Synthesis of Novel Organic Ni (II) N-isonicotinoylhydrazine-Carbothioamide Complexes and their Application in the Oxygen Evolution Reactions

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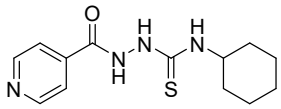
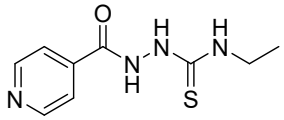
1. General Information

Reagent were purchased from commercial sources and used as directly without further purification unless mentioned otherwise. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra are recorded on Bruker 400 MHz spectrometer. Ultra-pure water (18.2 MΩ cm^{-1}) was purified throughout the work with a Mill-Q water purification system (Millipore, Bedford, France). Chemical shifts were reported in parts per million (ppm) referenced to tetramethylsilane (0.00 ppm) or residue of $CHCl_3$ (7.26 ppm). The spectra were collected in $CDCl_3$. Data are indicated as follows: s = singlet; d = doublet; dd = doublet of doublet; t= triplet; m = multiplet; q = quartet. The infrared （IR）spectra were measured The infrared （IR）spectra were measured for a sample dispersed in a KBr disk or charged between KBr disks and are reported in cm^{-1} for a sample dispersed in a KBr disk or charged between KBr disks and are reported in cm^{-1}. Raman spectra were obtained from High-Resolution Rama spectrometer. The electrochemical activities were evaluated using an electro chemical workstation (CHI 660E, Chen-Hua, China).

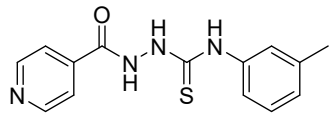
2. Characterizations of Ligand 1-5.



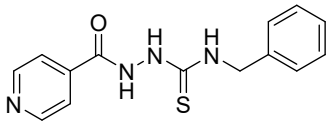
N-cyclohexyl -2-isonicotinoylhydrazine-1-carbothioamide (white solid, 2.49 g, 89% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.57 (s, 1H), 9.30 (s, 1H), 8.92-8.65 (m, 2H), 7.83 (d, J = 11.2 Hz, 2H), 7.80 (s, 1H), 4.13 (s, 1H), 1.93-1.51 (m, 5H), 1.37-0.97 (m, 5H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 180.51, 164.35, 150.24, 139.65, 121.71, 53.23, 31.90, 25.24, 25.04.



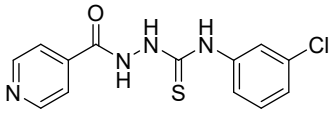
N-ethyl-2-isonicotinoylhydrazinocarbothioamides (white solid, 2.09 g, 93.1%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 9.38 (s, 1H), 8.89-8.73 (m, 2H), 8.20 (s, 1H), 7.92-7.77 (m, 2H), 3.47 (p, J = 6.8 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 181.30, 164.47, 150.22, 139.58, 121.70, 38.59, 14.51.



N-(m-tolylbenzene)-2-isonicotinoylhydrazinocarbothioamide: (white solid, 2.35g, 82.1%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 10.09 – 9.69 (m, 2H), 8.78 (d, J = 1.6 Hz, 1H), 8.77 (d, J = 1.7 Hz, 1H), 7.99-7.75 (m, 2H), 7.23 (dt, J = 14.4, 6.9 Hz, 3H), 7.09-6.93 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 180.84, 164.51, 150.21, 139.62, 139.01, 137.31, 127.91, 126.58, 125.89, 123.28, 121.73, 20.97.



N-benzyl-2-isonicotinoylhydrazinocarbothioamide (white solid, 2.55 g, 89.1%) ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 9.61 (s, 1H), 8.85-8.77 (m, 1H), 8.77-8.60 (m, 2H), 7.92-7.77 (m, 2H), 7.31 (s, 4H), 7.22 (q, J = 4.1 Hz, 1H), 4.75 (d, J = 5.1 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 182.14, 164.55, 150.22, 139.54, 139.32, 128.09, 127.05, 126.66, 121.71, 46.77.



O-(3-Chlorophenyl)-2-isonicotinoylhydrazinocarbothioamide (white solid, 2.09 g, 68.1%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 (s, 1H), 10.02 (s, 1H), 9.92 (s, 1H), 8.86-8.74 (m, 2H), 7.86 (d, J = 5.9 Hz, 2H), 7.58 (s, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 180.87, 164.50, 150.27, 140.65, 139.46, 132.09, 129.63, 125.38, 124.93, 124.36, 121.69.

3. IR spectra of the Ligand-1

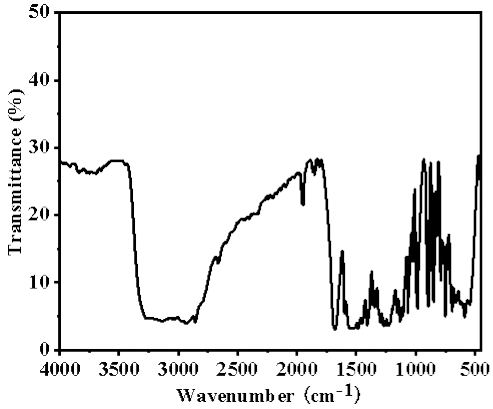


Figure S1. IR spectra of the **Ligand-1**

4. The CV curves s of Ni complexes

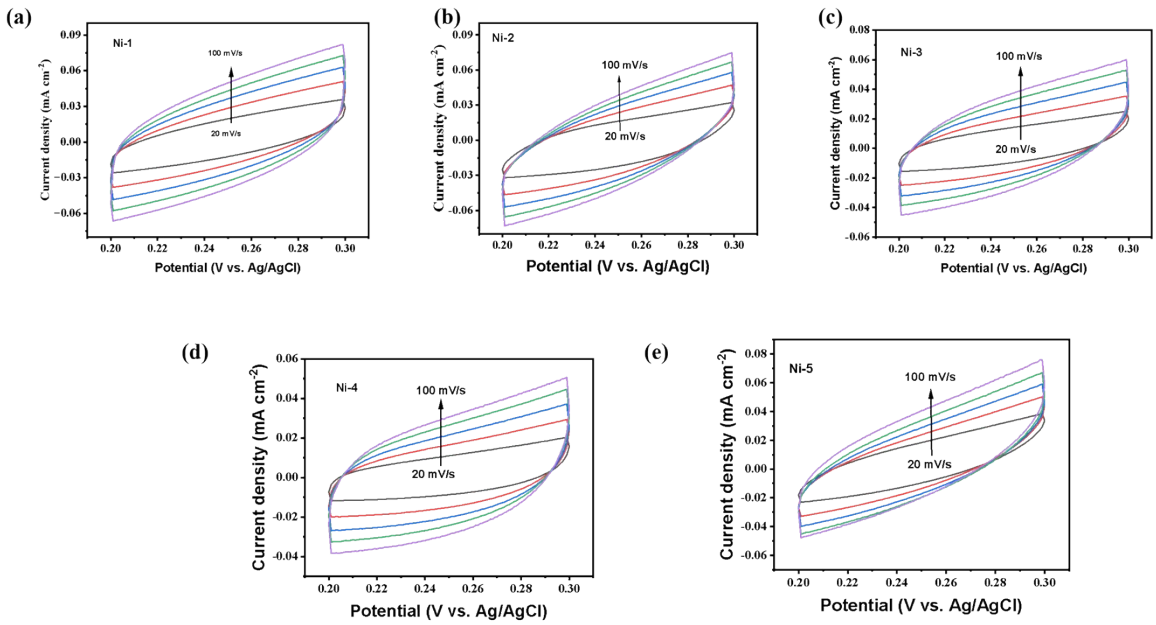


Figure S2. The **CV** curves with different scan rates of **Ni-1**~**Ni-5** complexes

5. XPS of Ni-1 complex

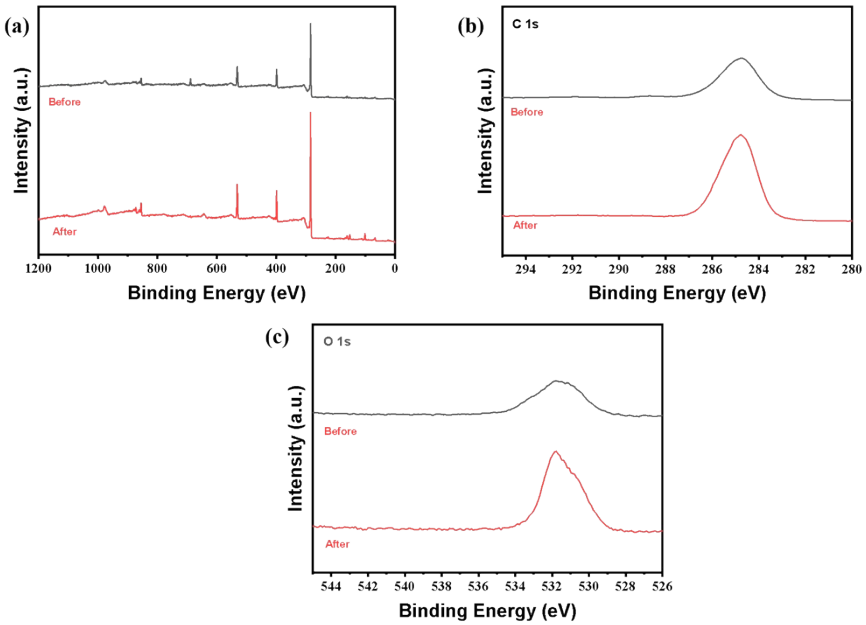


Figure S3. (a) XPS of **Ni-1** complex survey, (b) C 1s scan, (c) O 1s scan.

6. Infrared spectra of Ni-1 complex

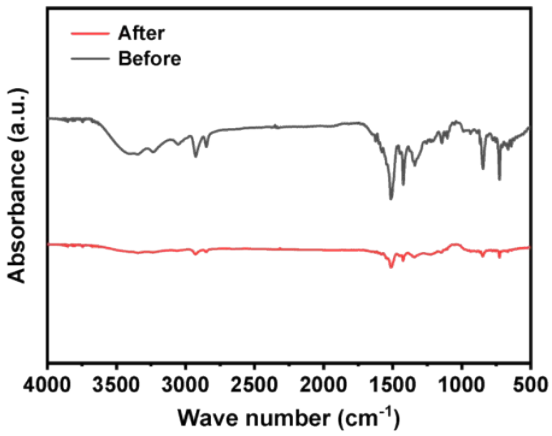


Figure S4. Infrared spectra before and after stability testing of **Ni-1** complex

NMR spectra

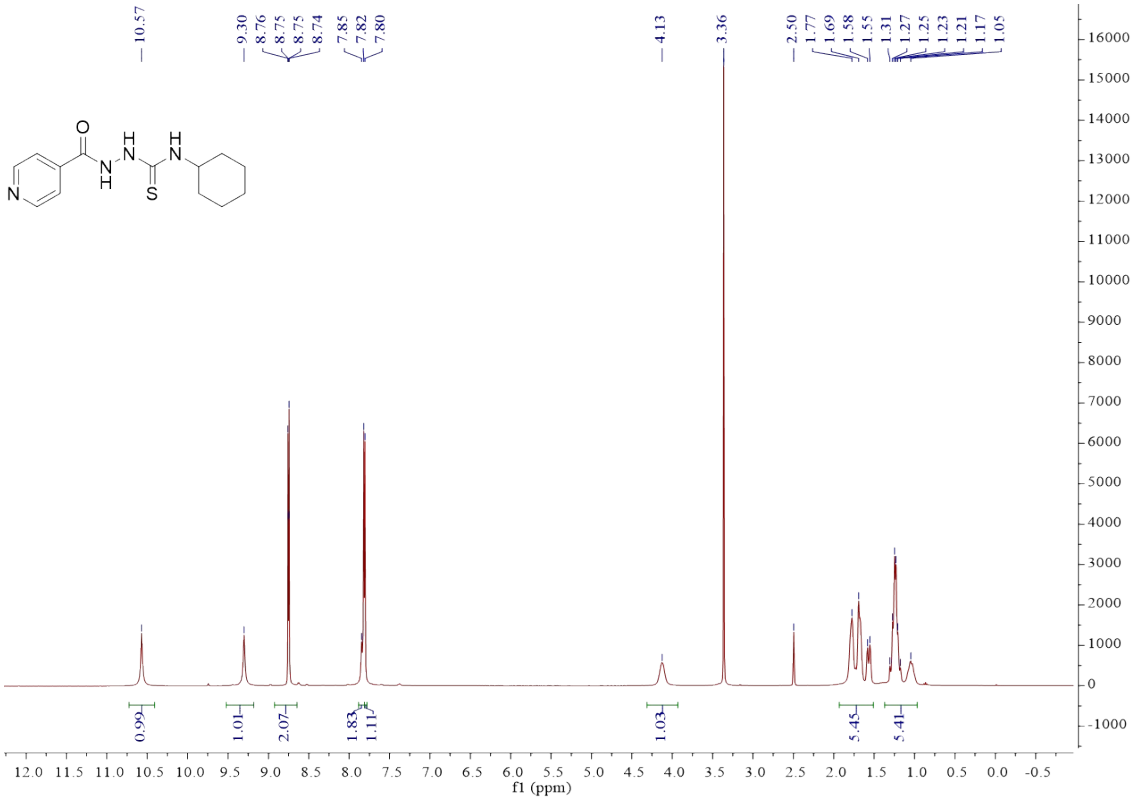


Figure S5. ^{1}H NMR spectrum of N-cyclohexyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)

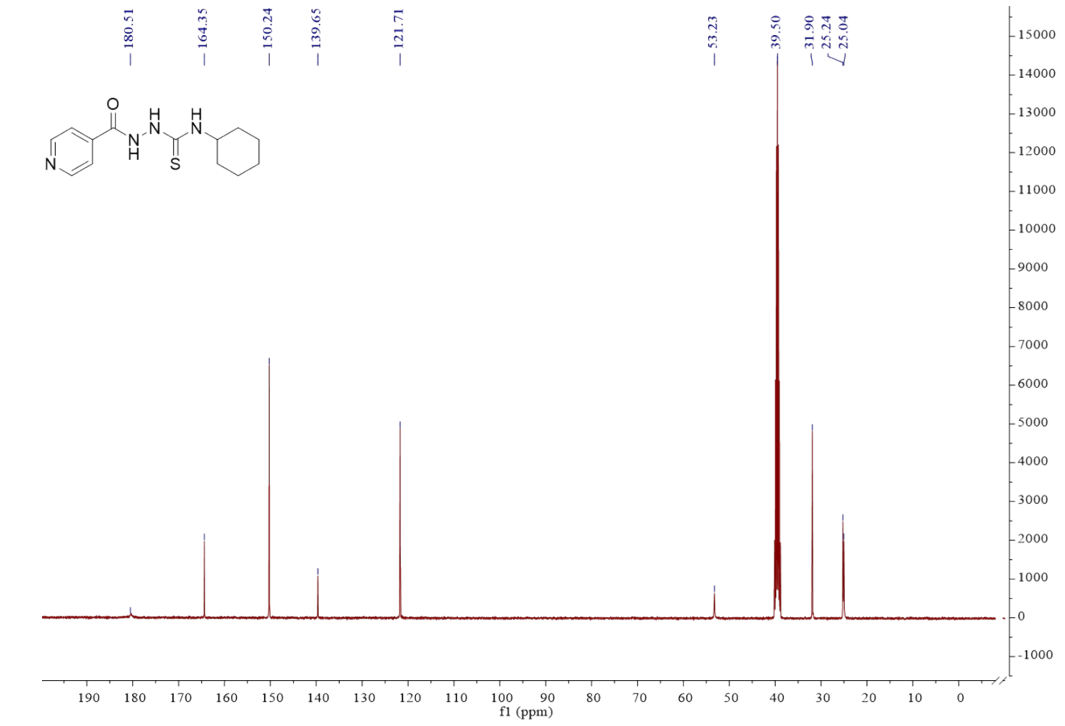


Figure S6. ^{13}C NMR spectrum of N-cyclohexyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)

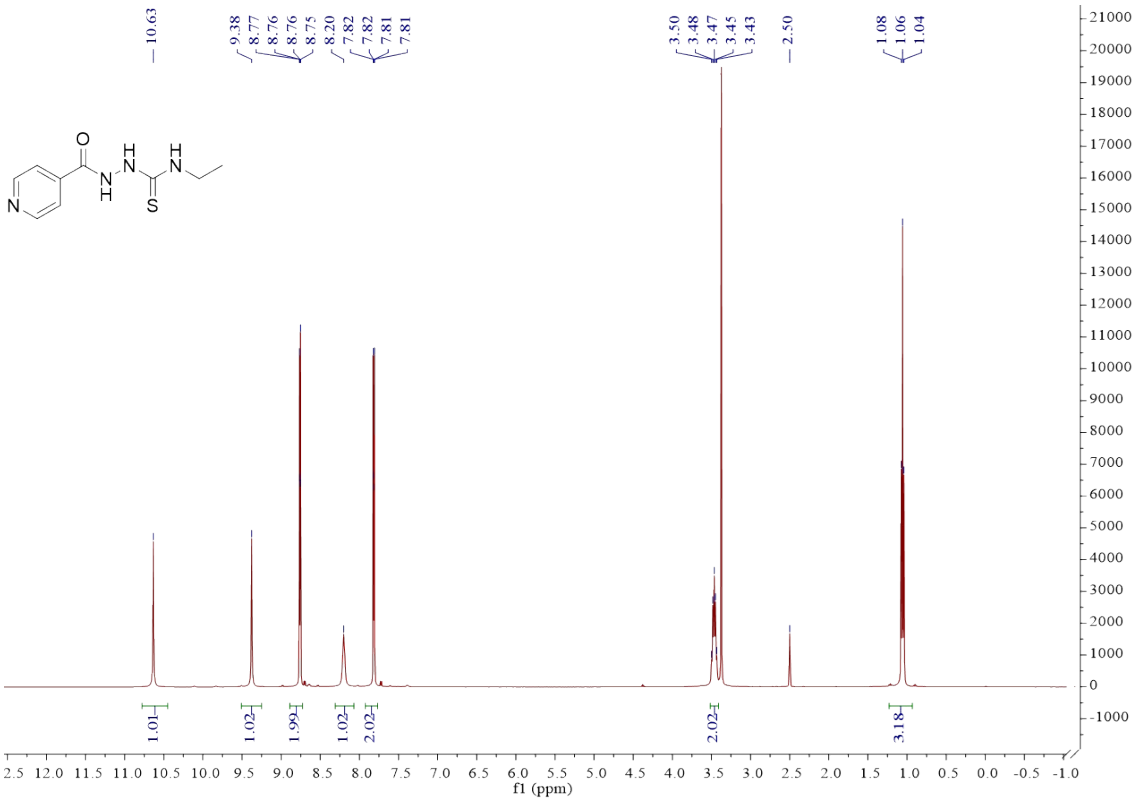


Figure S7. ^{1}H NMR spectrum of N-ethyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 400 M)

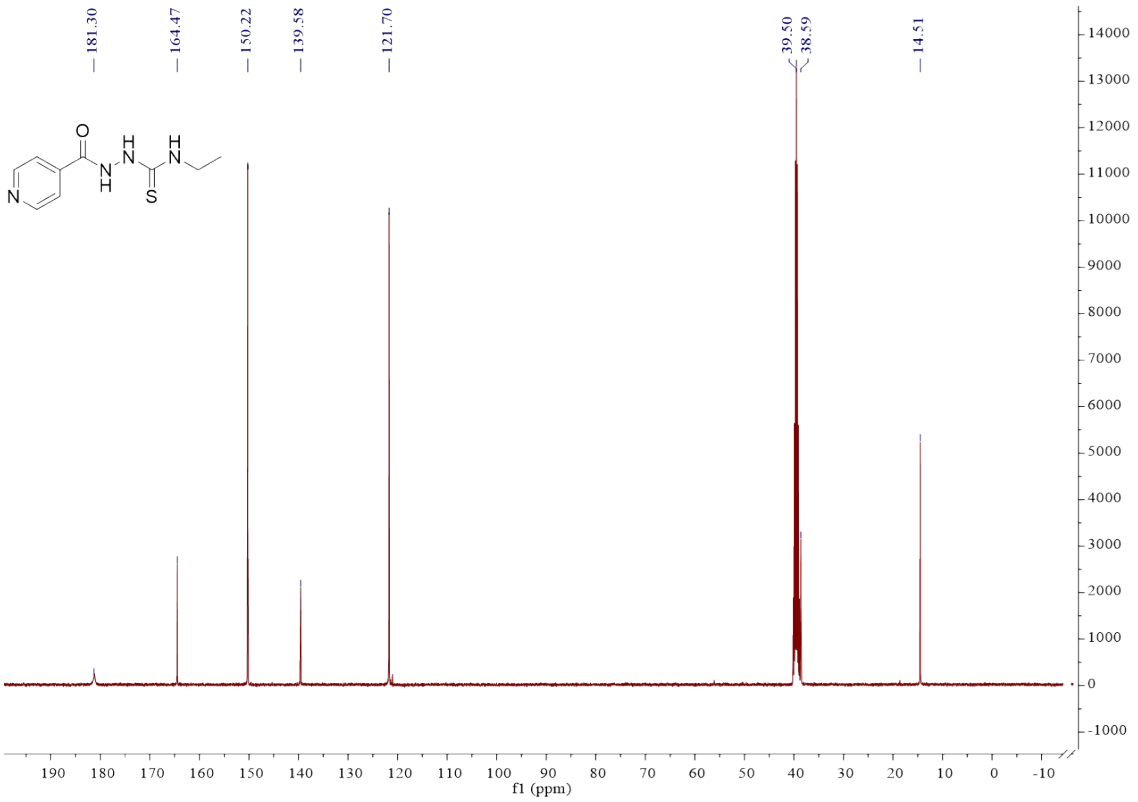
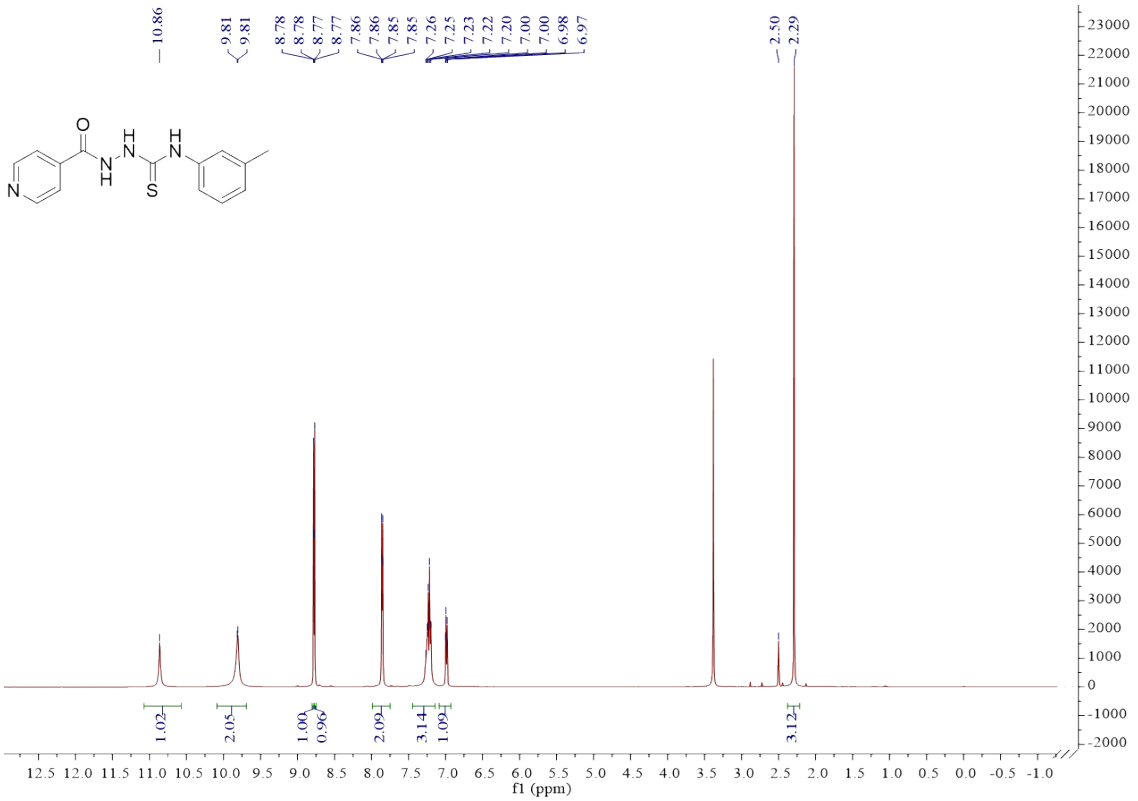


Figure S8. ^{13}C NMR spectrum of N-ethyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)



Figue S9. ^{1}H NMR spectrum of N-(m-tolylbenzene)-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 400 M)

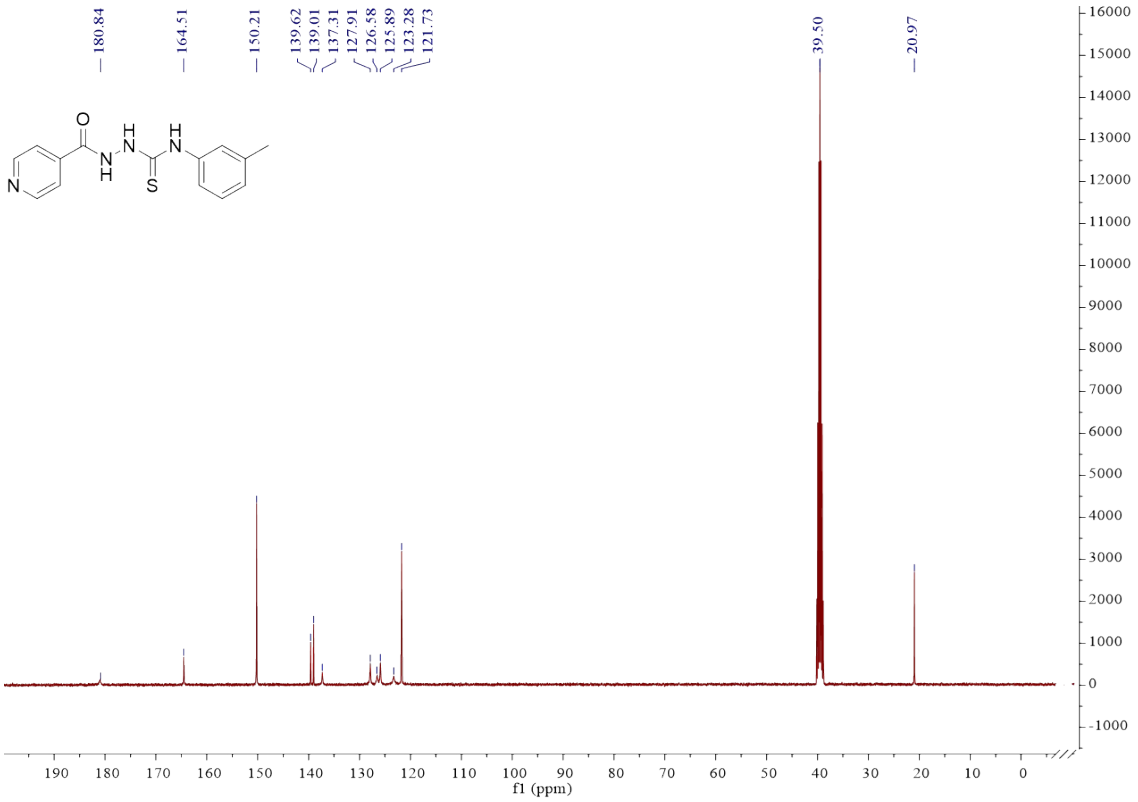


Figure S10. ^{13}C NMR spectrum of N-(m-tolylbenzene)-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)

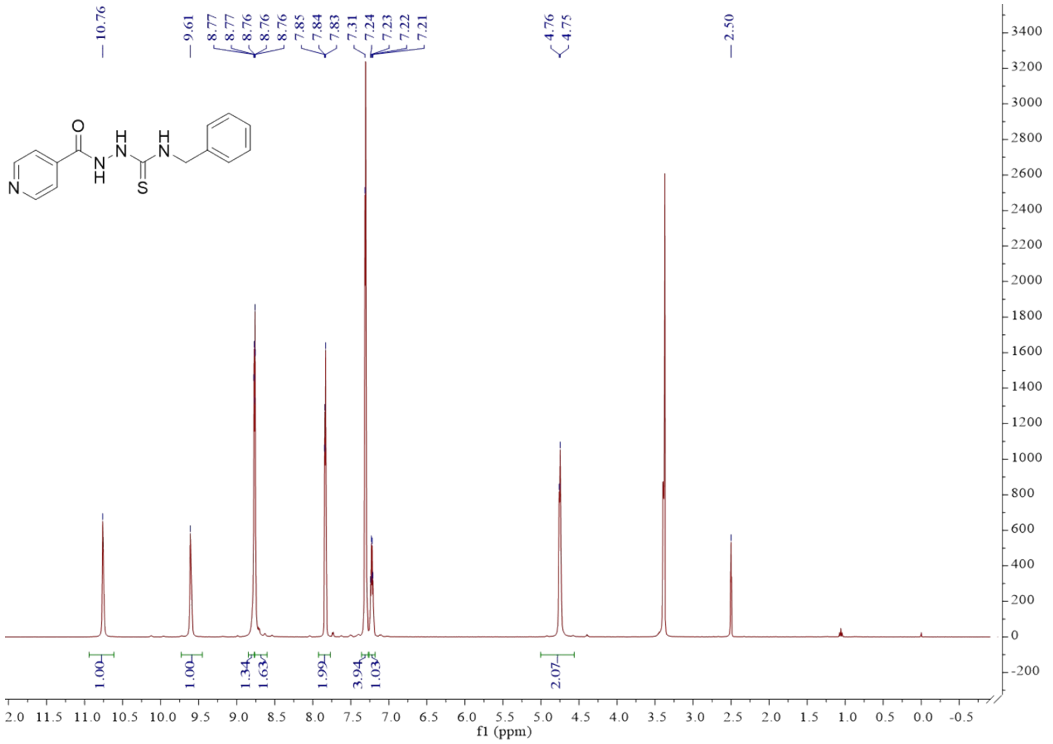


Figure S11. ^{1}H NMR spectrum of N-benzyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 400 M)

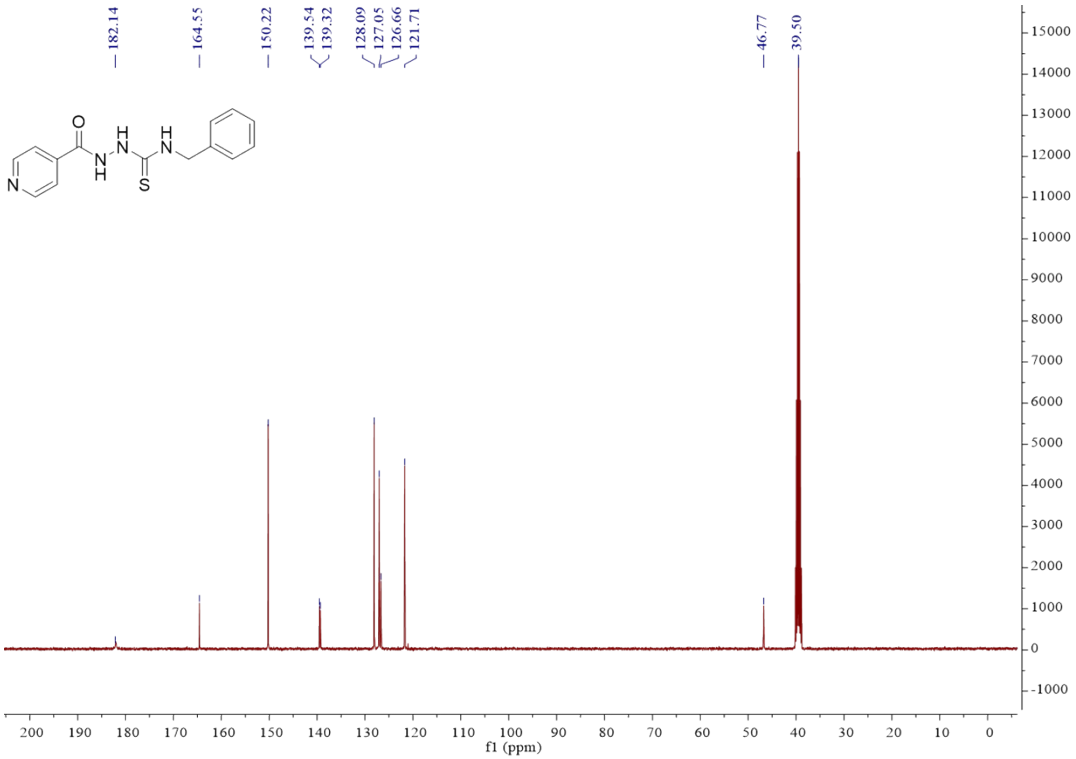


Figure S12. ^{13}C NMR spectrum of N-benzyl-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)

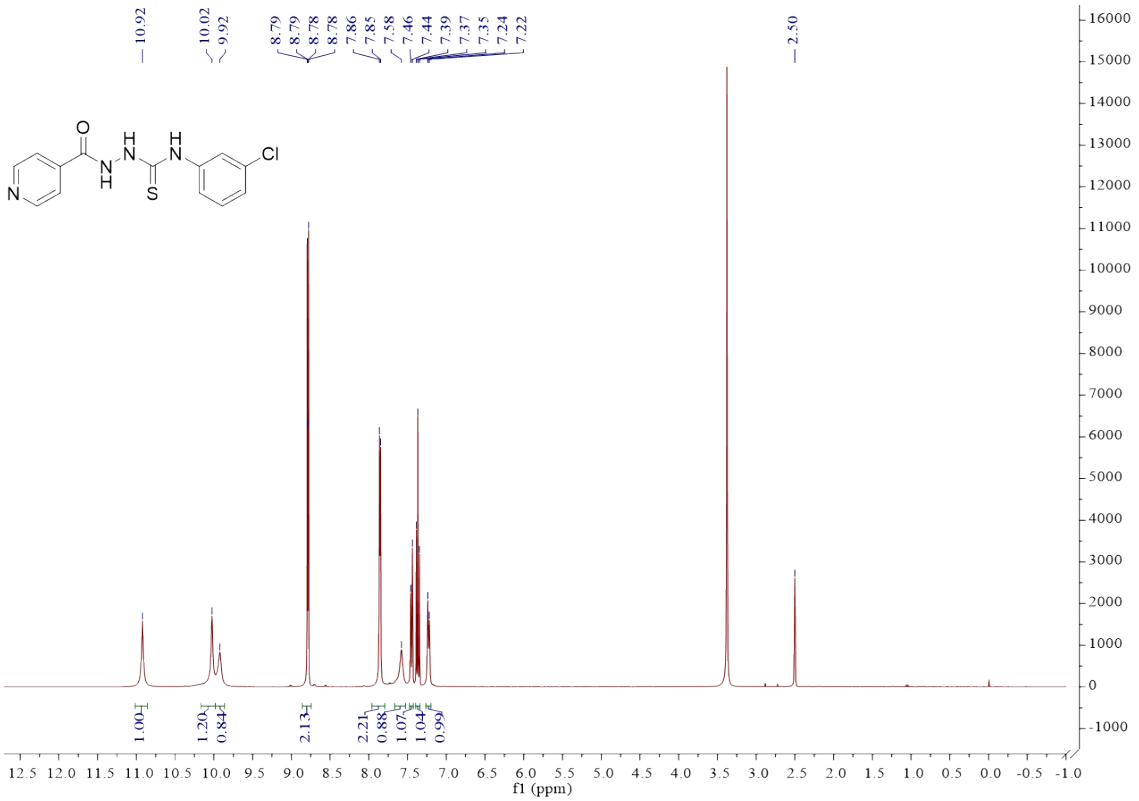


Figure S13. [1]H NMR spectrum of N-(3-Chlorophenyl)-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 400 M)

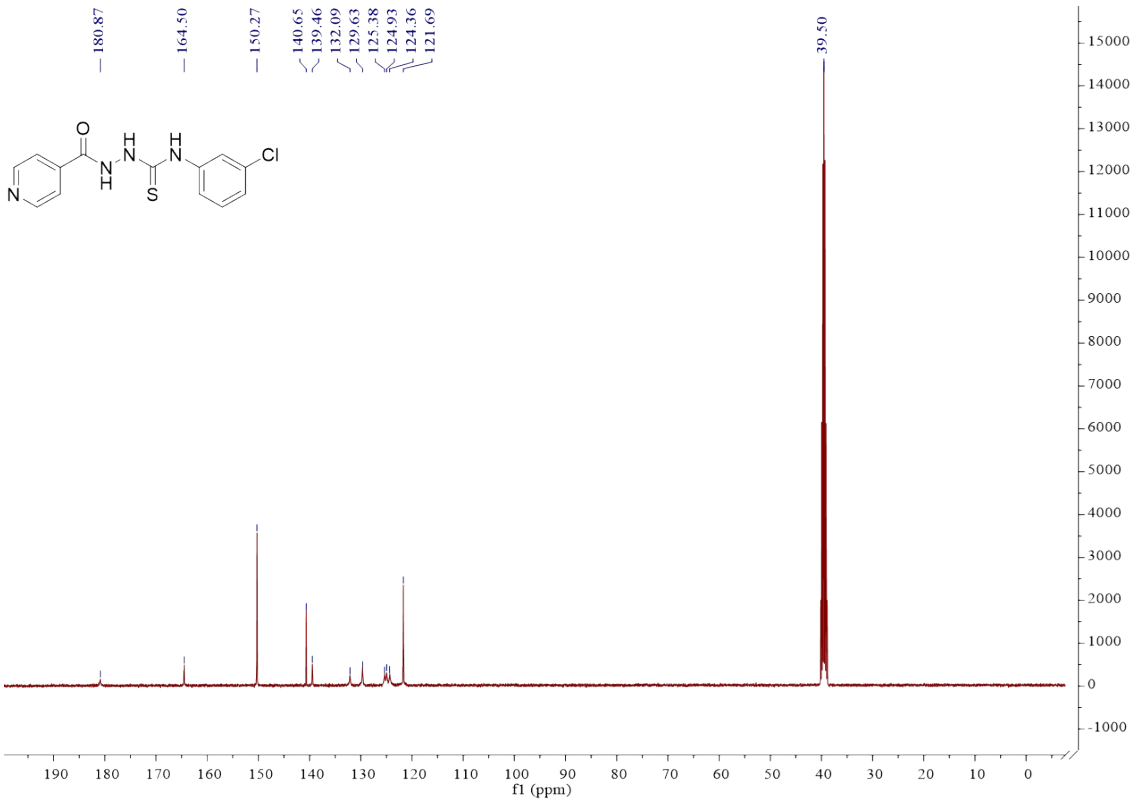


Figure S14. [13]C NMR spectrum of N-(3-Chlorophenyl)-2-isonicotinoylhydrazinocarbothioamides (DMSO-d_6, 100 M)