Supplementary Information (SI) for New Journal of Chemistry.

Sustainable Access to (E)-2-(2-benzylidenehydrazinyl)-4-phenylthiazoles by Ruthenium(II) Catalyst via Dehydrogenative Coupling of Alcohols

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1. Experimental section

Methods and materials

CHNS elemental Vario EL III elemental analyzer instrument was used to perform elemental analyses (C, H, and N). Perkin-Elmer 597 spectrophotometers have been used to record FT-IR spectra of the complexes in the range 4000−400 cm^{-1}. Melting points were determined by Boetius micro heating table melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in Bruker 400 MHz in using TMS as an internal standard. Spectrometer using $CDCl_3$/d_6-DMSO as solvents on 400 and 100 MHz instruments respectively. The mass spectral data for all the complexes were obtained by a Micro mass Thermo scientific LTQ XL mass spectrometer. Ruthenium precursor, (97%), Benzhydrazides (95−98%), solvents, Thiosemicarbazide, 2-bromoactophenoneand primary alcohols were purchased from commercial suppliers and used as received. Reagent grade solvents purchased from standard suppliers were purified and dried according to standard procedures.[1]The gas chromatograph analysis for the dtection of hydrogen gas was performed on an Agilent GC 8890 and a TCD detector, injection temperature = 50 °C, column temperature = 80 °C, detector temperature (TCD) = 180 °C, carrier gas = He_2.

2. X-ray Crystallography

A single crystal with high quality and exhibiting good morphology was chosen for X-ray diffraction intensity measurements. The X-ray diffraction intensity data was collected at room temperature (293 K) on a Bruker D8 Quest Eco diffractometer using MoKα radiation (0.71073 A˚). During the data collection, the crystal to detector distance was set to 4.5 cm. The data collection was monitored by APEX-III program suit.[2] further, the integration, Lorentz and polarization corrections and merging of data were carried out using SAINT. The absorption correction was performed by SADABS and the data was averaged using SORTAV software.[3] The hydrogen atoms of all C−H, N−H and O−H hydrogen bonds were located from the difference Fourier map and were refined isotropically. Idealized methyl group H-atom position was calculated geometrically [C−H = 0.96 A]˚and refined using riding model with Uiso(H) = 1.5 Ueq (C). The structure was solved by direct methods using SHELXS-2014[4] and refined by SHELXL-2014 [5] programs incorporated to WINGX package.[6] The ORTEP of the molecule with displacement ellipsoids drawn at 50% probability level are shown in (Fig. 1). The molecular and packing diagrams were generated using the software MERCURY.The CCDC number ofcomplex**1** is **2424426.**

Crystal Structure of Ruthenium(II) Complex 1

The molecular structure of ruthenium(II) complex **1** were confirmed by single-crystal X-ray diffraction study. The single crystals were grown by slow evaporation with a 1:1 ratio of petroleum ether and dichloromethane solvent at room temperature. The complex **1** was crystallized in a monoclinic crystal system with a"$P2_1/n$" space group. The solid state structure was revealed that the hydrazone ligand is coordinated to ruthenium ion via hydrazide nitrogen and carbonyl oxygen atoms via bidentate N^O fashion with the formation of one six membered chelated ring with chlorine and phenyl ring. The bite angles and bond distance of the complex **1**O1-Ru1-Cl1, 84.42(6); O1-Ru1-N1, 88.68(8); O1-Ru1-C18, 108.21(9); O1-Ru1-C19, 85. 54 (9); O1-Ru1-C20, 91.91(9); N1-Ru1-Cl1, 83.95(6); N1-Ru1-C18, 99.36(10); N1-Ru1-C19, 129.82(10) and Ru1-Cl1, 2.4081 (7); Ru1-O1 2.0879(18); Ru1-N1, 2.093(2); Ru1-C18, 2.213(18); Ru1-C19,2.164(3): Ru1-C20, 2.188(3)are respectively. The ORTEP representation of the ruthenium complex is illustrated in**Figure1**. One molecule ligand has donor sites of the atoms forms a octahedron coordination around the ruthenium ion. The bond lengths and angles of the Ru(II) complex was comparable with other reported ruthenium complex.[26] The X-ray crystallographic parameters, details of data collection, structure refinements and selected bond lengths / angles are summarized in supporting information.

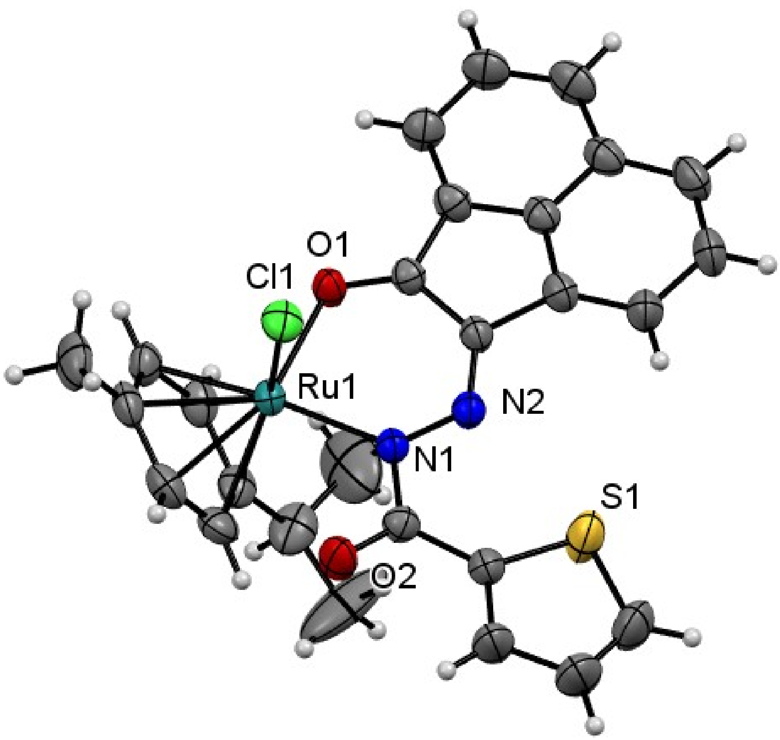


Figure 1.ORTEP view of the Complex 1 (CCDC: 2424426). The thermal ellipsoids are drawn with a 30% probability level. The selected bond distances (Å) and angles (°) O1-Ru1-Cl1, 84.42(6); O1-Ru1-N1, 88.68(8); O1-Ru1-C18, 108.21(9); O1-Ru1-C19, 85. 54 (9); O1-Ru1-C20, 91.91(9); N1-Ru1-Cl1, 83.95(6); N1-Ru1-C18, 99.36(10); N1-Ru1-C19, 129.82(10); O1-

C1-C2, 127.4(2); O1-C1-Cl1, 125.7(2) and Ru1-Cl1, 2.4081 (7); Ru1-O1 2.0879(18); Ru1-N1, 2.093(2); Ru1-C18, 2.213(18); Ru1-C19,2.164(3): Ru1-C20, 2.188(3); O1-C1, 1.237(3), O2-C13, 1.207(3); S1-C14, 1.703(3); S1-C17, 1.692(3).

Table S1. Crystal data and structure refinement for complex

Identification code	**Complex 1**
Empirical formula	$C_{30}H_{26}ClN_2O_2RuS$
Formula weight	576.05
Temperature/K	295(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.7959(9)
b/Å	7.7136(3)
c/Å	19.3582(10)
α/°	90
β/°	111.100(6)
γ/°	90
Volume/Å^3	2618.4(2)
Z	4
ρ_{calc}g/cm^3	1.461
μ/mm^{-1}	0.806
F(000)	1168.0
Crystal size/mm^3	0.27 × 0.17 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.79 to 59.004
Index ranges	$-26 \leq h \leq 22$, $-10 \leq k \leq 10$, $-23 \leq l \leq 26$
Reflections collected	15153
Independent reflections	6310 [R_{int} = 0.0340, R_{sigma} = 0.0453]
Data/restraints/parameters	6310/0/310
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0533, wR_2 = 0.0875
Largest diff. peak/hole / e Å^{-3}	0.45/-0.42

Table S2. Selected bond angles and lengths

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru1	Cl1	2.4081(7)		C5	C6	1.360(4)
Ru1	O1	2.0879(18)		C6	C7	1.416(4)
Ru1	N1	2.093(2)		C7	C8	1.404(4)
Ru1	C18	2.213(3)		C7	C12	1.399(4)
Ru1	C19	2.164(3)		C8	C9	1.364(5)
Ru1	C20	2.188(3)		C9	C10	1.411(4)
Ru1	C21	2.208(3)		C10	C11	1.372(4)
Ru1	C22	2.163(3)		C11	C12	1.398(4)
Ru1	C23	2.165(3)		C13	C14	1.478(4)
S1	C14	1.703(3)		C14	C15	1.381(4)
S1	C17	1.692(3)		C15	C16	1.406(5)
O1	C1	1.237(3)		C16	C17	1.318(5)
O2	C13	1.207(3)		C18	C19	1.419(4)
N1	N2	1.320(3)		C18	C23	1.414(4)
N1	C13	1.407(3)		C18	C24	1.503(4)
N2	C2	1.302(3)		C19	C20	1.399(4)
C1	C2	1.472(4)		C20	C21	1.393(4)
C1	C11	1.464(4)		C21	C22	1.411(4)
C2	C3	1.467(4)		C21	C27	1.490(4)
C3	C4	1.364(4)		C22	C23	1.386(4)
C3	C12	1.412(4)		C24	C25	1.483(6)
C4	C5	1.416(4)		C24	C26	1.499(5)

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ru1	Cl1	84.42(6)		C3	C4	C5	118.8(3)
O1	Ru1	N1	88.68(8)		C6	C5	C4	123.1(3)
O1	Ru1	C18	108.21(10)		C5	C6	C7	119.9(3)
O1	Ru1	C19	85.54(9)		C8	C7	C6	128.6(3)
O1	Ru1	C20	91.91(9)		C12	C7	C6	116.0(3)
O1	Ru1	C21	121.76(10)		C12	C7	C8	115.4(3)
O1	Ru1	C22	158.53(10)		C9	C8	C7	121.7(3)
O1	Ru1	C23	145.63(10)		C8	C9	C10	121.9(3)
N1	Ru1	Cl1	83.95(6)		C11	C10	C9	117.8(3)
N1	Ru1	C18	99.36(10)		C10	C11	C1	133.2(3)
N1	Ru1	C19	129.82(10)		C10	C11	C12	119.8(3)
N1	Ru1	C20	167.09(10)		C12	C11	C1	106.9(2)
N1	Ru1	C21	148.08(10)		C7	C12	C3	124.2(3)
N1	Ru1	C22	112.74(10)		C11	C12	C3	112.5(2)
N1	Ru1	C23	93.15(10)		C11	C12	C7	123.3(3)
C18	Ru1	Cl1	166.92(8)		O2	C13	N1	119.7(2)
C19	Ru1	Cl1	144.44(8)		O2	C13	C14	118.8(2)
C19	Ru1	C18	37.81(11)		N1	C13	C14	121.4(2)
C19	Ru1	C20	37.50(11)		C13	C14	S1	129.6(2)
C19	Ru1	C21	67.54(11)		C15	C14	S1	110.5(2)
C19	Ru1	C23	67.14(11)		C15	C14	C13	119.9(3)
C20	Ru1	Cl1	108.95(8)		C14	C15	C16	111.9(3)
C20	Ru1	C18	68.22(11)		C17	C16	C15	113.1(3)
C20	Ru1	C21	36.94(11)		C16	C17	S1	112.9(3)
C21	Ru1	Cl1	89.35(8)		C19	C18	Ru1	69.19(15)
C21	Ru1	C18	81.16(11)		C19	C18	C24	121.7(3)
C22	Ru1	Cl1	98.73(9)		C23	C18	Ru1	69.30(16)
C22	Ru1	C18	68.28(12)		C23	C18	C19	115.3(3)
C22	Ru1	C19	79.60(12)		C23	C18	C24	123.0(3)
C22	Ru1	C20	66.91(11)		C24	C18	Ru1	131.2(2)
C22	Ru1	C21	37.64(11)		C18	C19	Ru1	73.00(15)
C22	Ru1	C23	37.37(11)		C20	C19	Ru1	72.21(16)
C23	Ru1	Cl1	129.91(9)		C20	C19	C18	122.3(3)
C23	Ru1	C18	37.67(11)		C19	C20	Ru1	70.29(16)
C23	Ru1	C20	79.15(11)		C21	C20	Ru1	72.31(16)
C23	Ru1	C21	67.68(12)		C21	C20	C19	121.0(3)
C17	S1	C14	91.74(16)		C20	C21	Ru1	70.75(16)
C1	O1	Ru1	124.28(16)		C20	C21	C22	117.6(3)
N2	N1	Ru1	128.07(15)		C20	C21	C27	121.7(3)
N2	N1	C13	111.2(2)		C22	C21	Ru1	69.42(16)
C13	N1	Ru1	120.68(17)		C22	C21	C27	120.6(3)
C2	N2	N1	122.4(2)		C27	C21	Ru1	128.3(2)
O1	C1	C2	127.4(2)		C21	C22	Ru1	72.94(16)
O1	C1	C11	125.7(2)		C23	C22	Ru1	71.39(16)
C11	C1	C2	107.0(2)		C23	C22	C21	121.1(3)
N2	C2	C1	129.1(2)		C18	C23	Ru1	73.03(16)
N2	C2	C3	123.6(2)		C22	C23	Ru1	71.24(16)
C3	C2	C1	107.3(2)		C22	C23	C18	122.6(3)
C4	C3	C2	135.8(3)		C25	C24	C18	112.8(3)
C4	C3	C12	118.0(3)		C25	C24	C26	110.5(4)

5. NMR spectra of Ru(II)complex

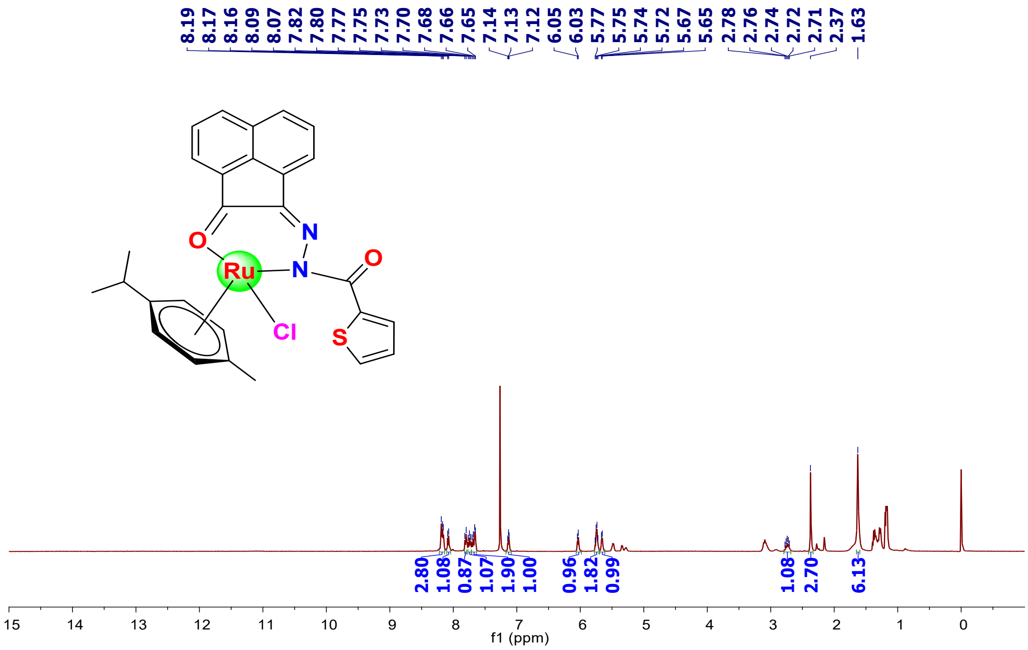


Figure S2. ^{1}H NMR spectrum of complex **1** in $CDCl_3$ (400 MHz, 300 K)

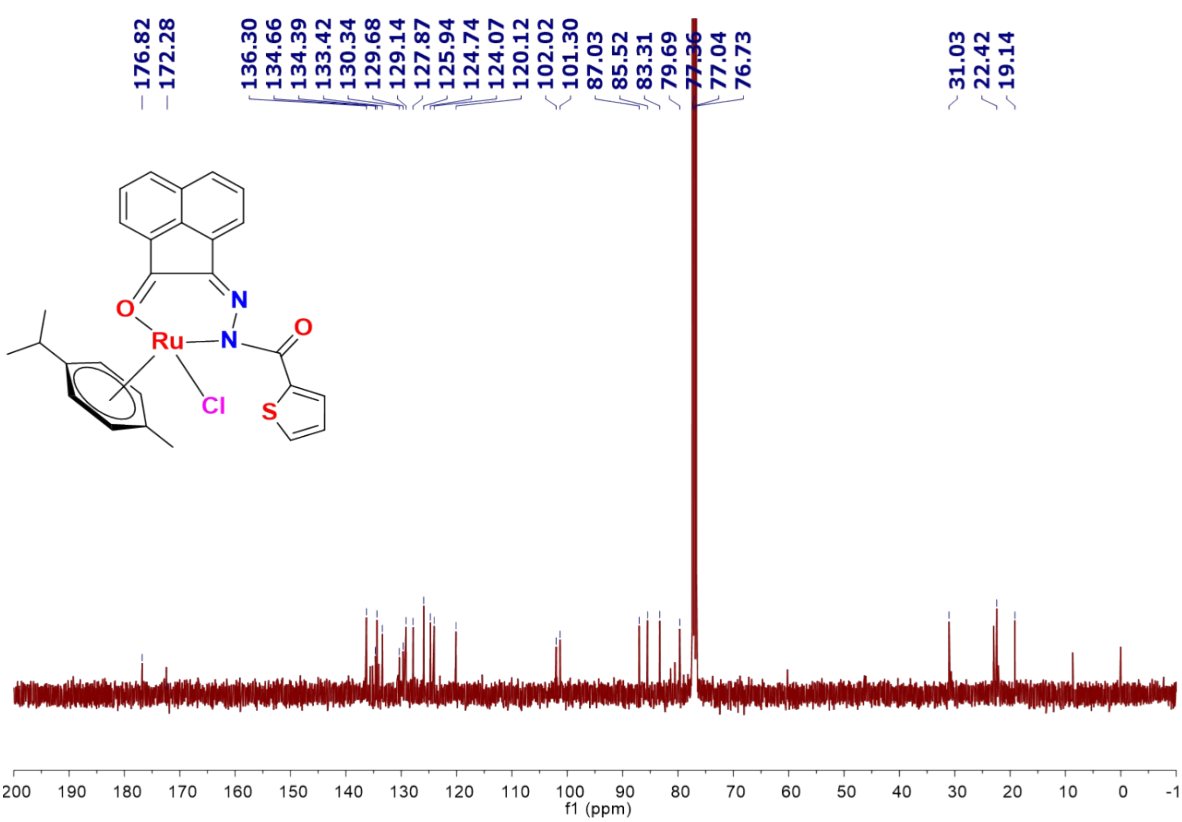


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$ (100 MHz, 300 K)

6. HRMS spectrum of Ru(II) complex

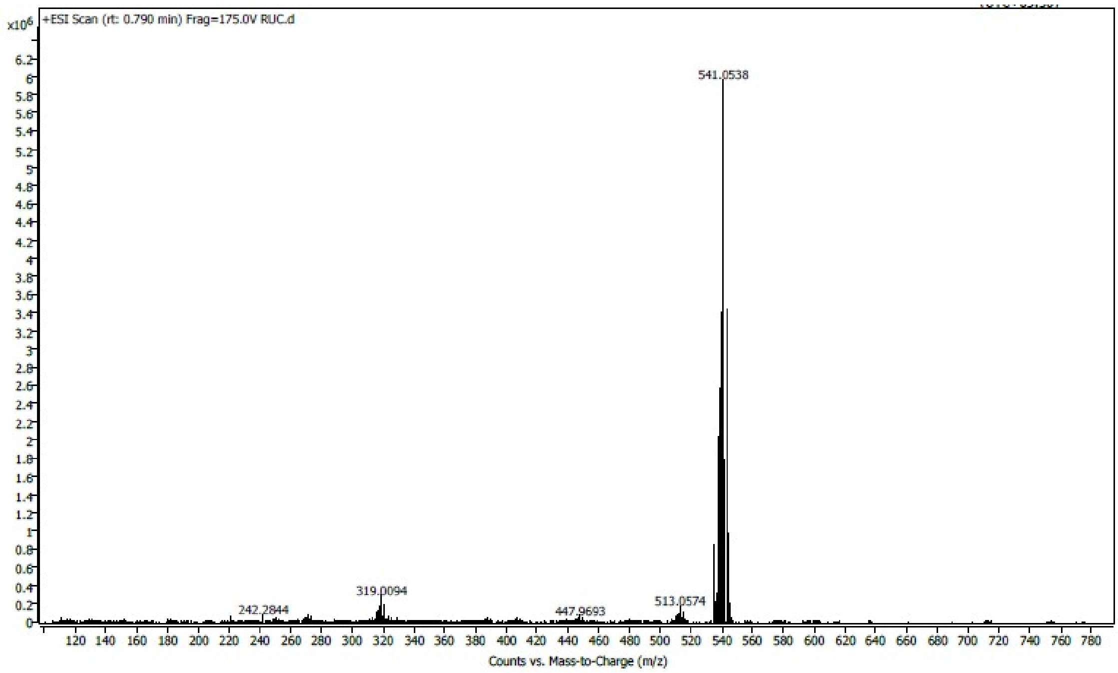
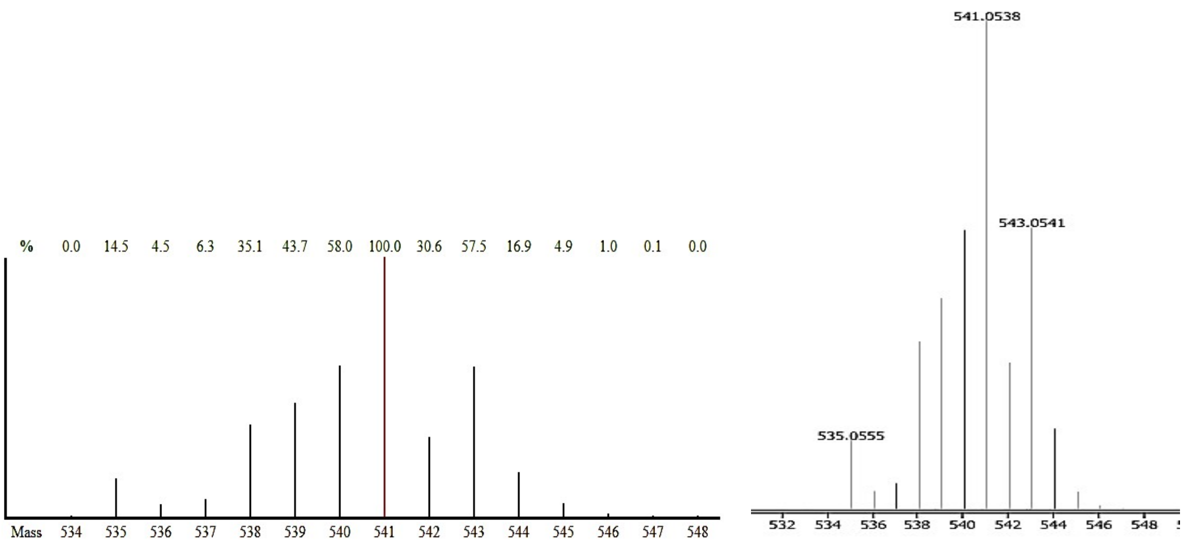


Figure S4.HRMS spectrum of complex **1**

(ESI-TOF) m/z: [M-Cl]+Calcd for $C_{27}H_{23}ClN_2O_2RuS$ 541.0524; Found 541.0538.



(a) **(b)**

Figure S4(i). Simulated (a) and experimental (b) pattern of the complex

7. NMR spectra of catalytic products

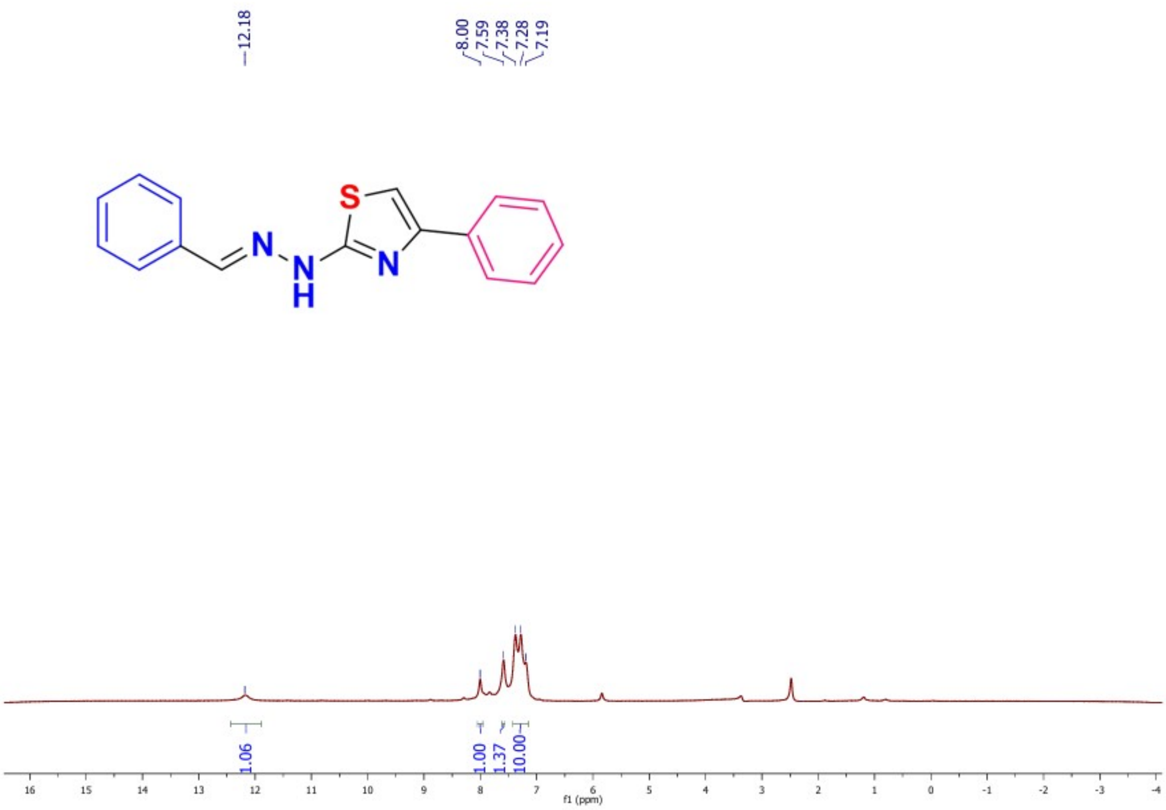


Figure S5. ^{1}H NMR spectrum of **4a** in DMSO-d_6(400 MHz, 300 K)

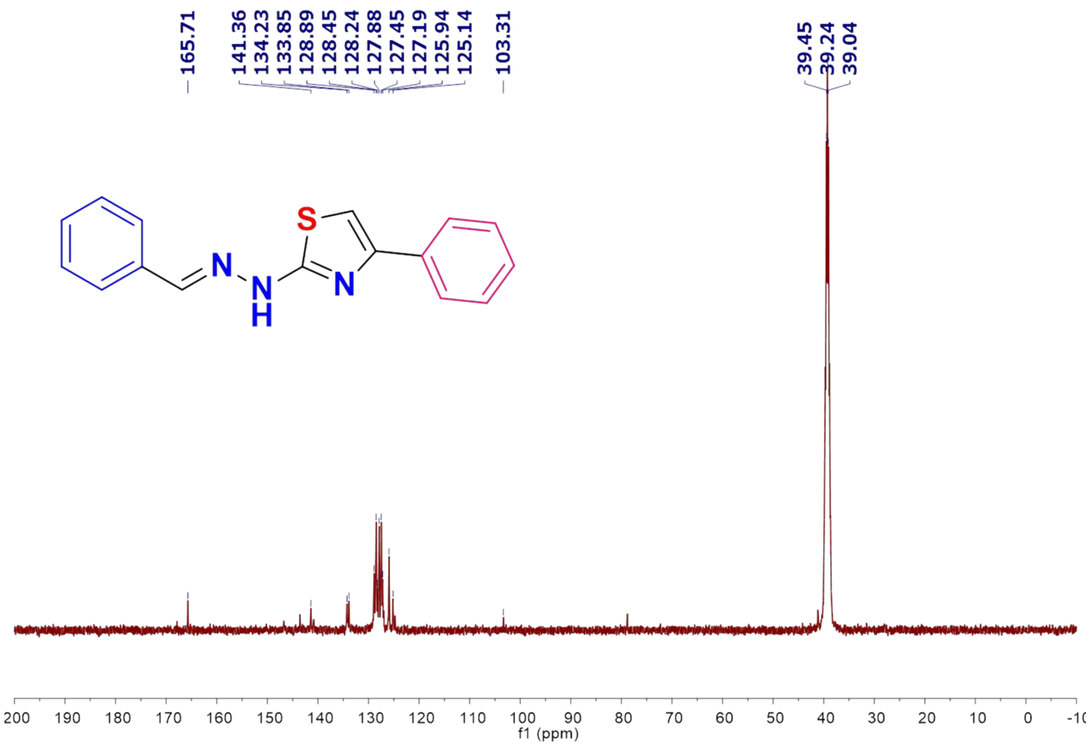


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in DMSO-d_6(100 MHz, 300 K)

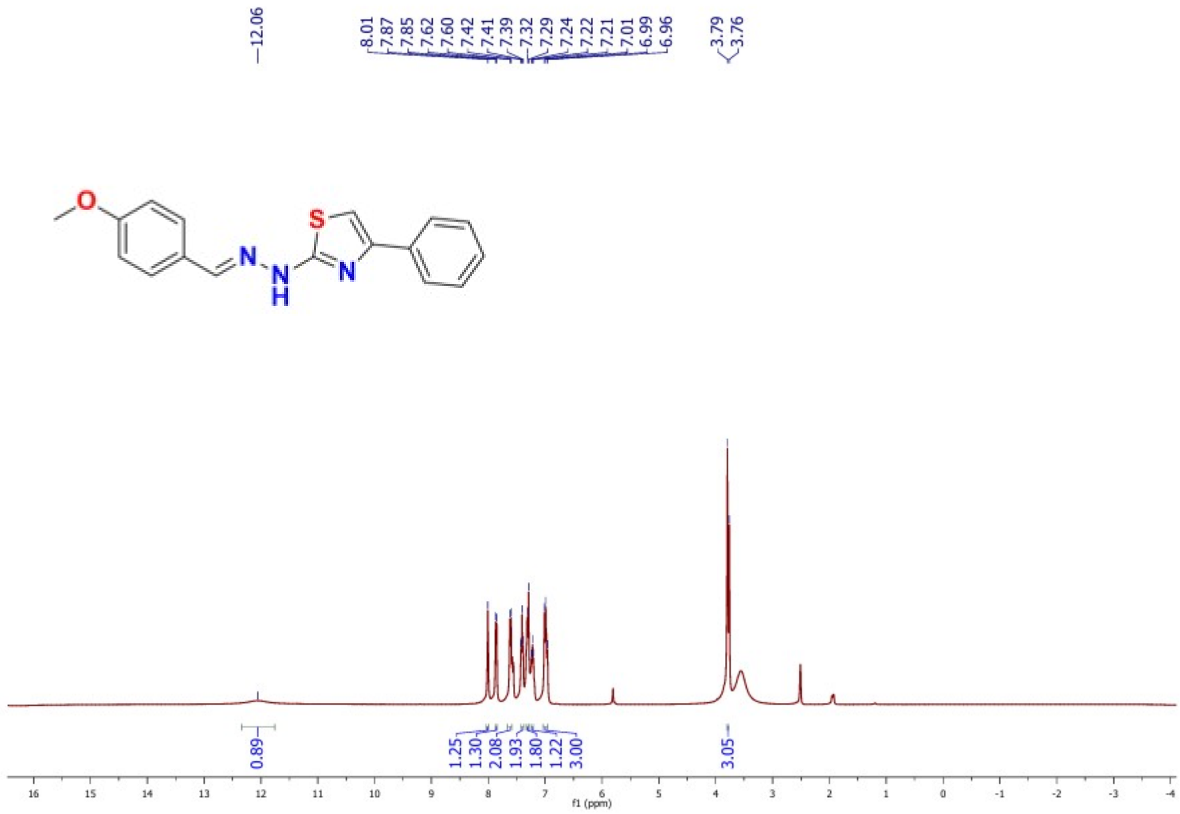


Figure S7. ^{1}H NMR spectrum of **4b** in DMSO-d_6(400 MHz, 300 K)

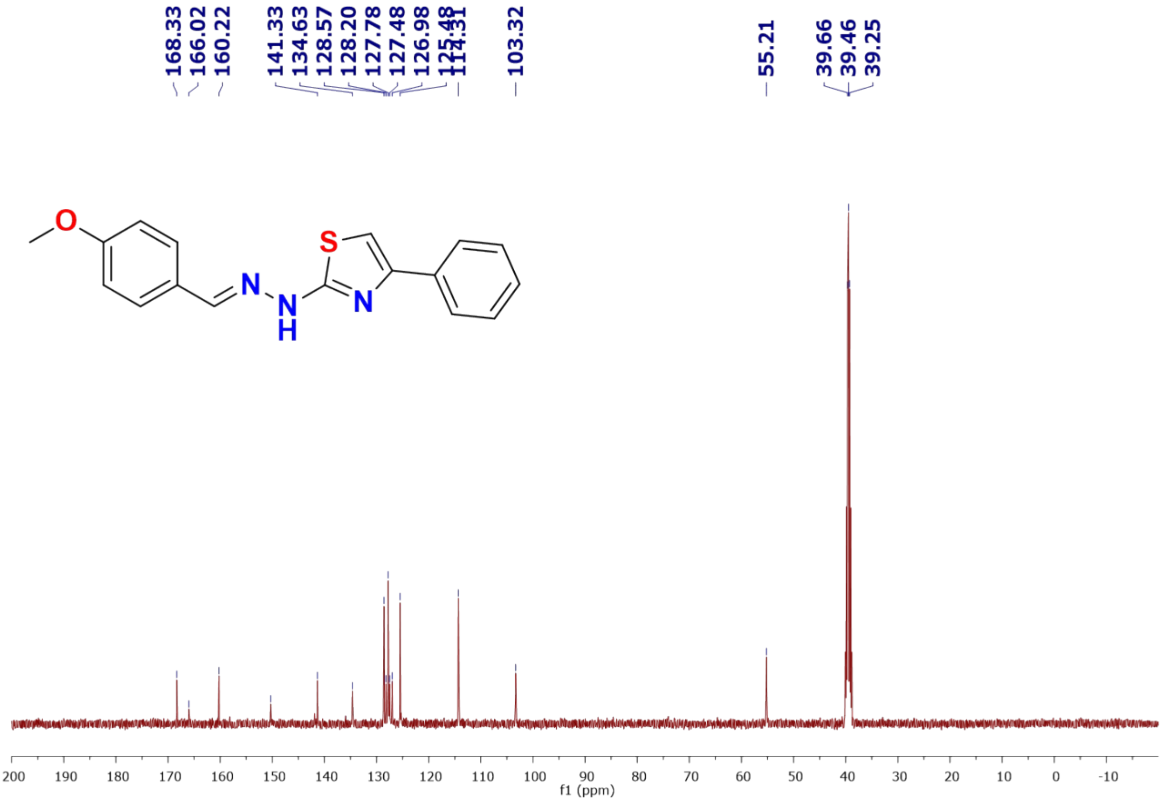


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **4b** in DMSO-d_6(100 MHz, 300 K)

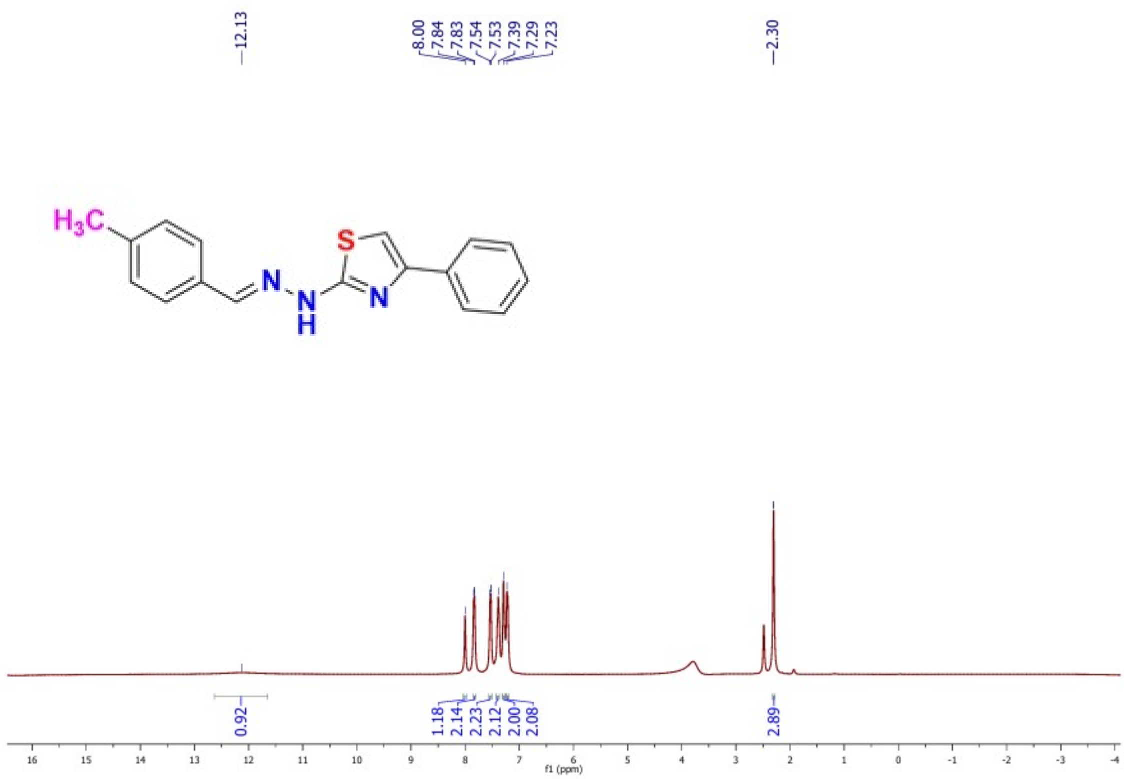


Figure S9. ^1H NMR spectrum of **4c** in DMSO-d_6(400 MHz, 300 K)

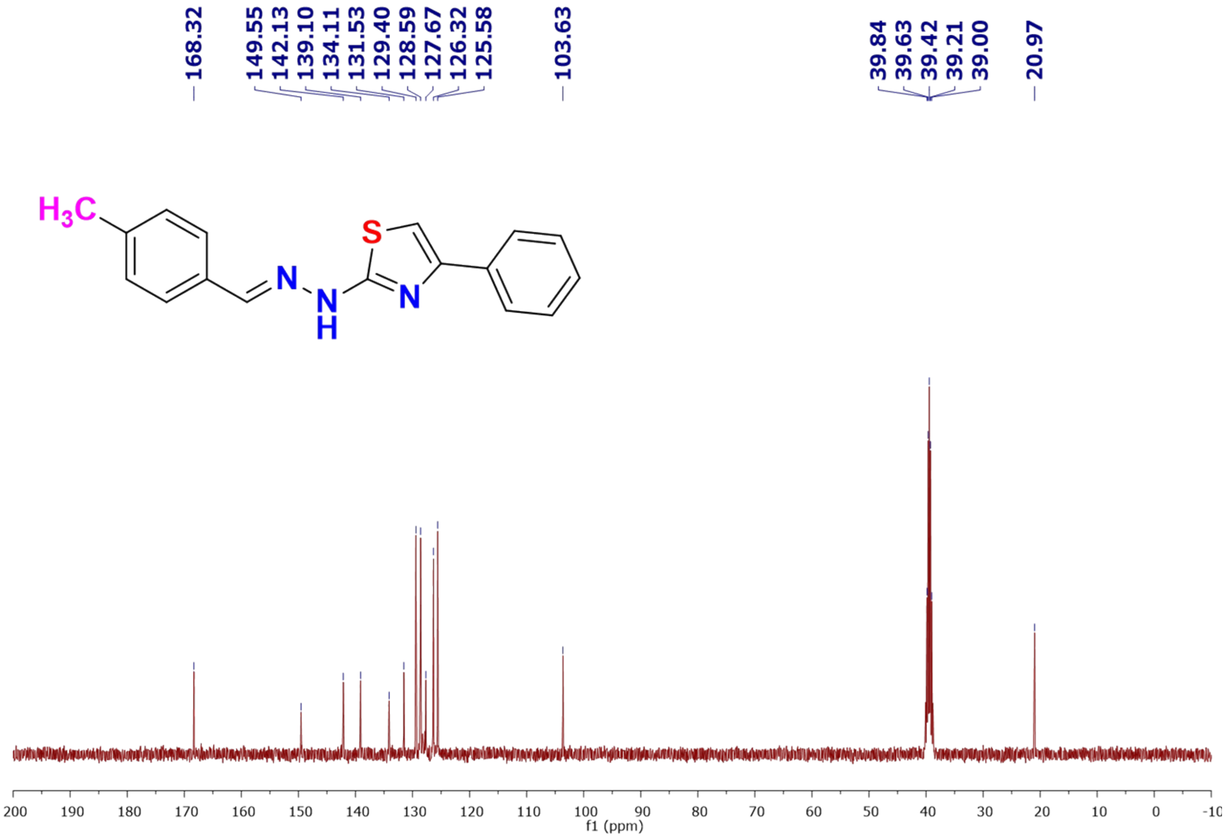


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in DMSO-d_6(100 MHz, 300 K)

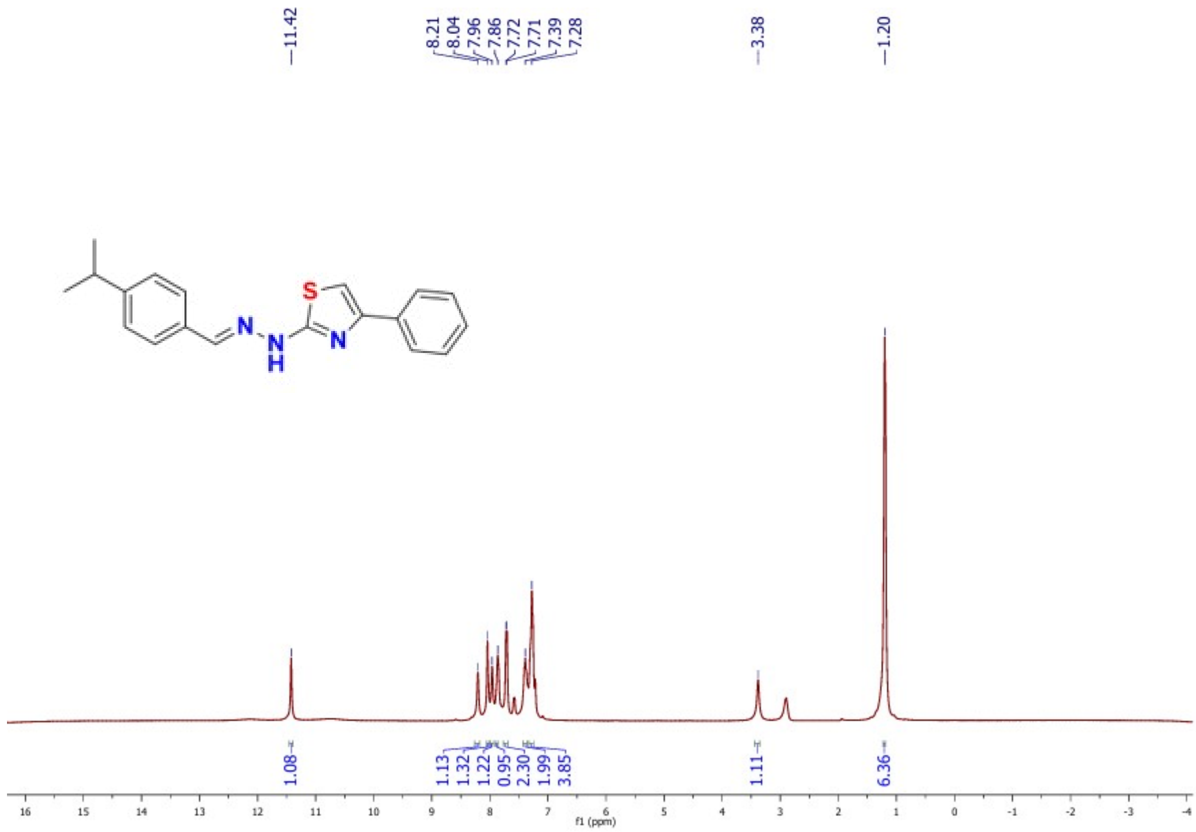


Figure S11. ^{1}H NMR spectrum of **4d** in DMSO-d_6(400 MHz, 300 K)

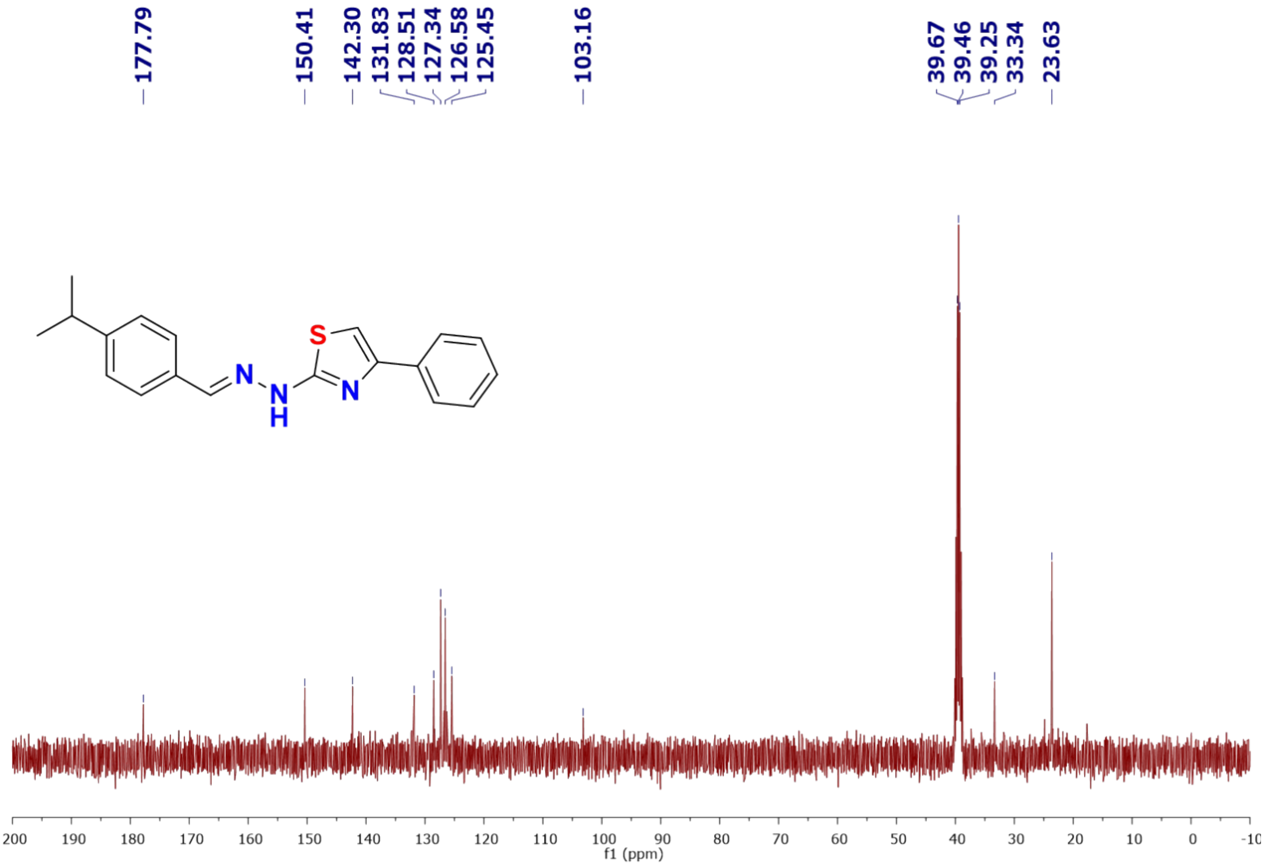


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in DMSO-d_6(100 MHz, 300 K)

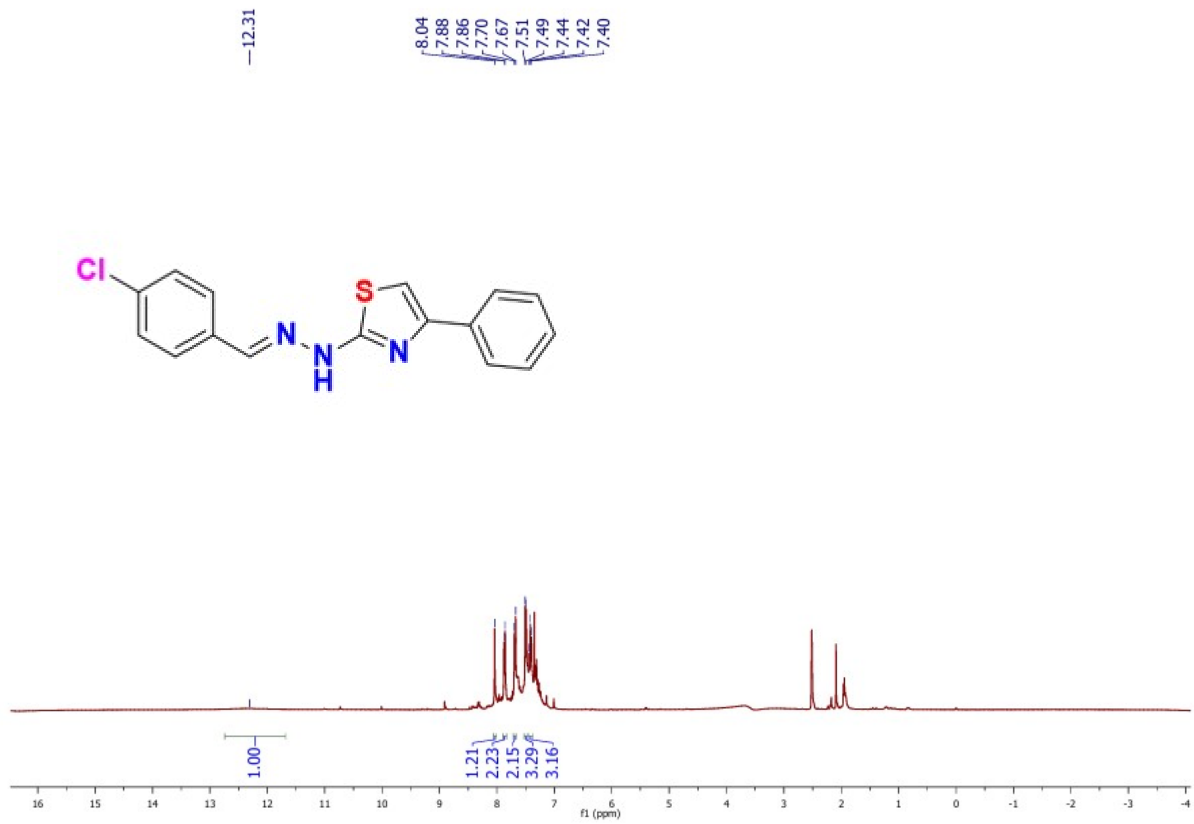


Figure S13. ^{1}H NMR spectrum of **4e** in DMSO-d_6(400 MHz, 300 K)

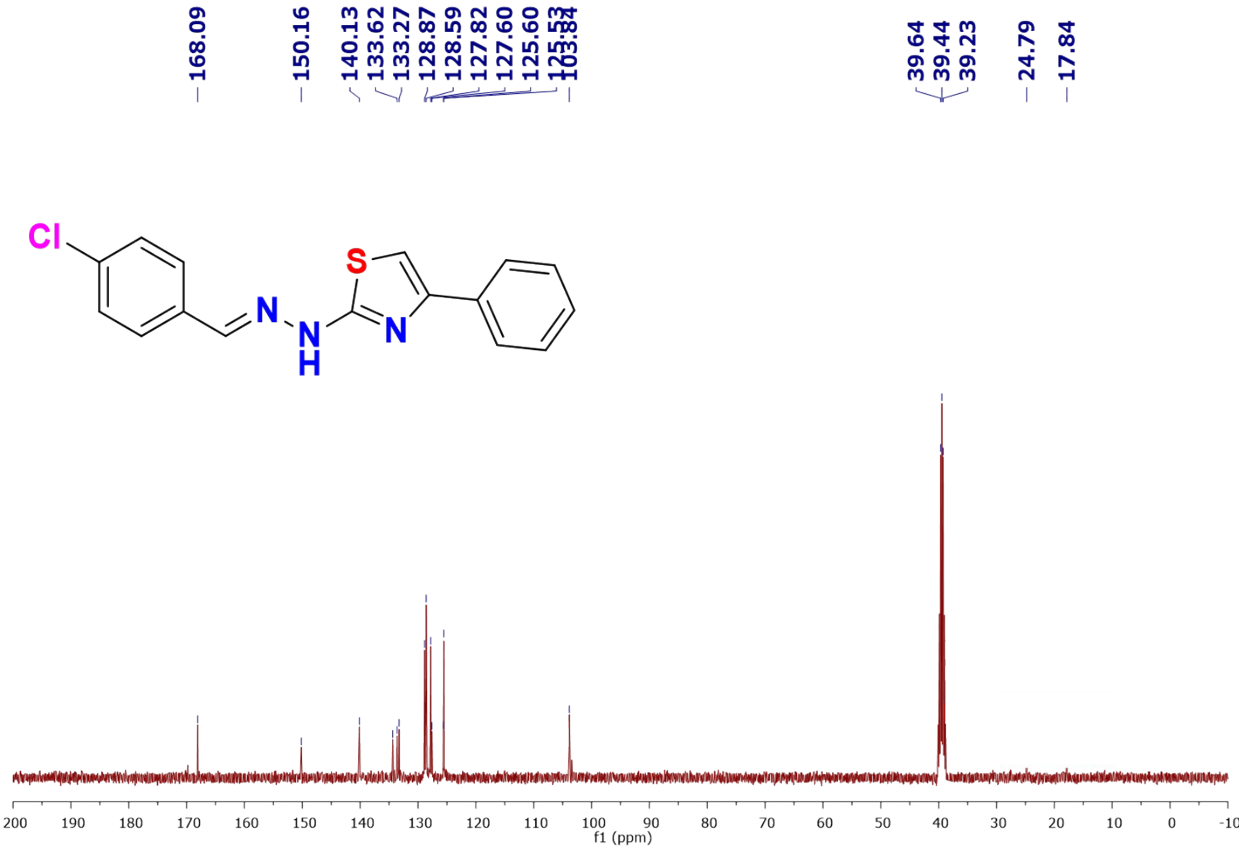


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** in DMSO-d_6(100 MHz, 300 K)

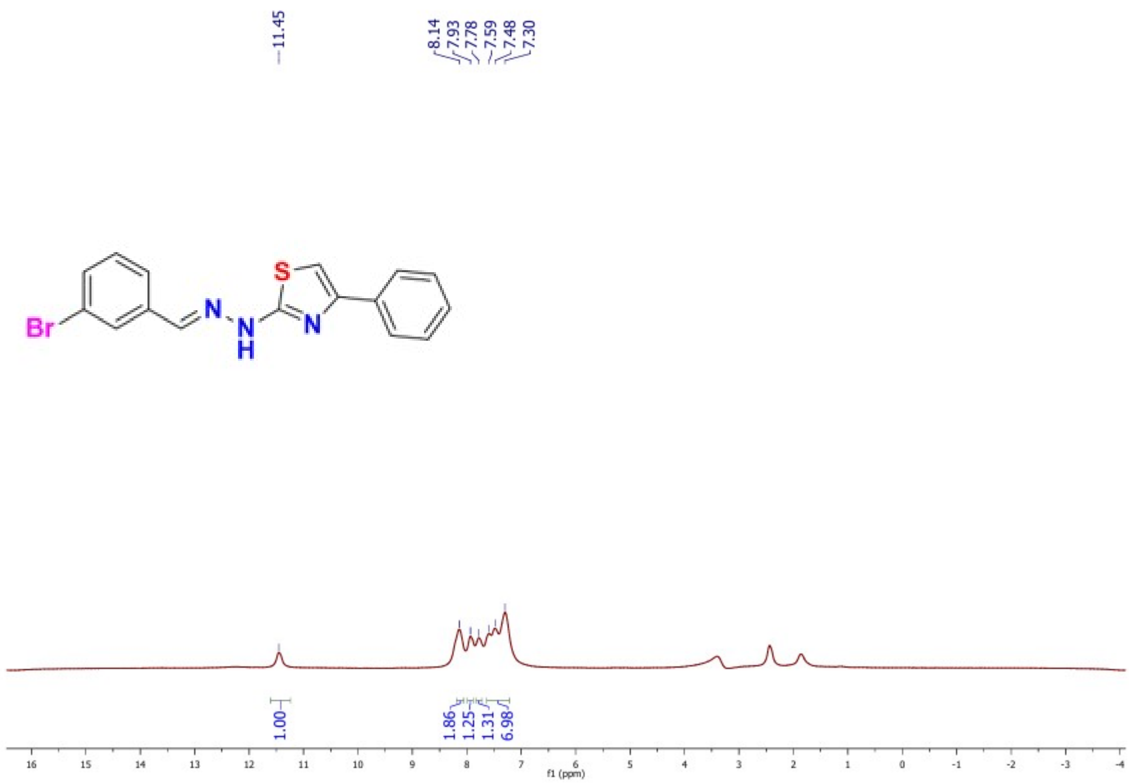


Figure S15. ^{1}H NMR spectrum of **4f** in DMSO-d_6(400 MHz, 300 K)

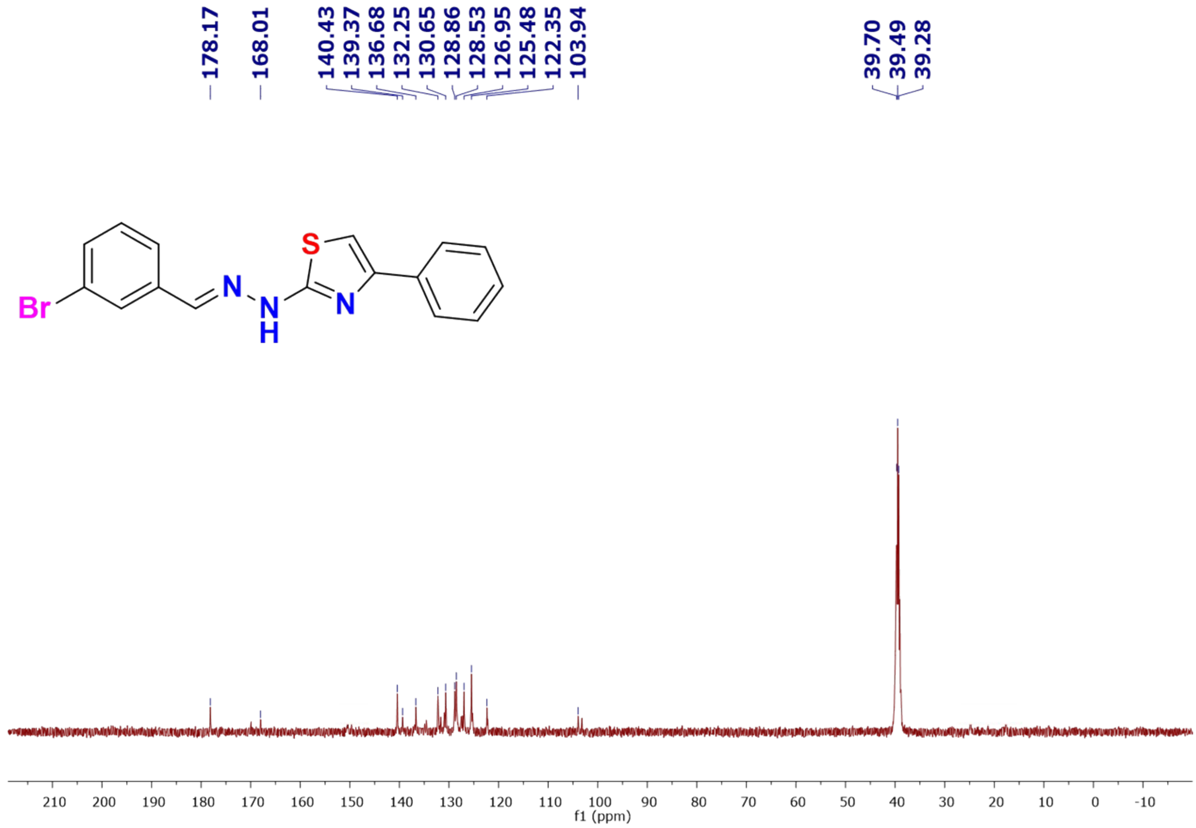


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** in DMSO-d_6(100 MHz, 300 K)

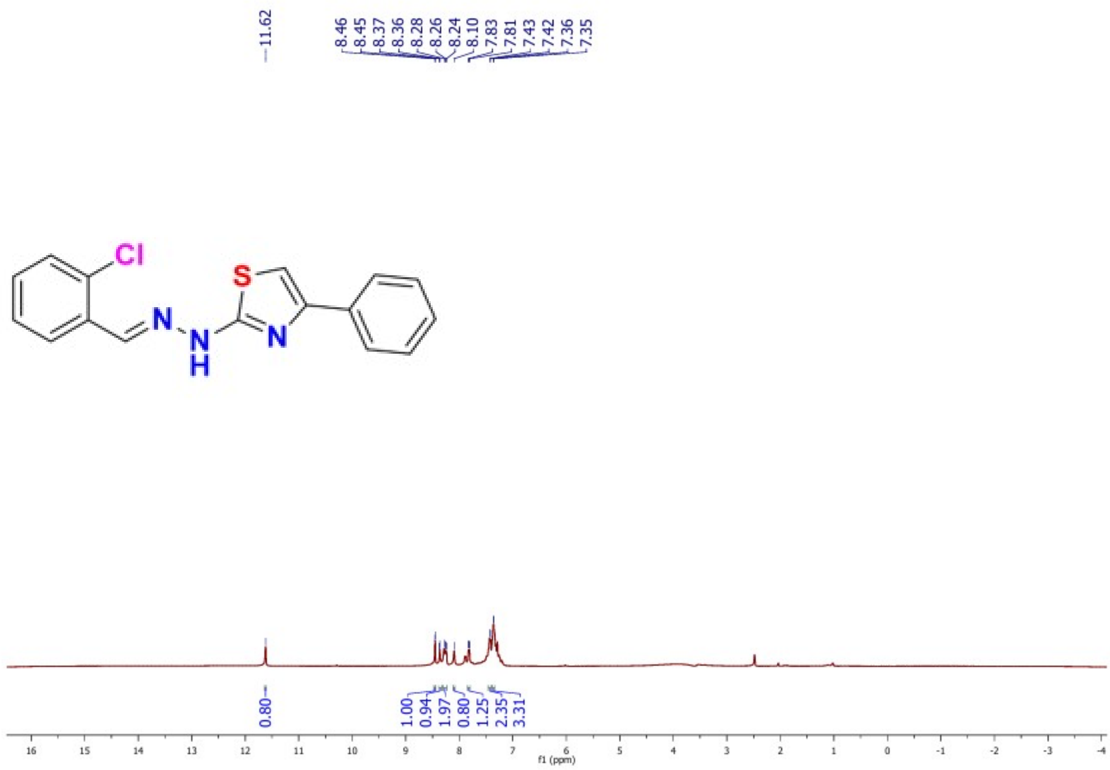


Figure S17. ^{1}H NMR spectrum of **4g** in DMSO-d_6(400 MHz, 300 K)

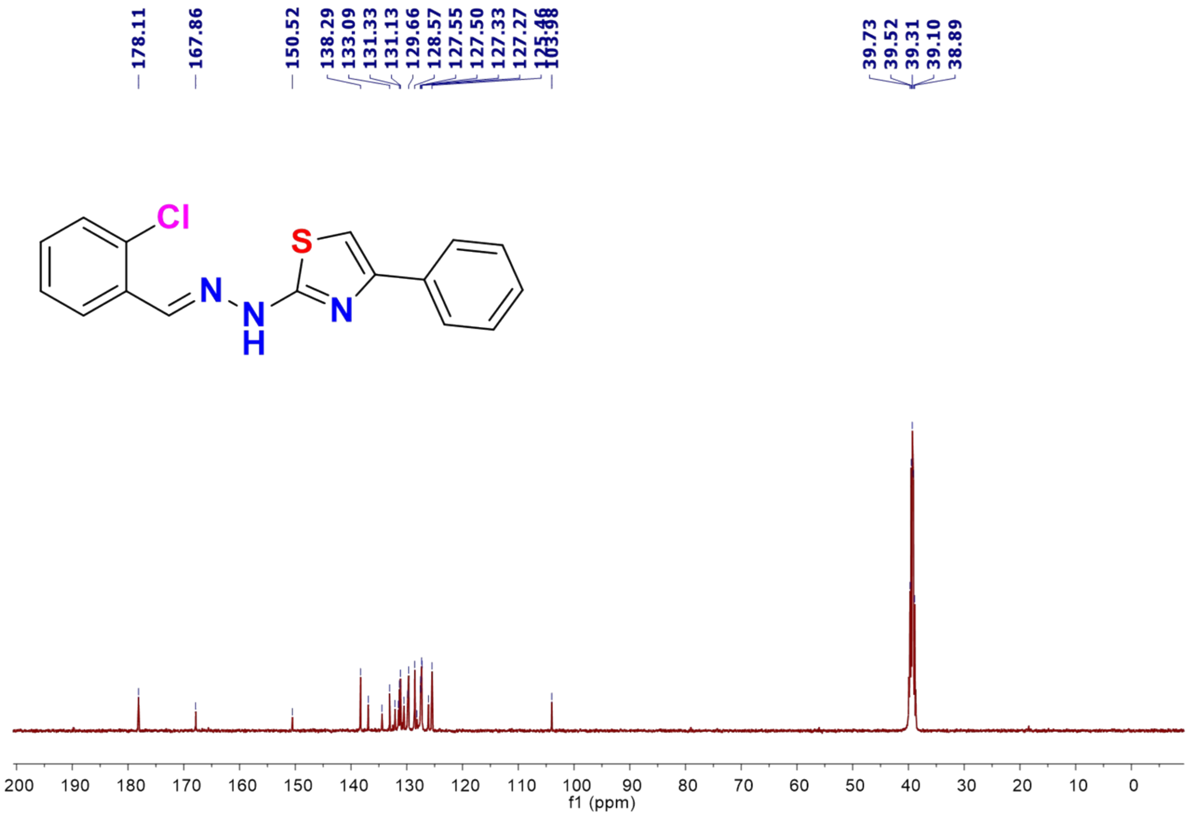


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **4g** in DMSO-d_6(100 MHz, 300 K)

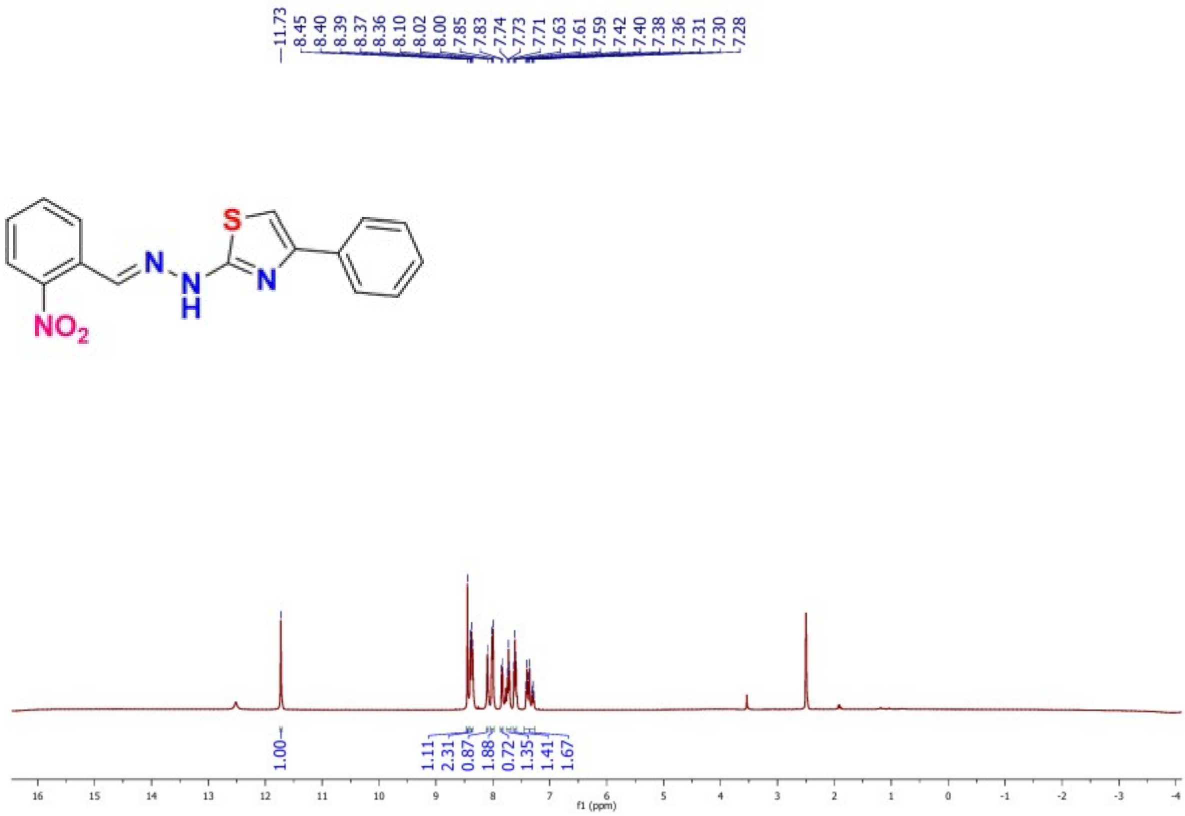


Figure S19. ^{1}H NMR spectrum of **4h** in DMSO-d_6(400 MHz, 300 K)

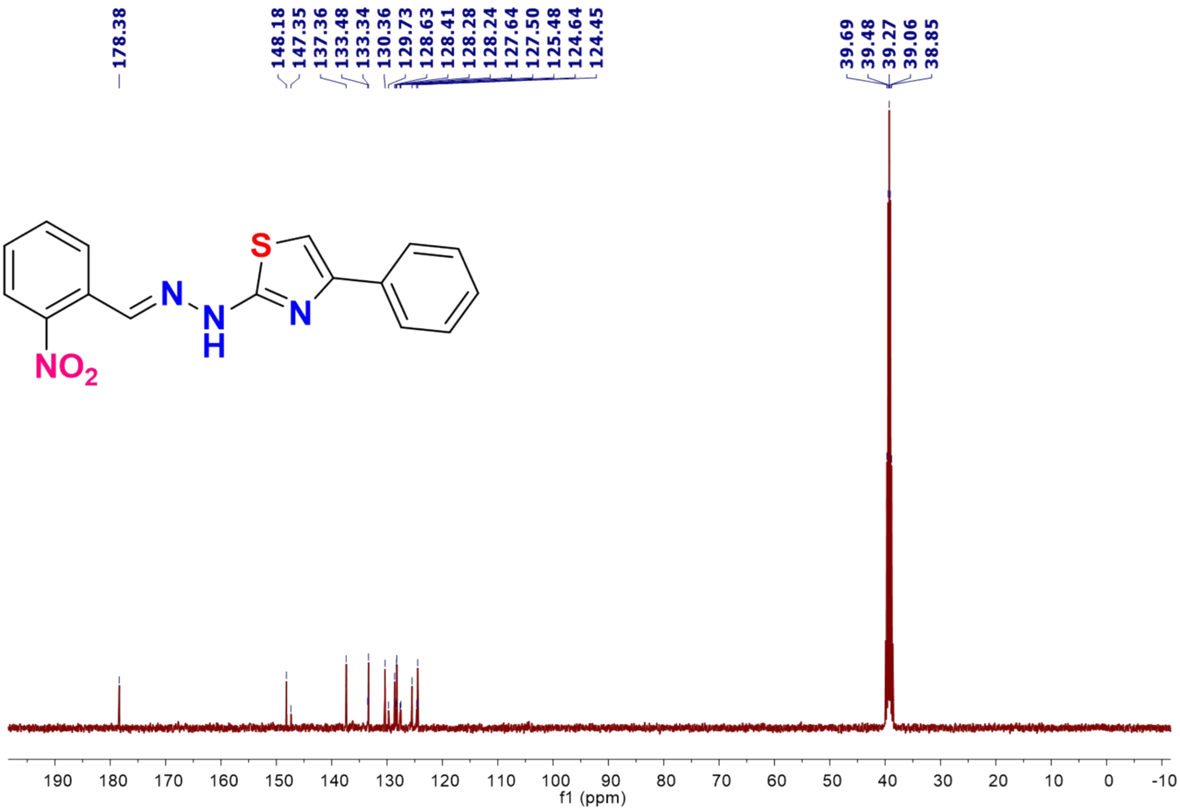


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **4h** in DMSO-d$_6$(100 MHz, 300 K)

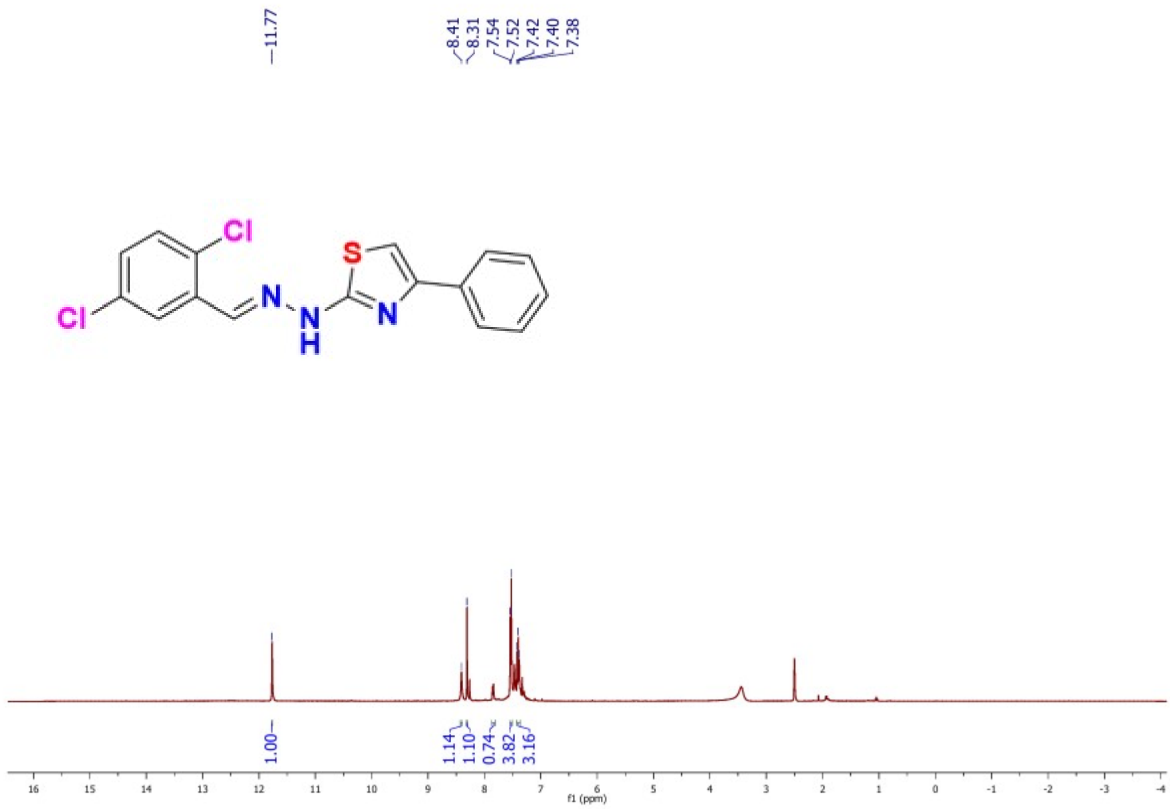


Figure S21. ^{1}H NMR spectrum of **4i** in DMSO-d$_6$(400 MHz, 300 K)

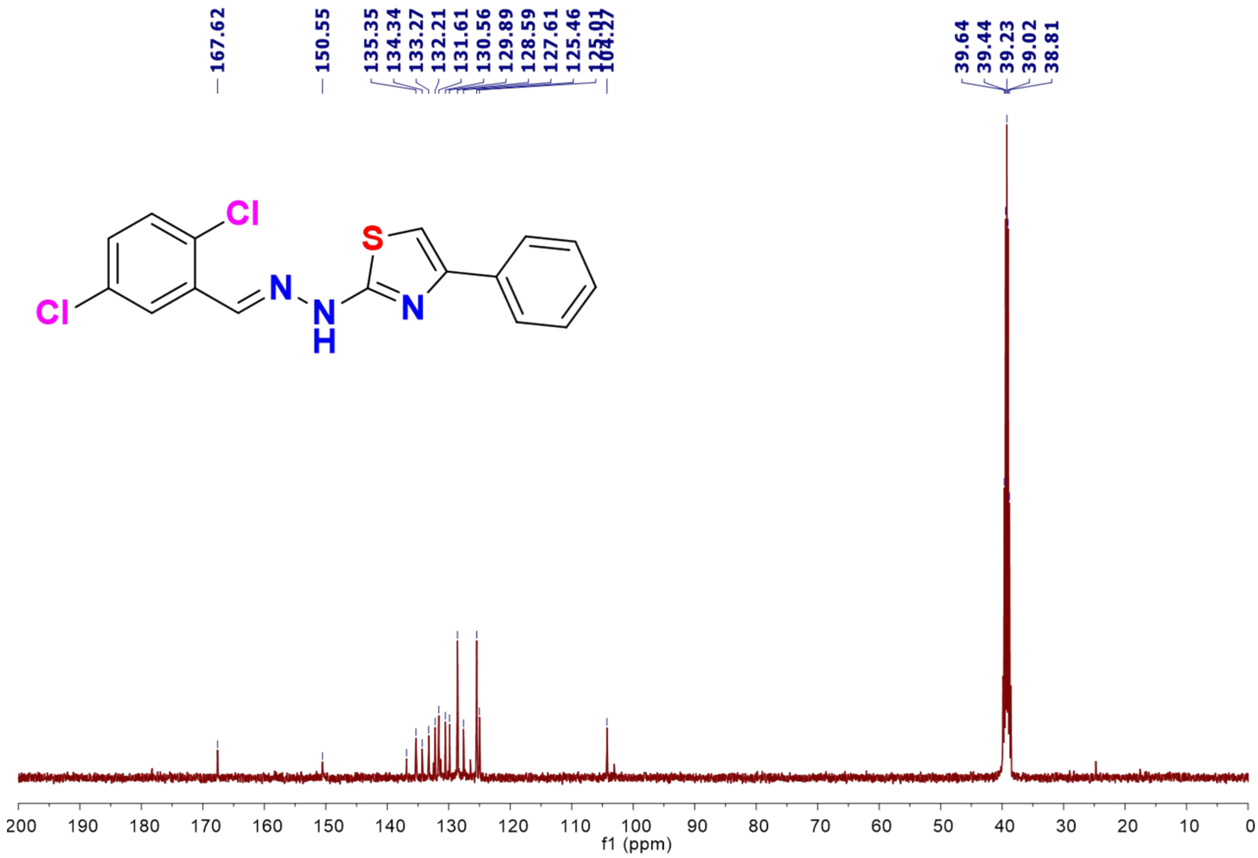


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **4i** in DMSO-d_6(100 MHz, 300 K)

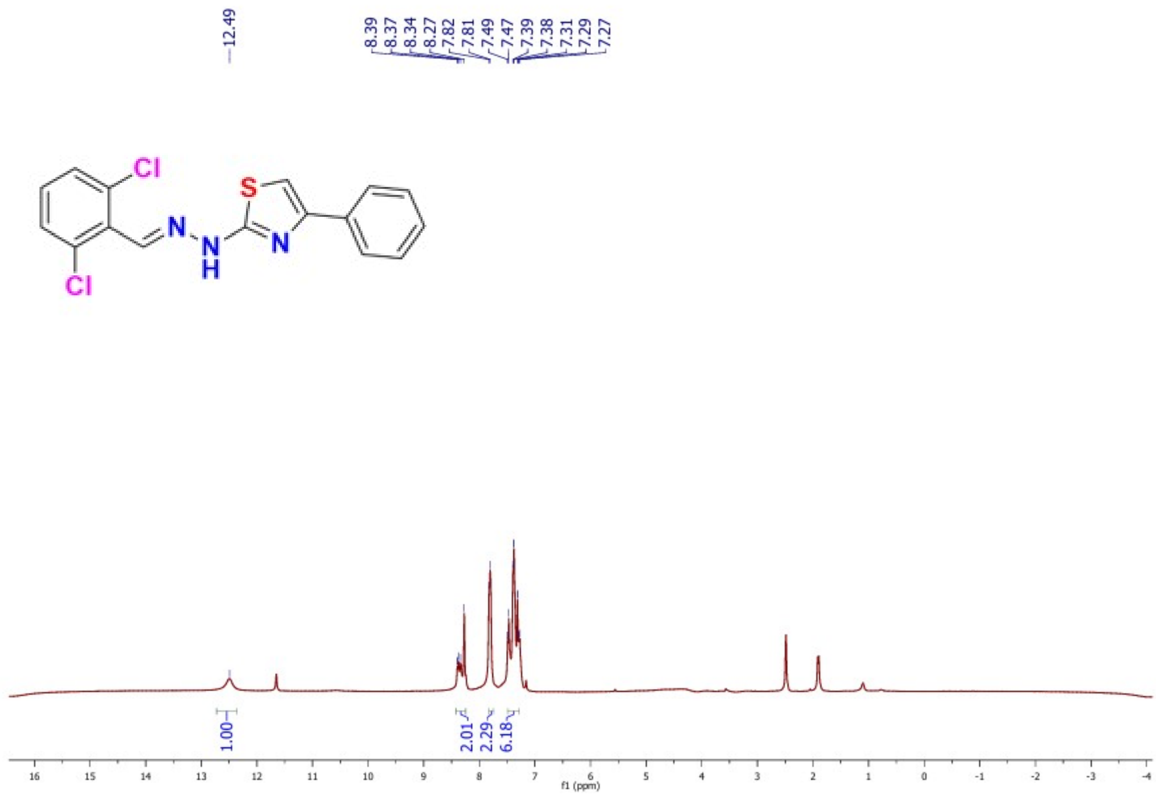


Figure S23. ^{1}H NMR spectrum of **4j** in DMSO-d_6(400 MHz, 300 K)

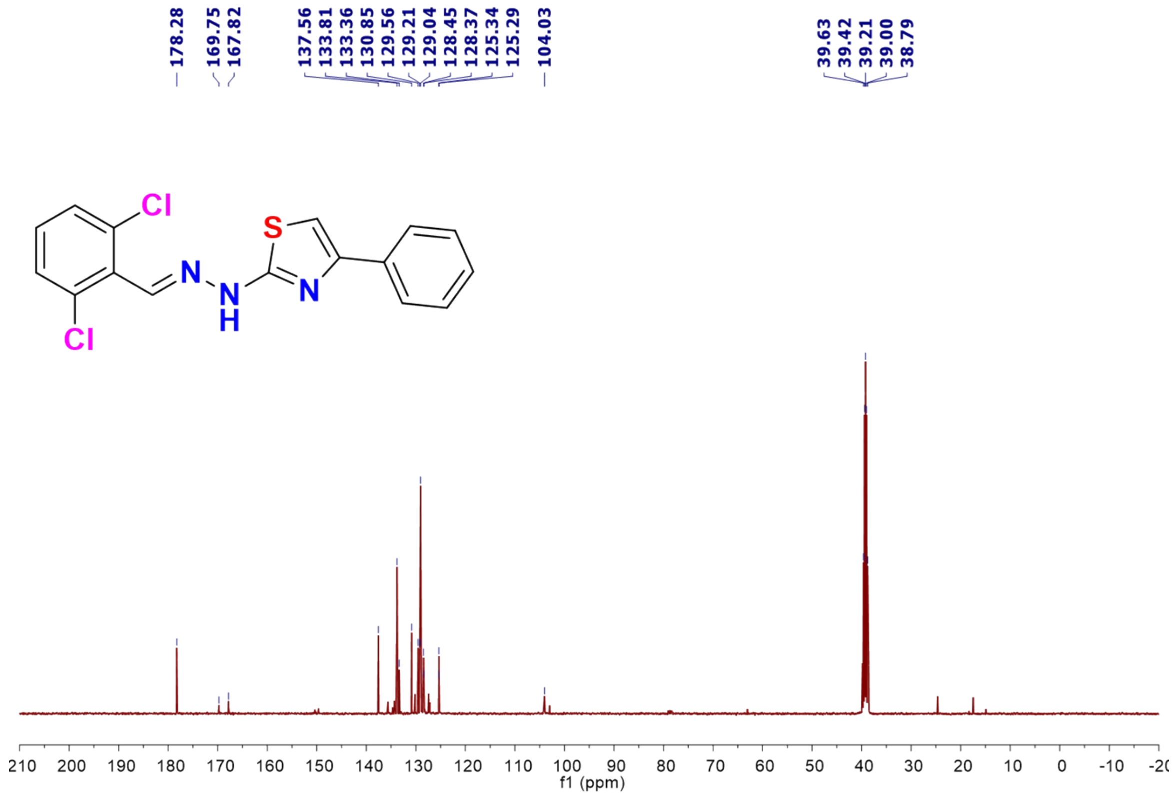


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **4j** in DMSO-d_6(100 MHz, 300 K)

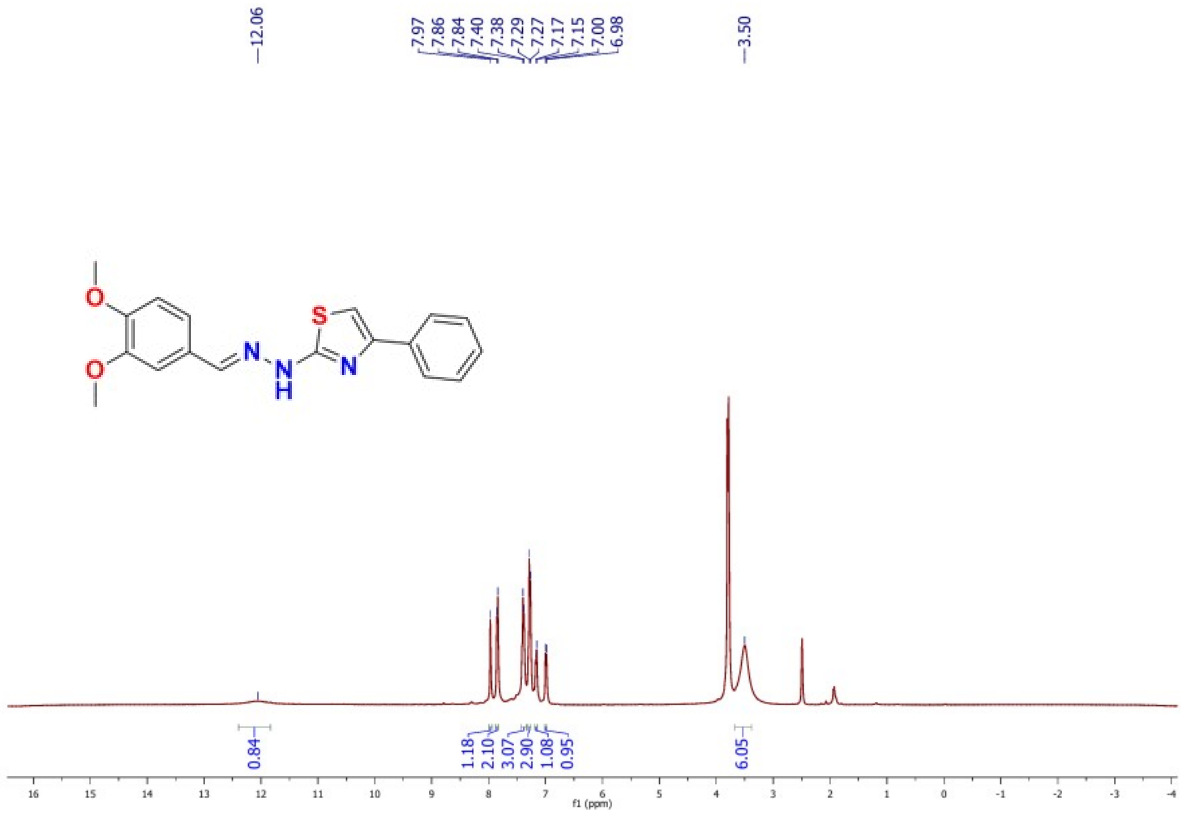


Figure S25. ^{1}H NMR spectrum of **4k** in DMSO-d_6(400 MHz, 300 K)

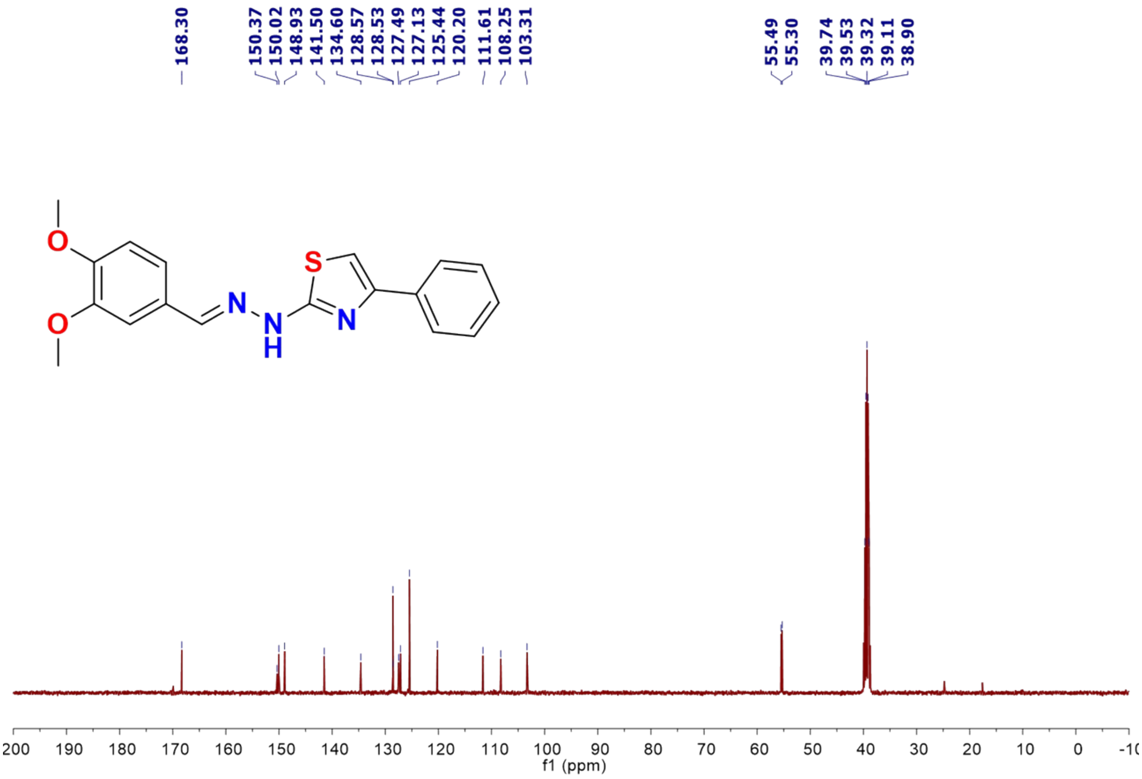


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **4k** in DMSO-d$_6$(100 MHz, 300 K)

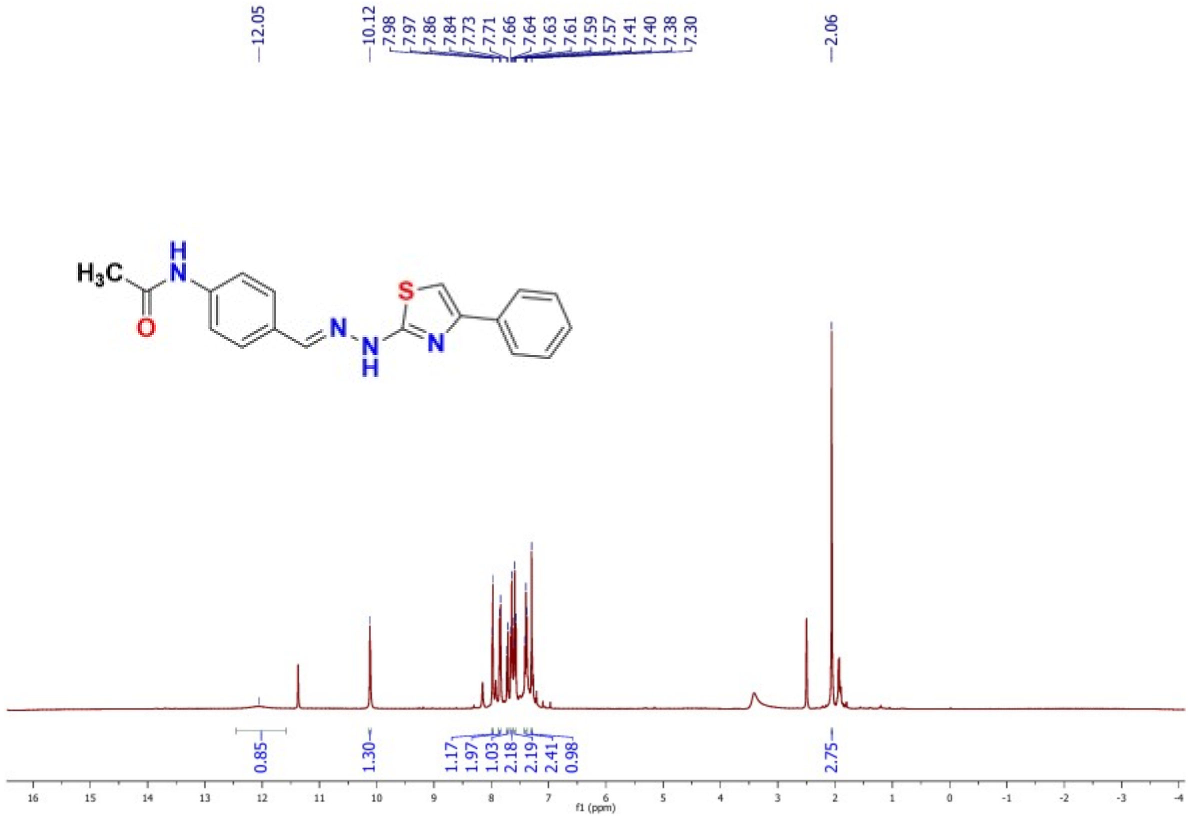


Figure S27. ^{1}H NMR spectrum of **4l** in DMSO-d$_6$(400 MHz, 300 K)

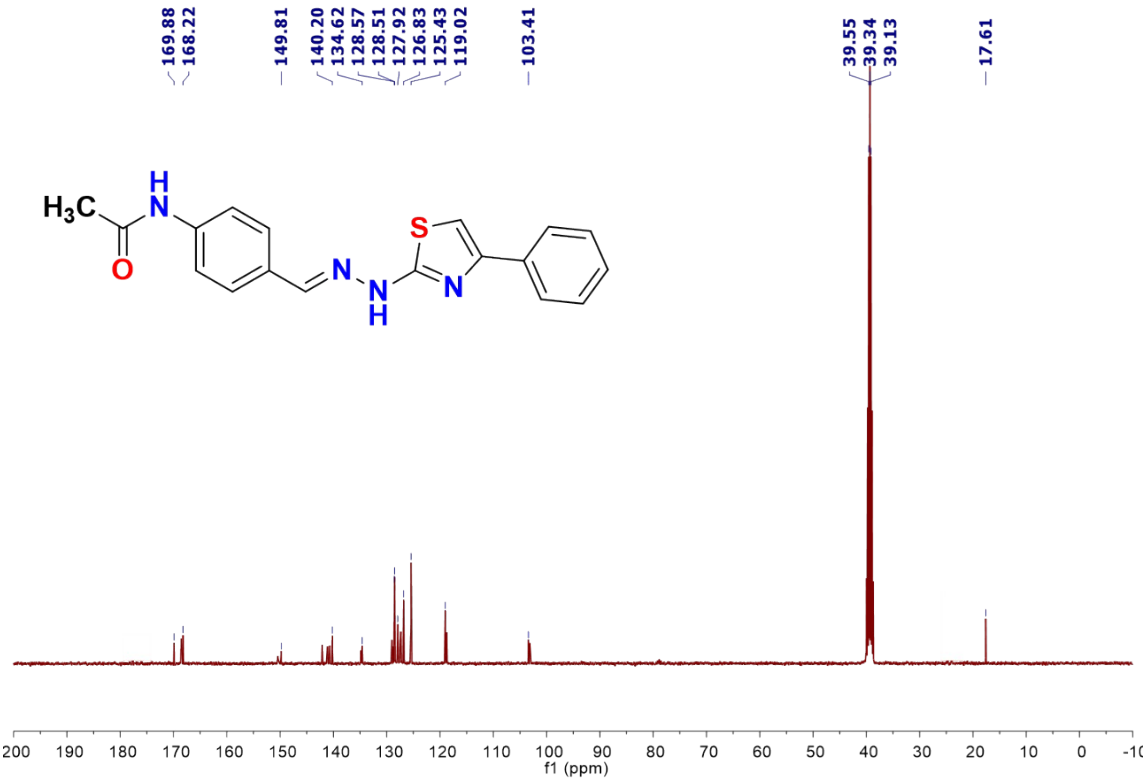


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **4l** in DMSO-d_6(100 MHz, 300 K)

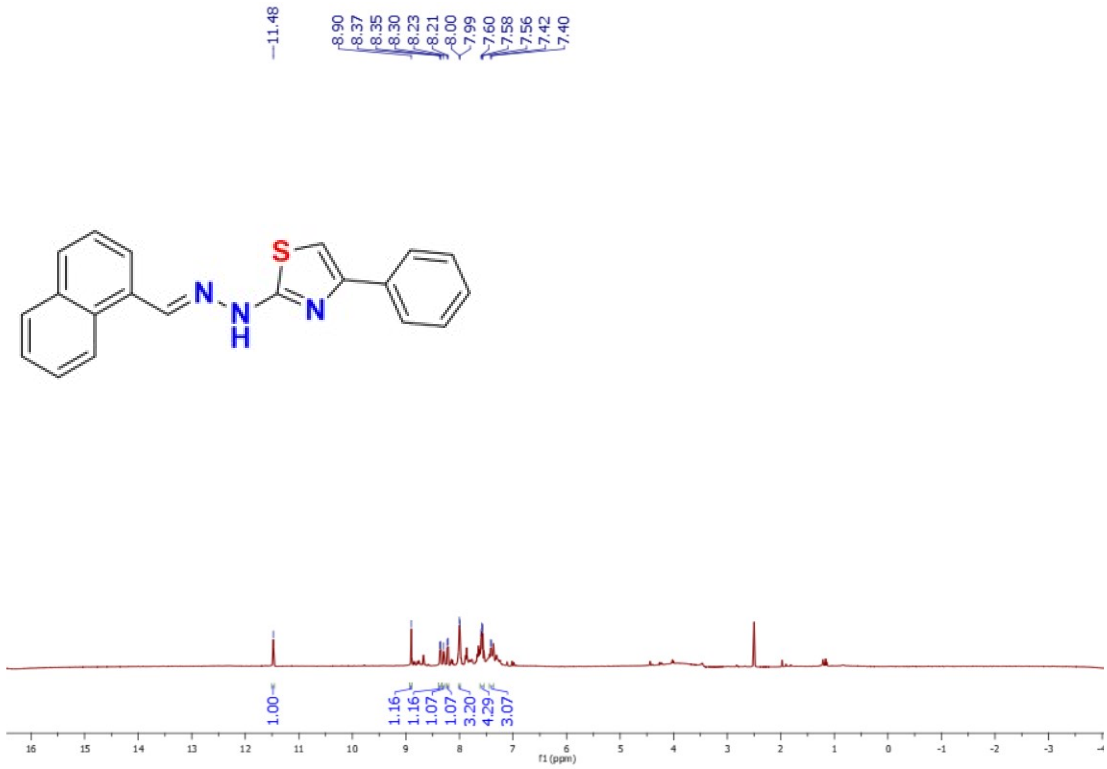


Figure S29. ^{1}H NMR spectrum of **4m** in DMSO-d_6(400 MHz, 300 K)

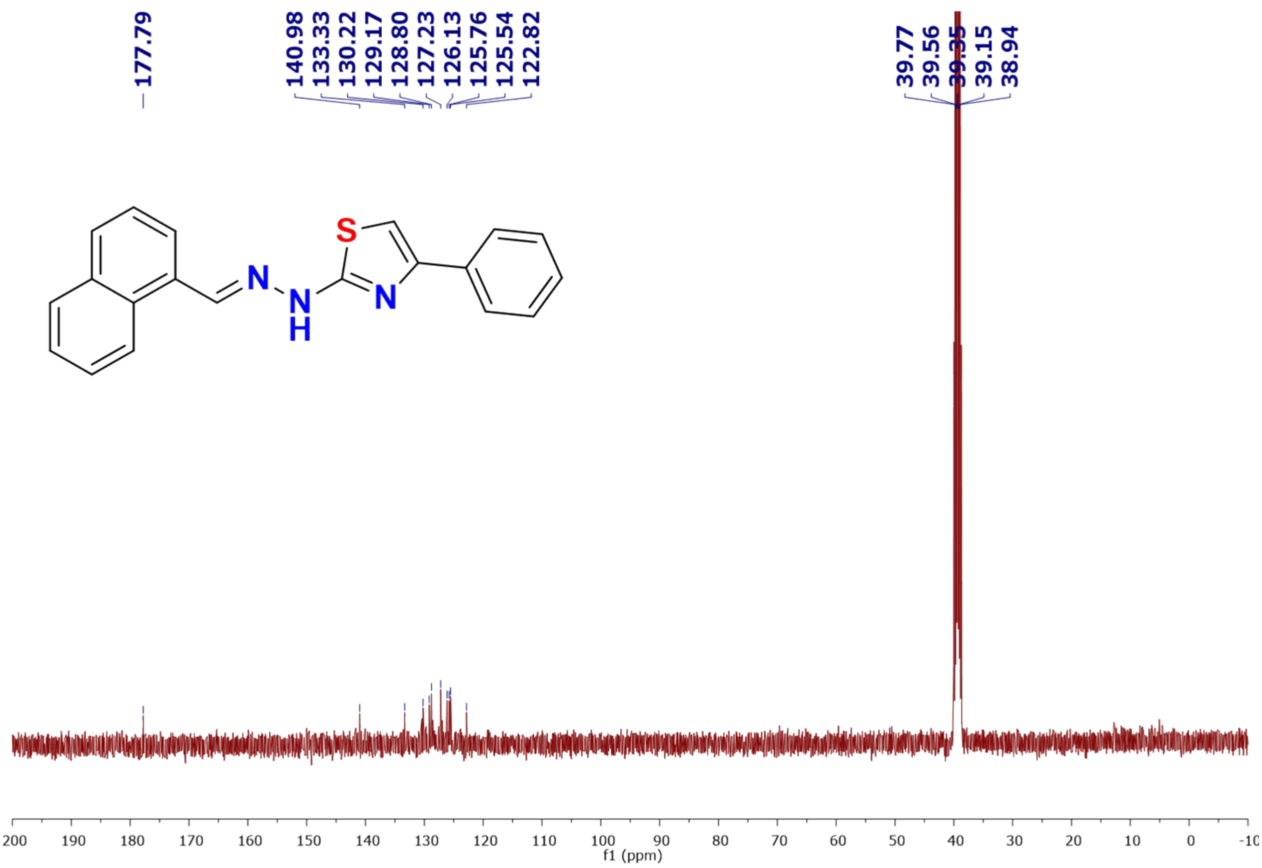


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **4m** in DMSO-d_6(100 MHz, 300 K)

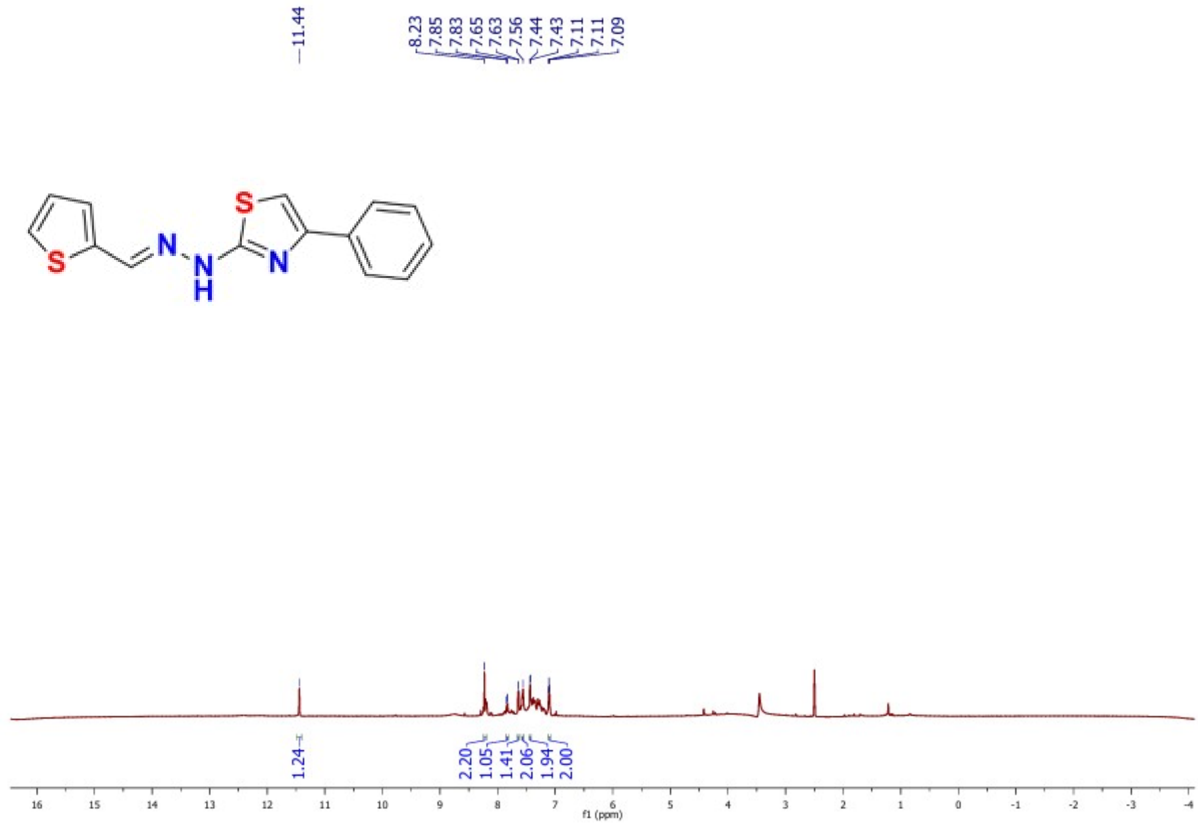


Figure S31. ^{1}H NMR spectrum of **4n** in DMSO-d_6(400 MHz, 300 K)

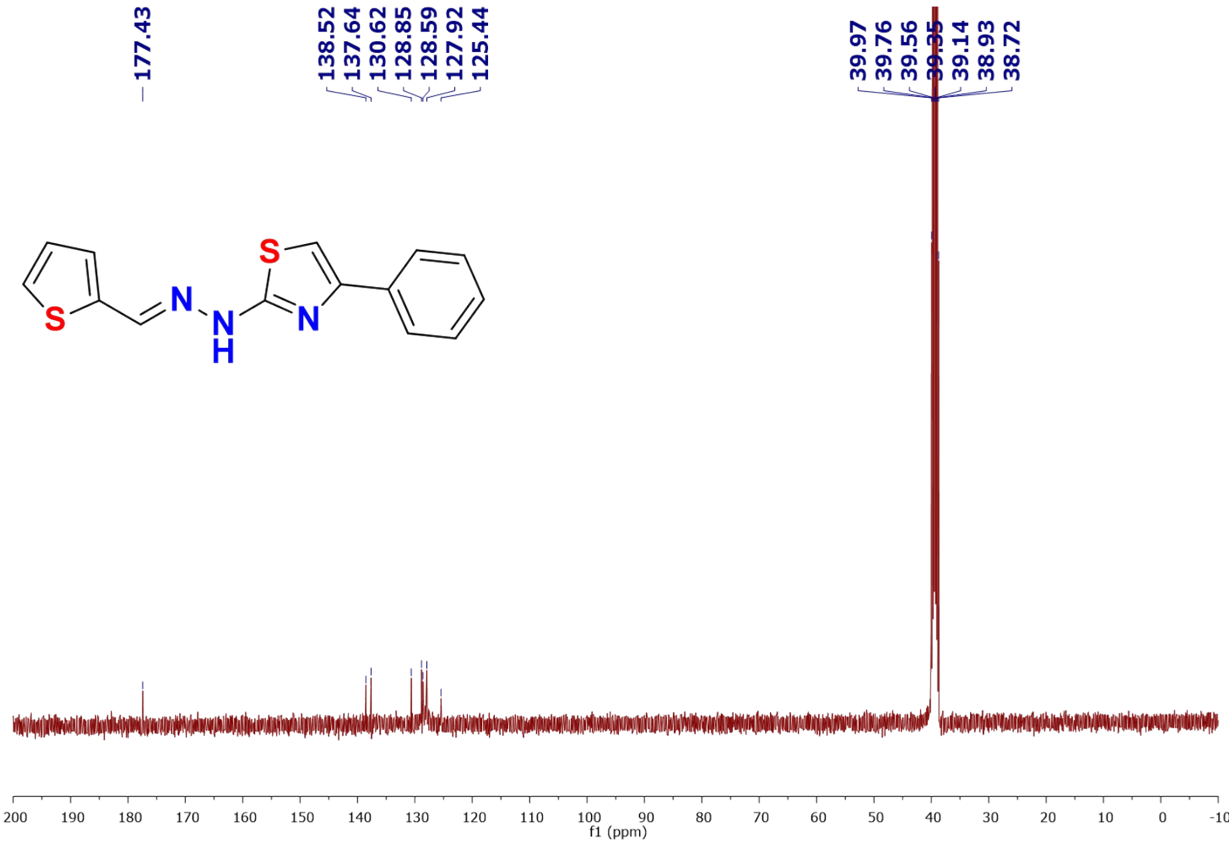


Figure S32. $^{13}C\{^1H\}$ NMR spectrum of **4n** in DMSO-d_6(100 MHz, 300 K)

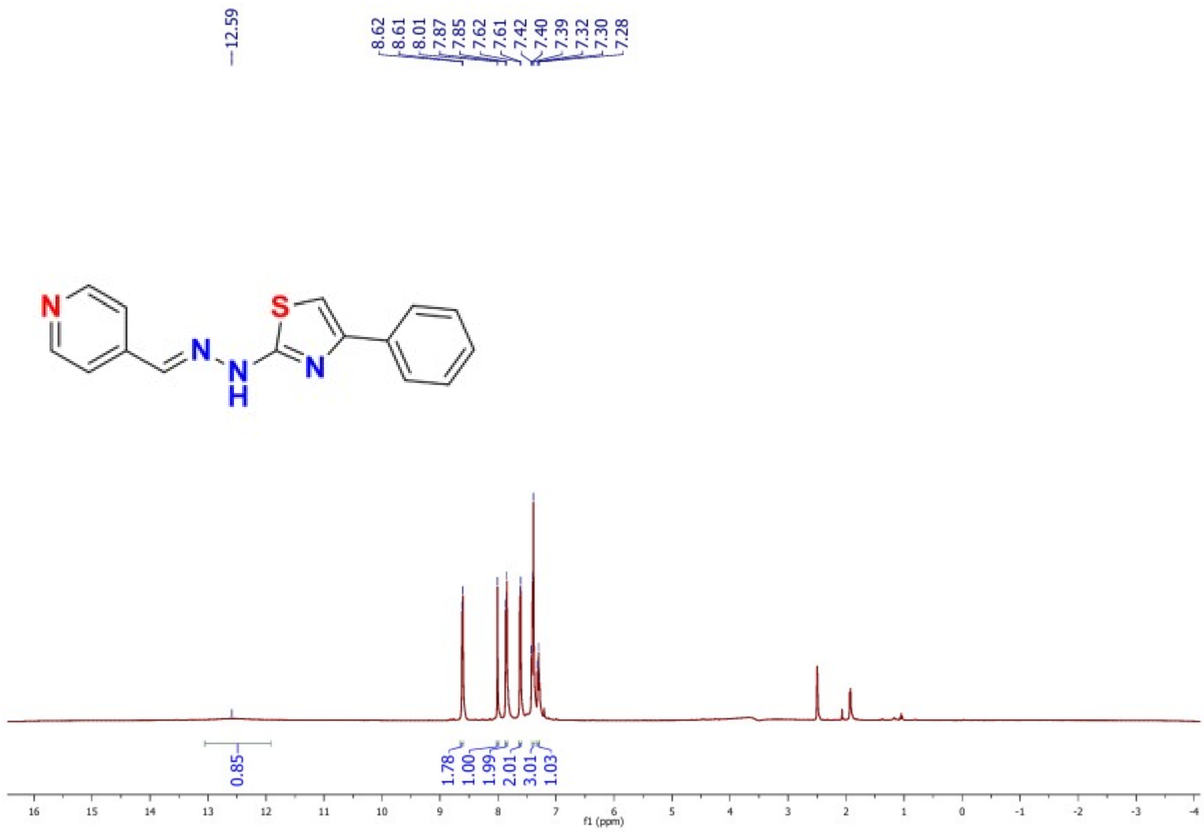


Figure S33. ^1H NMR spectrum of **4o** in DMSO-d_6(400 MHz, 300 K)

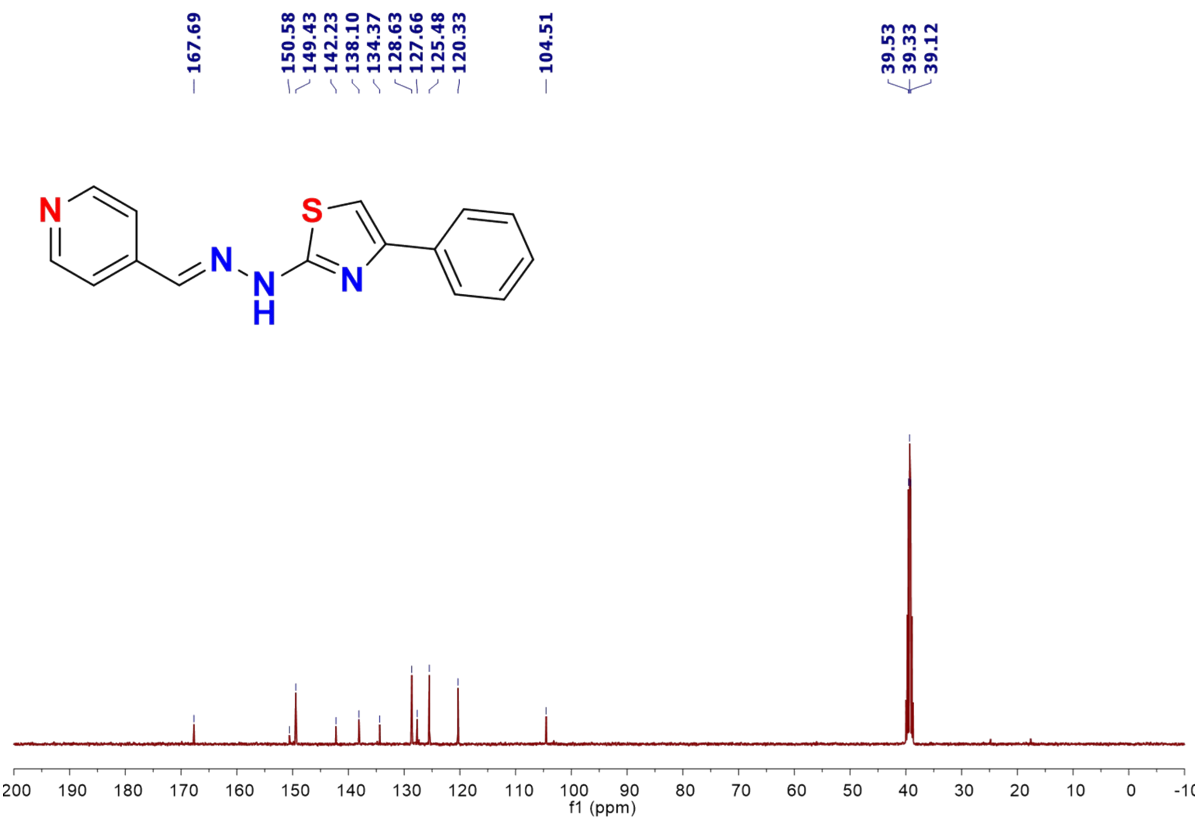


Figure S34. $^{13}C\{^1H\}$ NMR spectrum of **4o** in DMSO-d$_6$(100 MHz, 300 K)

8. NMR spectra of Intermediates:

(i) Benzaldehyde (1a')

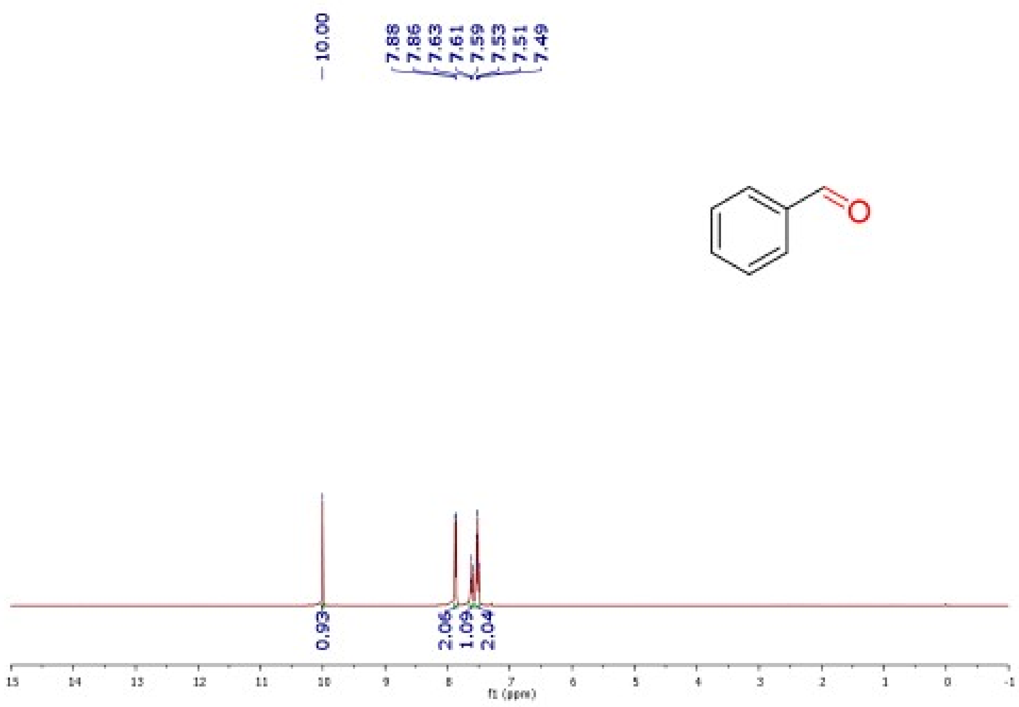


Figure S35. [1]H NMR spectrum of **1a’** in $CDCl_3$(400 MHz, 300 K)

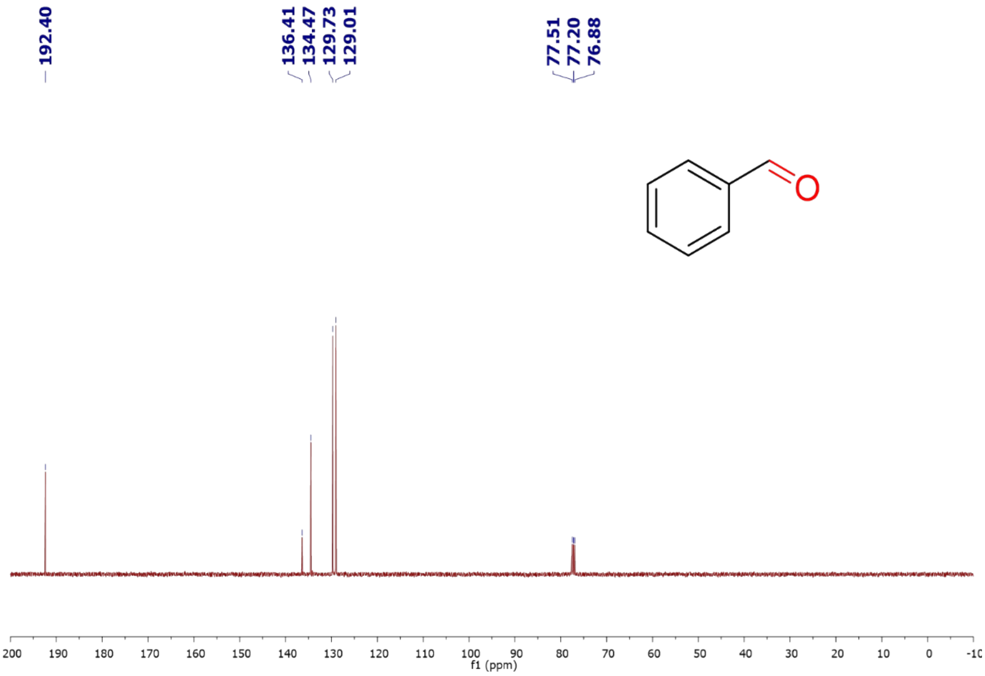


Figure S36. $^{13}C\{^1H\}$ NMR spectrum of**1a’** in $CDCl_3$(100 MHz, 300 K)

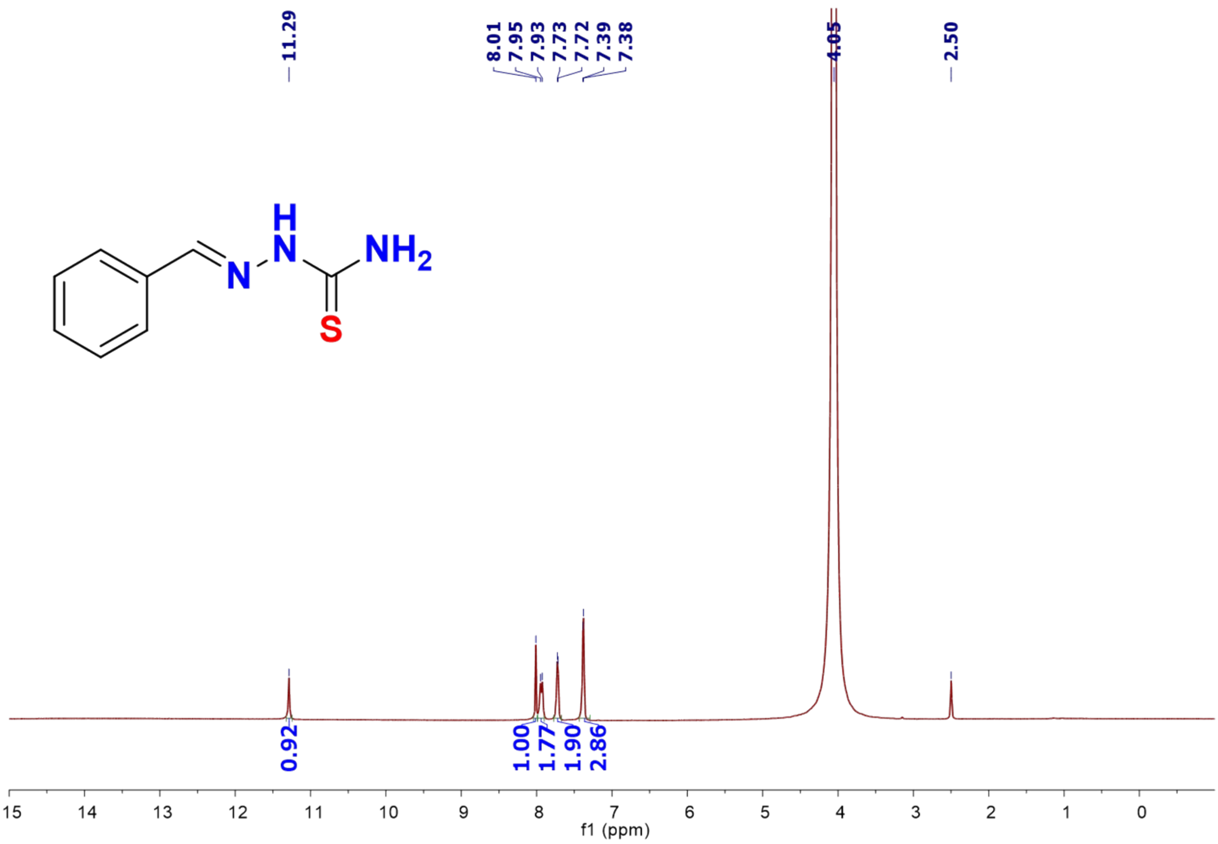


Figure S37. [1]H NMR spectrum of **1a’** in $CDCl_3$(400 MHz, 300 K)

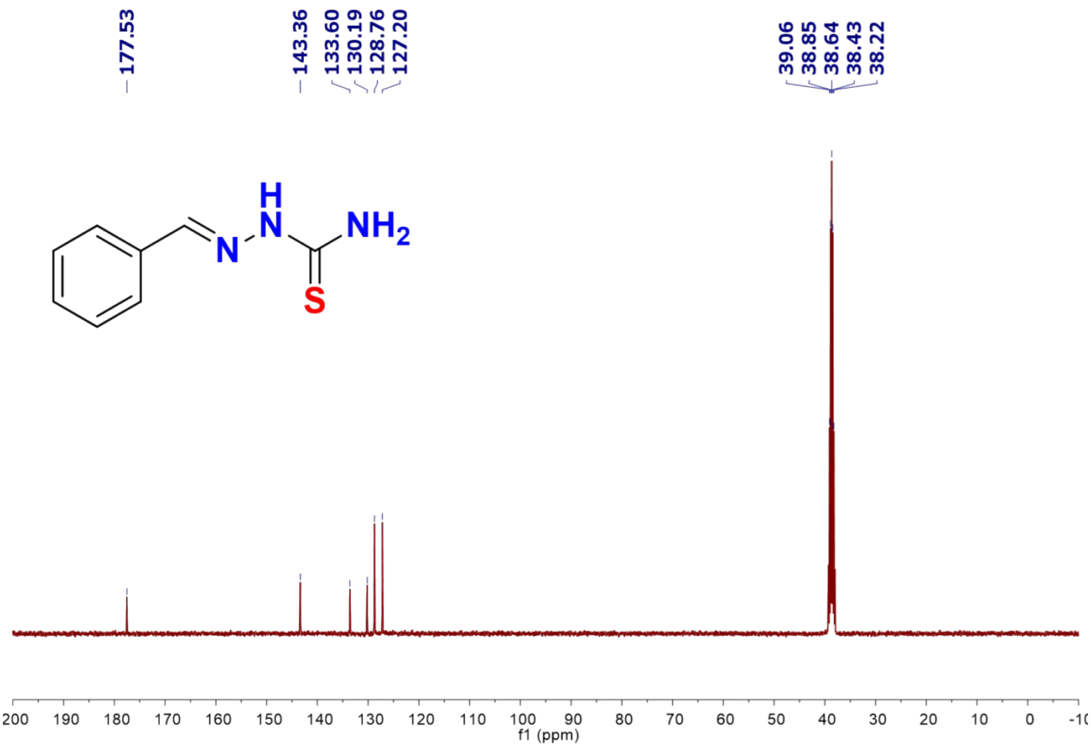


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of**1a'** in $CDCl_3$(100 MHz, 300 K)

9. HRMS Spectra of new catalytic products

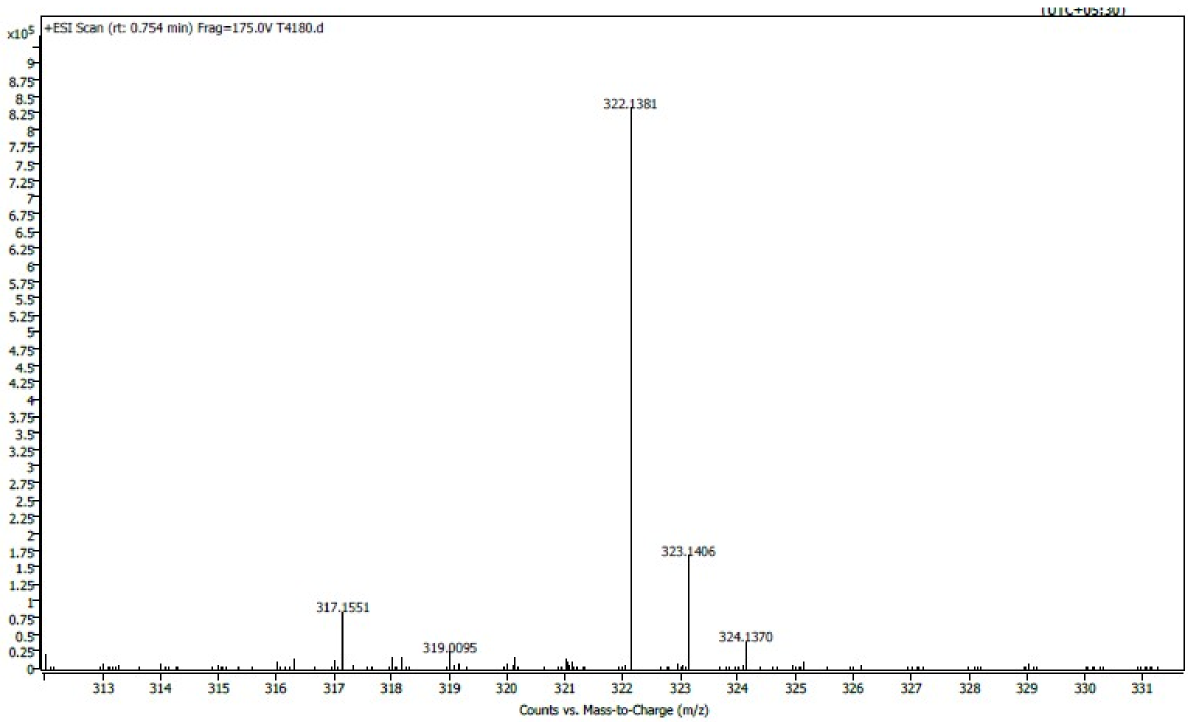


Figure S39. HRMS spectrum of catalytic product **4d ((ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{19}H_{19}N_3S$ 321.1300; Found 322.1381)**

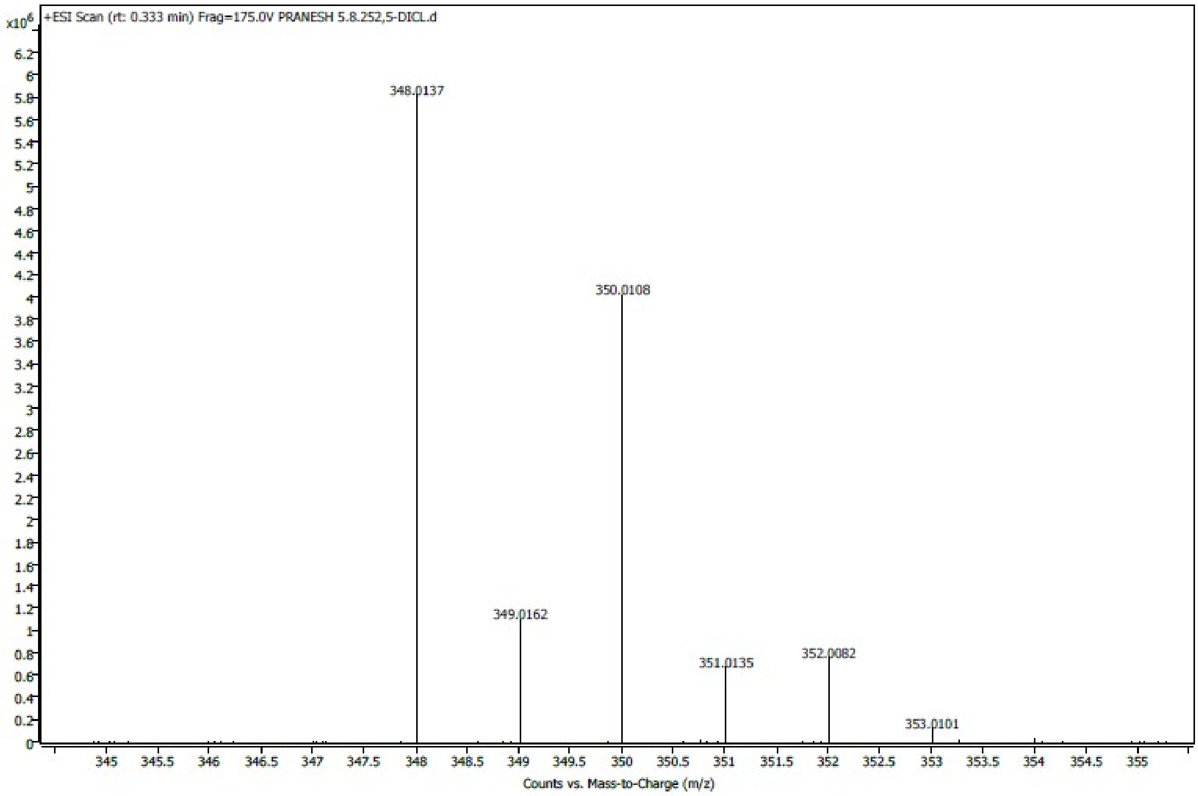


Figure S40. HRMS spectrum of catalytic product **4i((ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{11}Cl_2N_3S$ 347.0051; Found 348.0137)**

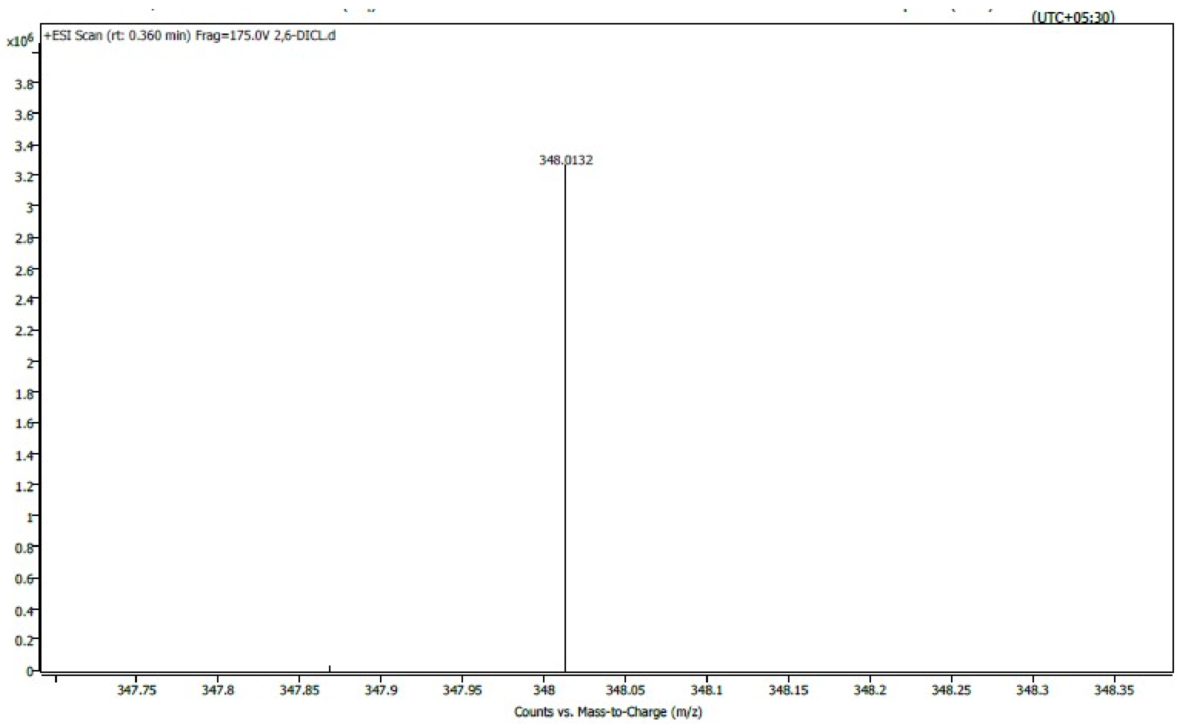


Figure S41. HRMS spectrum of catalytic product **4j ((ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{11}Cl_2N_3S$ 347.0051; Found 348.0132)**

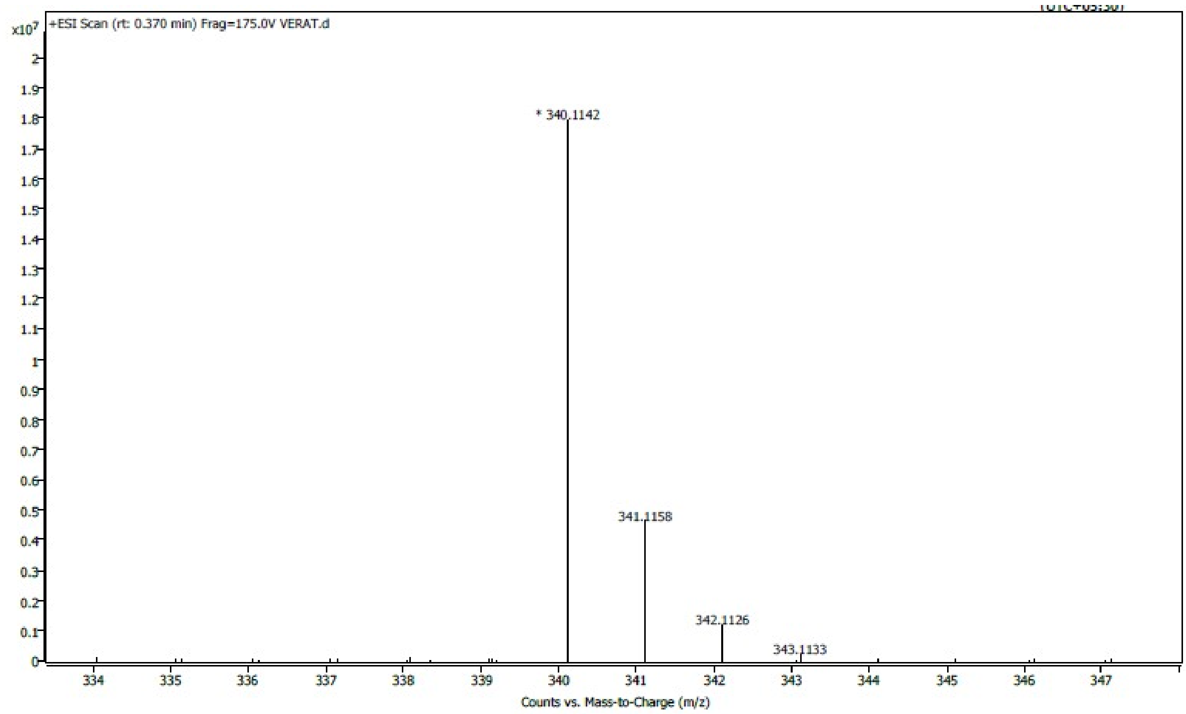


Figure S42. HRMS spectrum of catalytic product **4k ((ESI-TOF) m/z: [M+H]$^+$Calcd for $C_{18}H_{17}N_3O_2S$ 339.1041; Found 340.1142)**

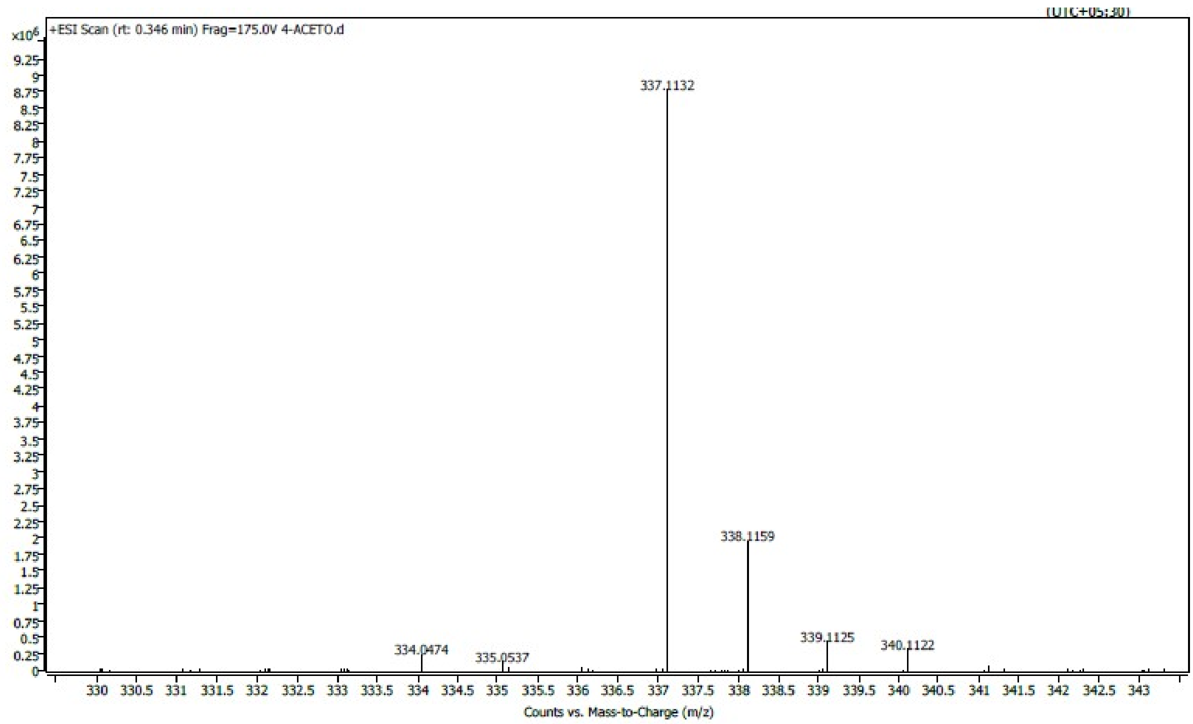


Figure S43. HRMS spectrum of catalytic product **4l((ESI-TOF) m/z: [M+H]$^+$Calcd for $C_{18}H_{16}N_4OS$ 336.1045; Found 337.1132)**

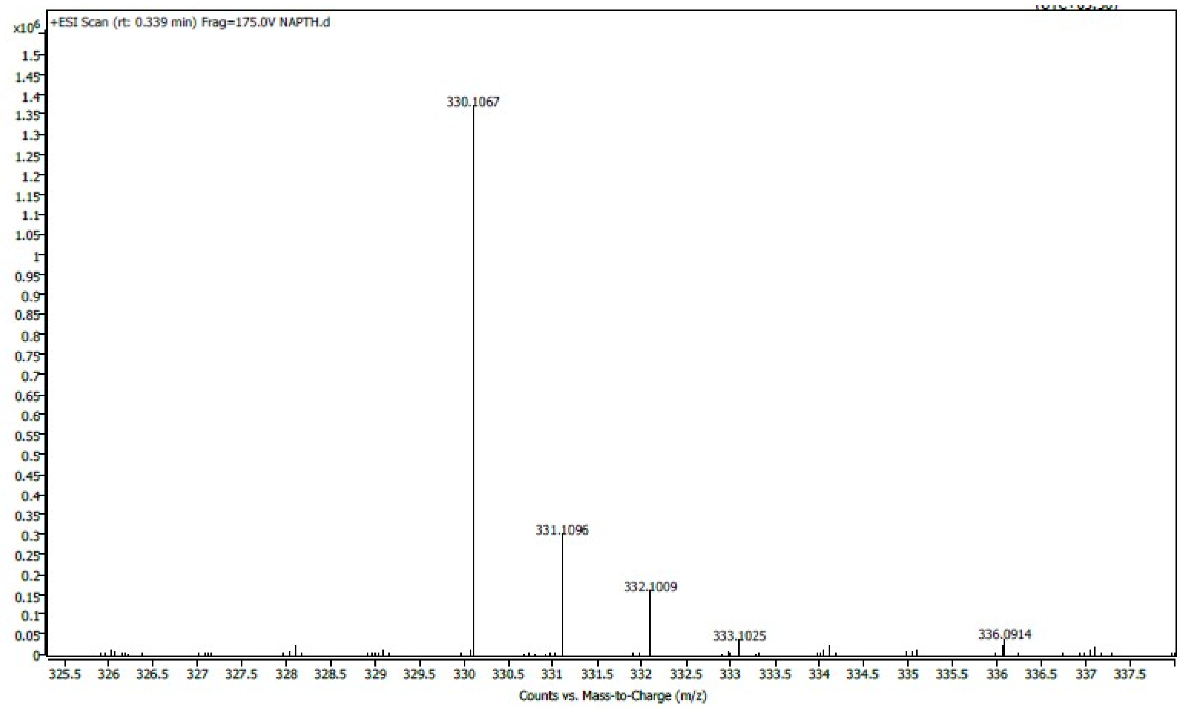


Figure S44. HRMS spectrum of catalytic product **4m((ESI-TOF) m/z: [M+H]$^+$Calcd for $C_{20}H_{15}N_3S$ 329.0987; Found 330.1065)**

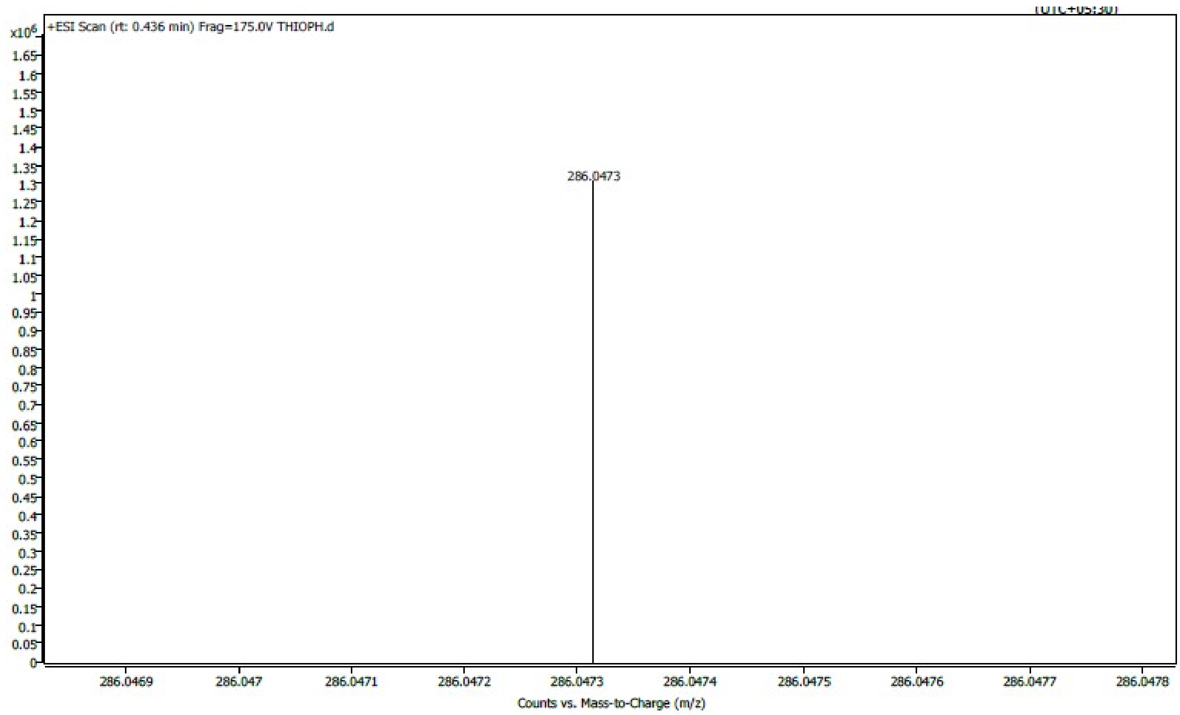


Figure S45. HRMS spectrum of catalytic product **4n ((ESI-TOF) m/z: [M+H]$^+$Calcd for $C_{14}H_{11}N_3S_2$ 285.0394; Found 286.0473)**

10. Confirmation of hydrogen gas

Under N_2 atmosphere, a mixture of Ru (II) catalyst (4 mol%), *t*-BuOK (0.50 mmol), benzyl alcohol (1.0 mmol), thiosemicarbazide (1.0 mmol) and 2-bromoacetophenone (1.0 mmol) was dissolved in 3 mL of toluene, and the mixture was placed in an oil bath and heated at 110 °C for 4 h. Then, the gaseous reaction mixture has been analyzed on GC-TCD detector to witness the liberation of hydrogen gas. Injection temperature = 50 °C, column temperature = 80 °C, detector temperature (TCD) = 180 °C, carrier gas = He_2.

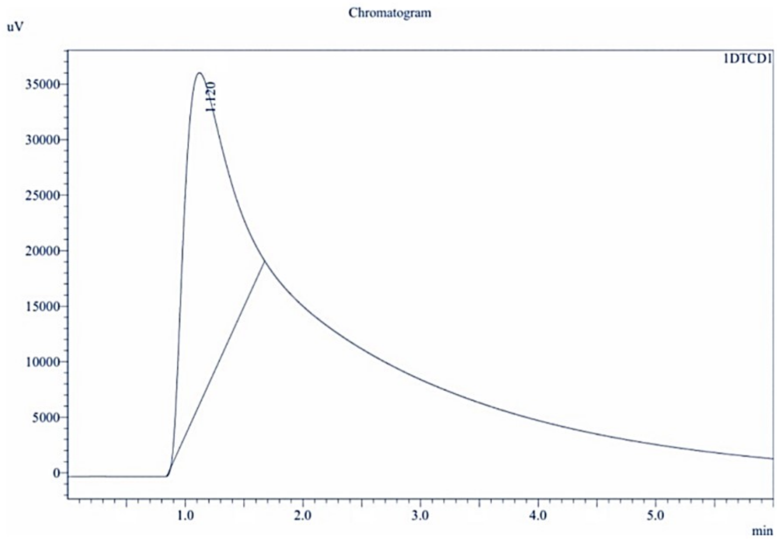


Figure S46. Chromatogram of H_2

11. CHARACTERIZATION OF CATALYTIC PRODUCTS

(E)-2-(2-benzylidenehydrazinyl)-4-phenylthiazole(4a)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and benzyl alcohol (108.14 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:241.13 mg, 86%). ^{1}H NMR (400 MHz, DMSO) δ 12.18 (s, 1H), 8.00 (s, 1H), 7.59 (s, 1H), 7.28 (t, 10H). ^{13}C NMR (100 MHz, DMSO) δ 165.7, 141.3, 134.2, 133.8, 128.8, 128.4, 128.2, 127.8, 127.4, 127.1, 125.9, 125.1, 103.3.TON= 21.5, TOF=1.79 h^{-1}

(E)-2-(2-(4-methoxybenzylidene)hydrazinyl)-4-phenylthiazole (4b)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 4-Methoxylbenzyl alcohol (138.16 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:287.07 mg, 92%). ^{1}H NMR (400 MHz, DMSO) δ 12.06 (s, 1H), 8.01 (s, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 16.6, 8.2 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.31 (d, *J* = 10.5 Hz, 2H), 7.22 (t, 1H), 6.99 (t, 3H), 3.79 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 168.3, 166.0, 160.2, 150.3, 141.3, 134.6, 128.5, 128.2, 127.7, 127.4, 126.9, 125.4, 114.3, 103.3, 55.2.TON= 23, TOF=1.91 h^{-1}

(E)-2-(2-(4-methylbenzylidene)hydrazinyl)-4-phenylthiazole (4c)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 4-Methylbenzyl alcohol (122.17 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:264.24 mg, 90%). ^{1}H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 8.00 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (s, 2H), 7.29 (s, 2H), 7.23 (s, 2H), 2.30 (s, 3H).^{13}C NMR (100 MHz, DMSO) δ 168.3, 149.5, 142.1, 139.1, 134.1, 131.5, 129.4, 128.5, 127.6, 126.3, 125.5, 103.6, 20.9.TON= 22.5, TOF=1.87 h^{-1}

(E)-2-(2-(4-isopropylbenzylidene)hydrazinyl)-4-phenylthiazole (4d): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 4-isopropylbenzyl alcohol (150.22 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:288.09 mg, 89%). ^{1}H NMR (400 MHz, DMSO) δ 11.42 (s, 1H), 8.21 (s, 1H), 8.04 (s, 1H), 7.96 (s, 1H), 7.86 (s, 1H), 7.72 (d, *J* = 6.4 Hz, 2H), 7.39 (s, 2H), 7.28 (s, 4H), 3.38 (s, 1H), 1.20 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 177.7, 150.4, 142.3, 131.8, 128.5, 127.3, 126.5, 125.4, 103.1, 33.3, 23.6.(ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{19}H_{19}N_3S$ 321.1300; Found 322.1381.TON= 22.2, TOF=1.85 h^{-1}

(E)-2-(2-(4-chlorobenzylidene)hydrazinyl)-4-phenylthiazole (4e)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 4-cholorobenzyl alcohol (142.58 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:268.09 mg, 84%). ^{1}H NMR (400 MHz, DMSO) δ 12.31 (s, 1H), 8.04 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.69 (d,*J* = 6.4 Hz, 2H), 7.50 (d, *J* = 6.4 Hz3H), 7.42 (t, 3H). ^{13}C NMR (100 MHz, DMSO) δ 168.0, 150.1, 140.1, 134.3, 133.6, 133.2, 128.8, 128.5, 127.8, 127.6, 125.6, 125.5, 103.8.

(E)-2-(2-(3-bromobenzylidene)hydrazinyl)-4-phenylthiazole (4f)[8]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 3-bromobenzyl alcohol (187.04 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:290.81 mg, 81%). ^{1}H NMR (400 MHz, DMSO) δ 11.45 (s, 1H), 8.14 (s, 2H), 7.93 (s, 1H), 7.78 (s, 1H), 7.59 - 7.30 (m, 7H). ^{13}C NMR (100 MHz, DMSO) δ 178.1, 168.0, 140.4, 139.3, 136.6, 132.2, 130.6, 128.8, 128.5, 126.9, 125.4, 122.3, 103.9.

(E)-2-(2-(2-chlorobenzylidene)hydrazinyl)-4-phenylthiazole (4g): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 2-cholorobenzyl alcohol (142.58 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:231.41 mg, 73%). ^{1}H NMR (400 MHz, DMSO) δ 11.62 (s, 1H), 8.46 (d, *J* = 2.8 Hz, 1H), 8.37 (d, *J* = 3.0 Hz, 1H), 8.26 (t, 2H), 8.10 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 3.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 178.1, 167.8, 150.5, 138.2, 136.8, 134.4, 133.0, 132.1, 131.5, 131.3, 131.1, 130.5, 129.8, 129.6, 128.5, 128.1, 127.5, 127.5, 127.3, 127.2, 126.1, 125.4, 103.9.

(E)-2-(2-(2-nitrobenzylidene)hydrazinyl)-4-phenylthiazole (4h)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 2-nitrobenzyl alcohol (153.114 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:318.62 mg, 59%). ^{1}H NMR (400 MHz, DMSO) δ 11.73 (s, 1H), 8.45 (s, 1H),8.40 - 8.38 (m, 2H), 8.10 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.28 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 178.3, 148.1, 147.3, 137.3, 133.4, 133.3, 130.3, 129.7, 128.6, 128.4, 128.2, 128.2, 127.6, 127.5, 125.4, 124.6, 124.4.

(E)-2-(2-(2,5-dichlorobenzylidene)hydrazinyl)-4-phenylthiazole (4i): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 2,5-dicholorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:188.06 mg, 54%). ^{1}H NMR (400 MHz, DMSO) δ 11.77 (s, 1H), 8.41 (s, 1H), 8.31 (s, 1H), 7.53 (d, *J* = 7.0 Hz, 4H), 7.40 (t, *J* = 38.2, 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 167.6, 150.5, 136.8, 135.3, 134.3, 133.2, 132.2, 131.6, 130.5, 129.8, 128.5, 127.6, 125.4, 125.0, 104.2.(ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{11}Cl_2N_3S$ 347.0051; Found 348.0137.

(E)-2-(2-(2,6-dichlorobenzylidene)hydrazinyl)-4-phenylthiazole (4j): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 2,6-dicholorobenzyl alcohol (177.03 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:176.18 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.49 (s, 1H), 8.38 (d, *J* = 5.3 Hz, 2H), 8.34-8.247 (m, 2H), 7.82-7.27 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 169.7, 167.8, 137.5, 133.8, 133.3, 130.8, 129.5, 129.2, 129.0, 128.4, 128.3, 125.3, 125.2, 104.0. (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{16}H_{11}Cl_2N_3S$ 347.0051; Found 348.0132.

(E)-2-(2-(3,4-dimethoxybenzylidene)hydrazinyl)-4-phenylthiazole (4k): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 3,4-dimethoxybenzyl alcohol (168.19 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:227.38 mg, 67%). ^{1}H NMR (400 MHz, DMSO) δ 12.06 (s, 1H), 7.97 (s, 1H), 7.85 (d, *J* = 5.9 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 3H), 7.29 – 7.27 (m, 3H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.98 (s, 2H), 3.50 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 168.3, 150.3, 150.0, 148.9, 141.5, 134.6, 128.5, 128.5, 127.4, 127.1, 125.4, 120.2, 111.6, 108.2, 103.3, 55.4, 55.3. (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{18}H_{17}N_3O_2S$ 339.1041; Found 340.1142.

(E)-N-(4-((2-(4-phenylthiazol-2-yl)hydrazono)methyl)phenyl)acetamide(4l):
According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol)

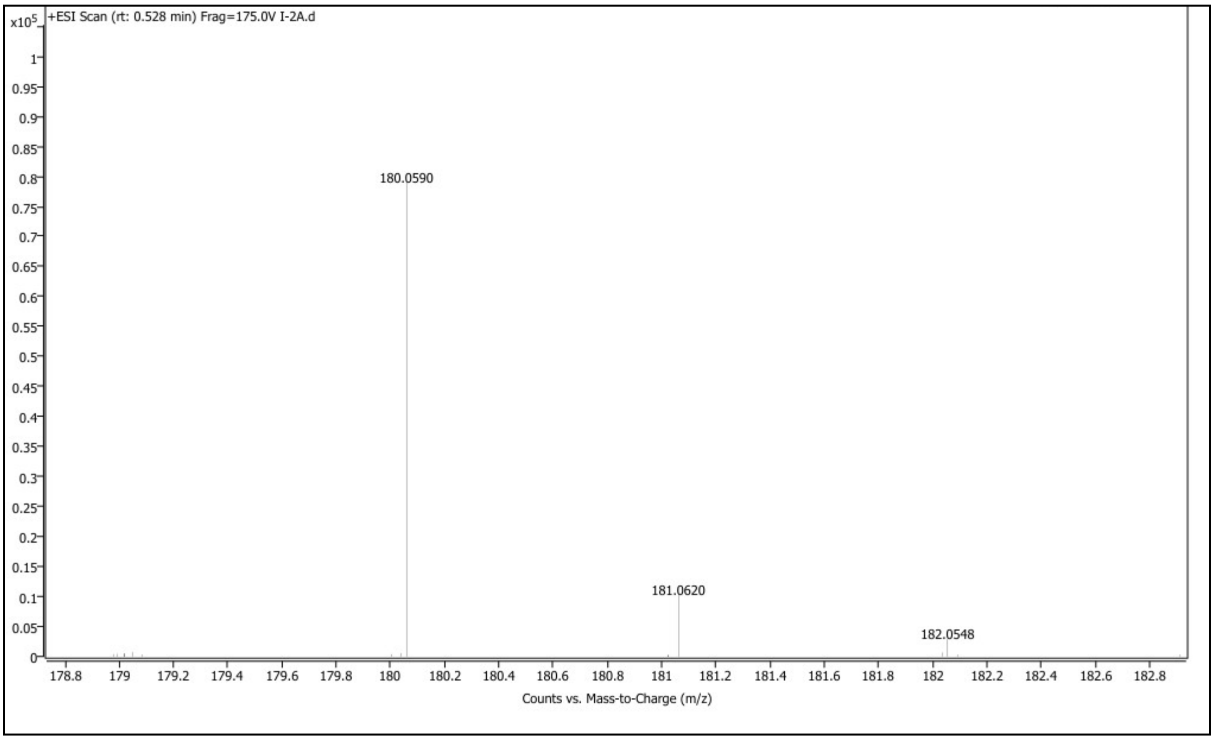
and 4-acetamidobenzyl alcohol (165.19 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:241.76 mg, 71%). ^{1}H NMR (400 MHz, DMSO) δ 12.05 (s, 1H), 10.12 (s, 1H), 7.98 (d, *J* = 4.8 Hz, 1H), 7.85 (d, *J* = 6.3, 2.3 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 14.7, 8.6 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.2 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 169.8, 168.2, 149.8, 140.2, 134.6, 128.5, 128.5, 127.9, 126.8, 125.4, 119.0, 103.4,17.6. (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{18}H_{16}N_4OS$ 336.1045; Found 337.1132.

(E)-2-(2-(naphthalen-1-ylmethylene)hydrazinyl)-4-phenylthiazole (4m): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 1-naphthalenemethanol (158.20 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:248.32 mg, 78%). ^{1}H NMR (400 MHz, DMSO) δ 11.48 (s, 3H), 11.48 (s, 1H), 8.90 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 2.3 Hz, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 4.3 Hz, 3H, 7.60 – 7.56 (m, 4H), 7.40 – 7.42 (m, 3H), 7.37 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 177.7, 140.9, 133.3, 130.2, 129.1, 128.80, 127.2, 126.1, 125.7, 125.5, 122.8s. (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{20}H_{15}N_3S$ 329.0987; Found 330.1065.

(E)-4-phenyl-2-(2-(thiophen-2-ylmethylene)hydrazinyl)thiazole (4n): According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and thiophene-2-methanol (144.17 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:189.32 mg, 66%). ^{1}H NMR (400 MHz, DMSO) δ 11.44 (s, 1H), 8.23 (s, 2H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.56 (s, 2H), 7.44 (d, *J* = 3.5 Hz, 1H), 7.56 (s, 1H), 7.43 (d, *J* = 4.7 Hz, 2H), 7.11 – 7.09 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 177.4, 138.5, 137.6, 130.6, 128.8, 128.5, 127.9, 125.4. (ESI-TOF) m/z: $[M+H]^+$Calcd for $C_{14}H_{11}N_3S_2$ 285.0394; Found 286.0473.

(E)-4-phenyl-2-(2-(pyridin-4-ylmethylene)hydrazinyl)thiazole (4o)[7]: According to the general procedure, the titled compound was synthesized by using 2-bromocaetophenone (199.04 mg, 1.0 mmol), thiosemicarbazide (91.13 mg, 1.0 mmol) and 4-pyridinebenzyl alcohol (109.13 mg, 1.0 mmol). Column chromatography (SiO_2-60-120 mesh, Eluent: *n*-hexane: EtOAc = 20:4) as white solid (yield:175.14 mg, 62%). ^{1}H NMR (400 MHz, DMSO) δ 12.59 (s, 1H), 8.62 (d, *J* = 6.0 Hz, 2H), 8.01 (s, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 6.0 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 167.6, 150.5, 149.4, 142.2, 138.1, 134.3, 128.6, 127.6, 125.4, 120.3, 104.51.

12.HRMS Spectra of 2-benzylidenehydrazinecarbothioamide (E)



12.HRMS Spectrum of 2-benzylidenehydrazinecarbothioamide (E) intermediate

(m/z: $[M+H]^+$Calcd for $C_8H_9N_3S$ 180.0595; Found 180.0590)

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