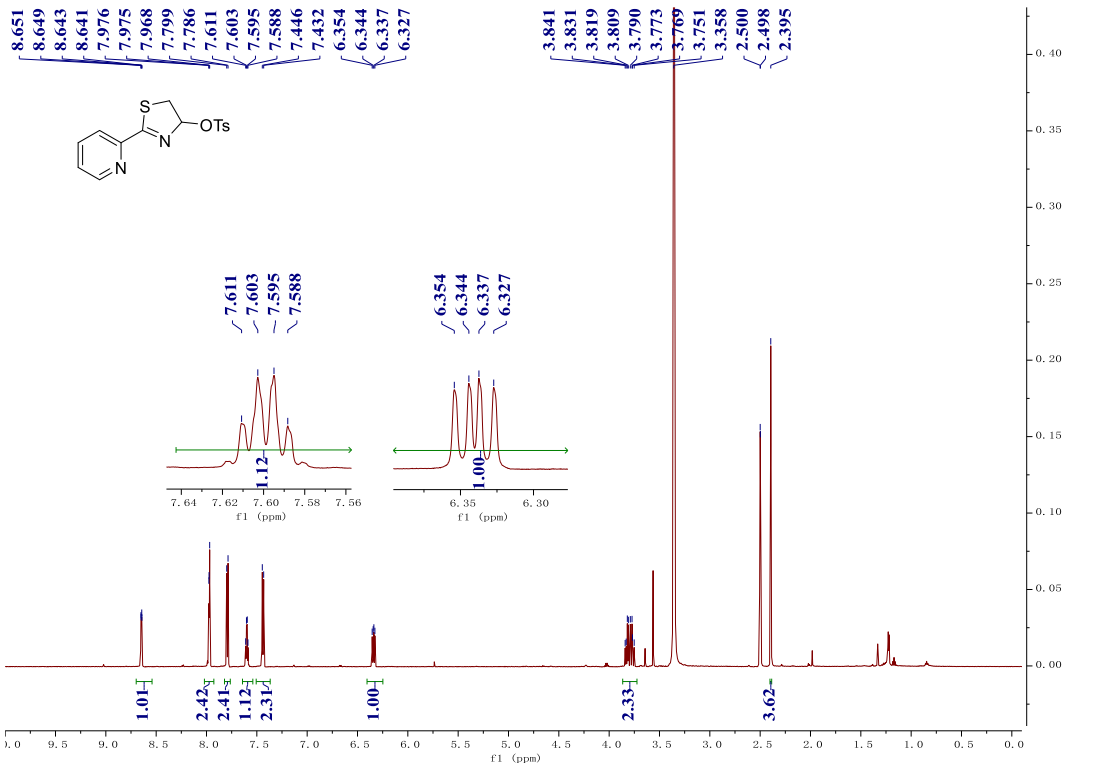
^{1}H NMR Spectrum of **8aa** (600 MHz, DMSO-D6)



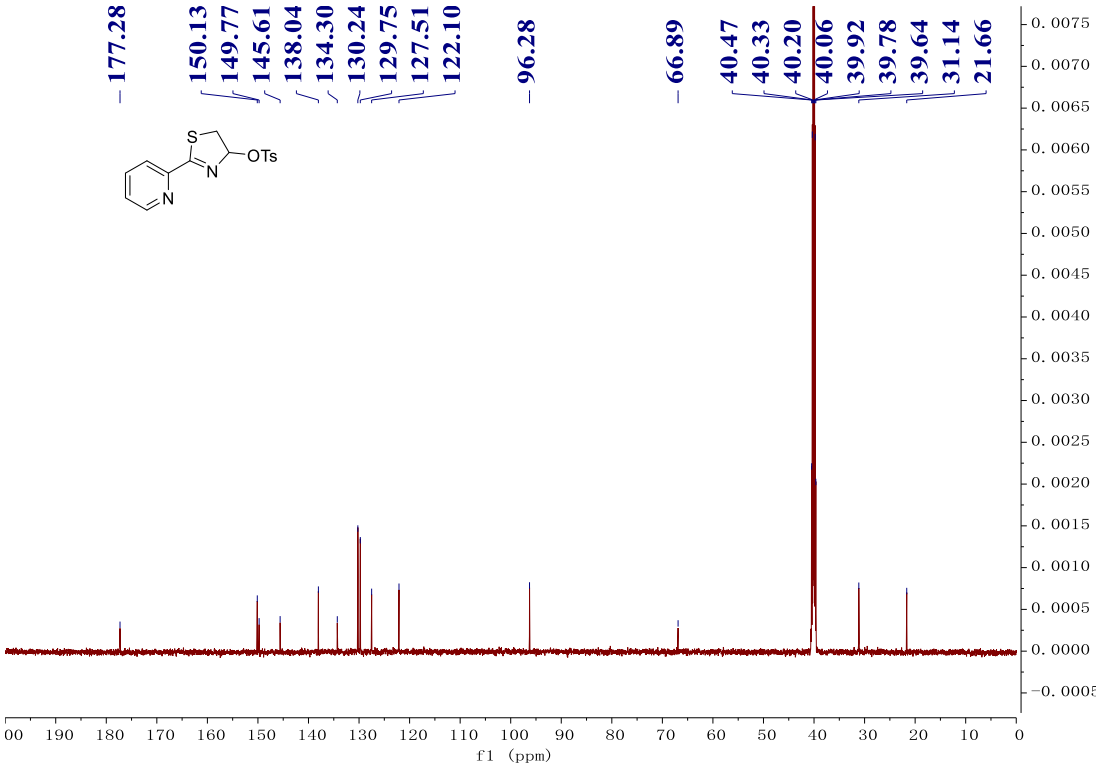
^{13}C NMR Spectrum of **8aa** (150 MHz, DMSO-D6)



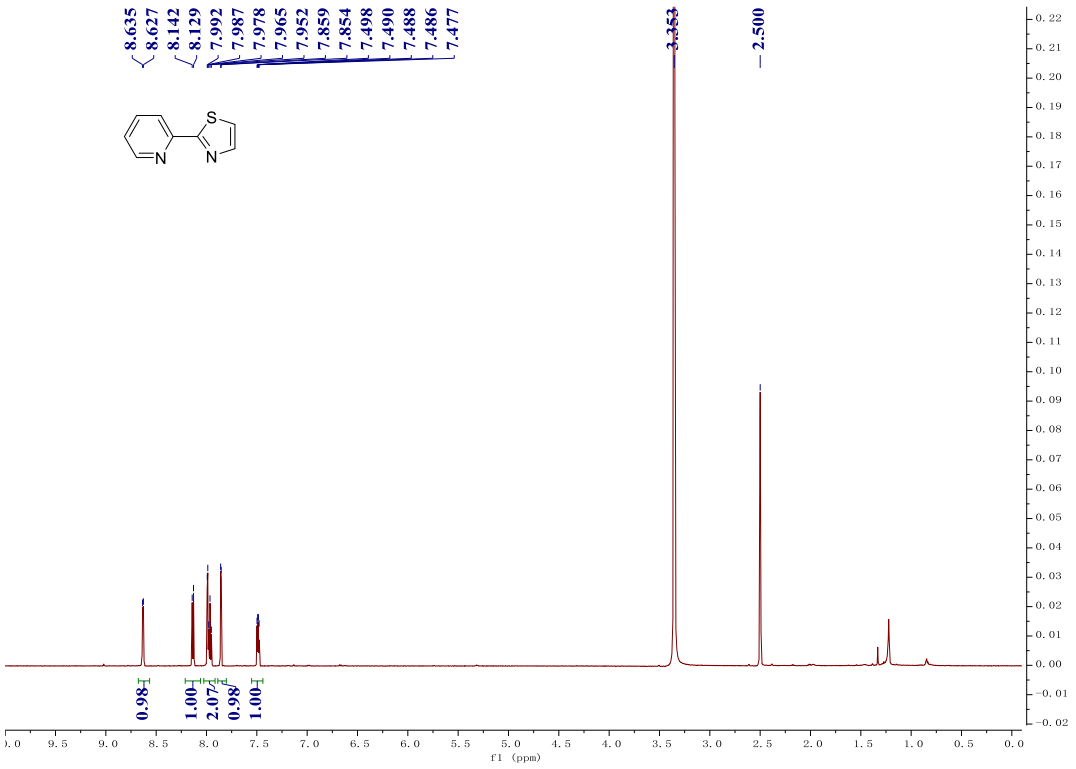
^{1}H NMR Spectrum of **9aa** (600 MHz, DMSO-D6)



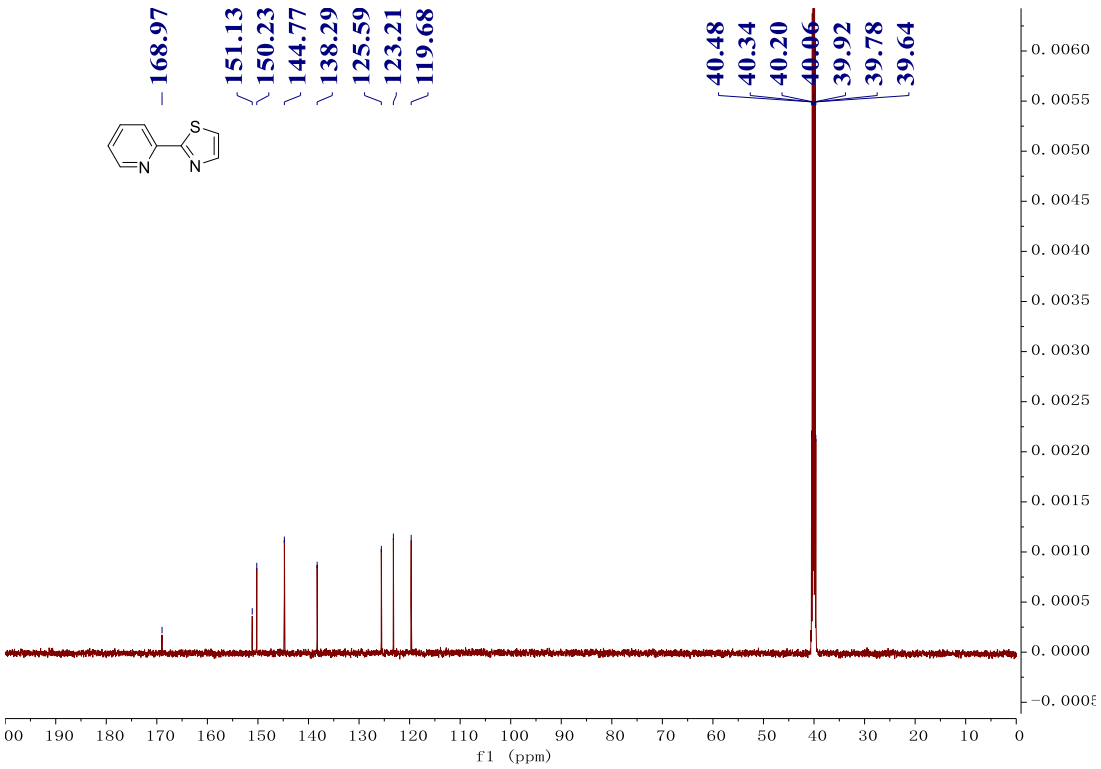
^{13}C NMR Spectrum of **9aa** (150 MHz, DMSO-D6)



^{1}H NMR Spectrum of **10aa** (600 MHz, DMSO-D6)



^{13}C NMR Spectrum of **10aa** (150 MHz, DMSO-D6)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150.23
144.77
138.29
125.59
123.21
119.68
40.48
40.34
40.20
40.06
39.92
39.78
39.64
S
N
N
f1 (ppm)