Supporting Information

Catalyst-free synthesis of thiazolidines *via* sequential hydrolysis/rearrangement reactions of 5-arylidenethiazolidin-4-ones at room temperature

Fanxun Zeng [a], Letian Zhang [a], Xusheng Shao [a], Zhong Li [a, b], Xiaoyong Xu * [a, b]

[a] *Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

[b] *Shanghai Collaborative Innovation Center for Biomanufacturing Technology, 130 Meilong Road, Shanghai 200237, China*

** Corresponding author. Tel.: +86-21-64252945; fax: +86-21-64252603. E-mail: xyxu@ecust.edu.cn.*

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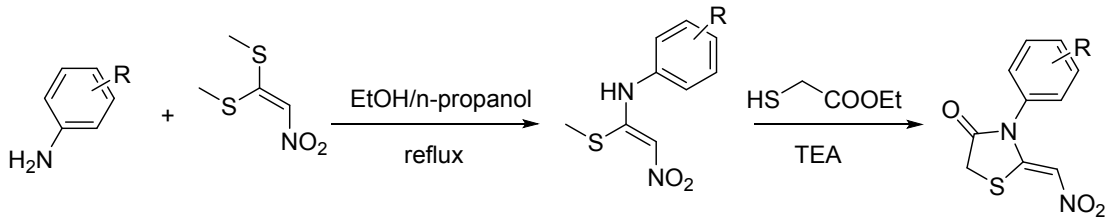
1. General Information

Unless otherwise indicated, all commercially available solvents and reagents were purchased directly from commercial suppliers and used as received without further purification. Melting points (m.p.) were recorded on Büchi B540 apparatus (Büchi Labortechnik AG, Flawil, Switzerland) and are uncorrected. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker AM-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{19}F at 376 MHz) spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the

internal standard. Chemical shifts are reported in δ (parts per million) values. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constant (Hz) and integration. High-resolution electron mass spectra (ESI-TOF) were performed on a Micromass LC-TOF spectrometer. High Resolution Mass Spectrometry (HRMS) EI were recorded under electron impact (70 eV) condition using a MicroMass GCT CA 055 instrument. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254) and spots were visualized with ultraviolet (UV) light. X-ray diffraction was performed with a Bruker Smart 1000. Chromatographic analysis was performed using an ACQUITY UPLC-H Class system (Waters Corp., USA), equipped with BEH C18 reversed phase column with 50 mm×2.1 mm i.d. and 1.7 µm particle size, equipped with a quaternary solvent delivery system, a 48-vial autosampler (10 µL loop), and a photodiode array detector (PDA). The UPLC separations were carried out using gradient separation at a flow rate of 0.4 mL min^{-1}. The mobile phase was a mixture of MilliQ ultrapure water (A) and acetonitrile (B). The following elution gradient totally lasted 15 min: initial mobile-phase composition, 90:10 (v/v) phase A:B; 0-8 min, linear change from 10 to 100% B; 8-10 min 100% B; 10-11 min, linear change from 100 to 10% B. The column and injection chamber were maintained at 40 and 25 °C, respectively. The sample injection volume was 3 µL and the detector was set at 363 nm for **2a**.

2. General procedure for the synthesis of thiazolidin-4-ones (IIIa–h)

To a solution of aniline derivative **Ia, Ie–h** (10 mmol) in EtOH (30 mL) or **Ib–d** (10 mmol) in n-propanol (30 mL) was added (2-nitroethene-1,1-diyl)bis(methylsulfane) (10 mmol). The mixture was stirred under reflux condition until the reaction was complete as indicated by TLC (typically 8 h). The mixture was cooled to room temperature. Then ethyl 2-mercaptoacetate (10 mmol) followed by TEA (1 mmol) were added. After completion of the addition, the reaction mixture was stirred at room temperature for 12 h. The resulting suspension of solid was filtered and washed with EtOH to give compounds **IIIa–h** in yields of 75–90%.

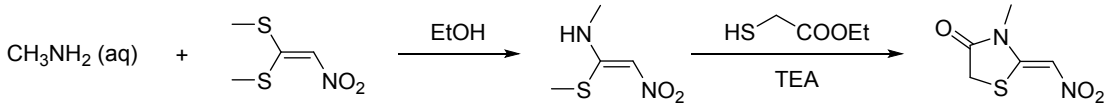


Ia-h **IIa-h** **IIIa-h**

3. Synthesis of (Z)-3-methyl-2-(nitromethylene)thiazolidin-4-one (IIIi)

A solution of (2-nitroethene-1,1-diyl)bis(methylsulfane) (30 mmol) in EtOH (60 mL) was heated to reflux and added methylamine solution (1.0 equiv) in EtOH (30 mL) dropwise over 30 min. Then the reaction was stirred under reflux condition overnight. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE : EA = 1:1) to afford the compound **IIi** in yield of 43%.

To a solution of compound **IIi** (10 mmol) in EtOH (30 mL) was added ethyl 2-mercaptoacetate (10 mmol) followed by TEA (1 mmol). The mixture was stirred at room temperature for 12 h. The resulting suspension of solid was filtered and washed with EtOH to give compound **IIIi** in yield of 75%.



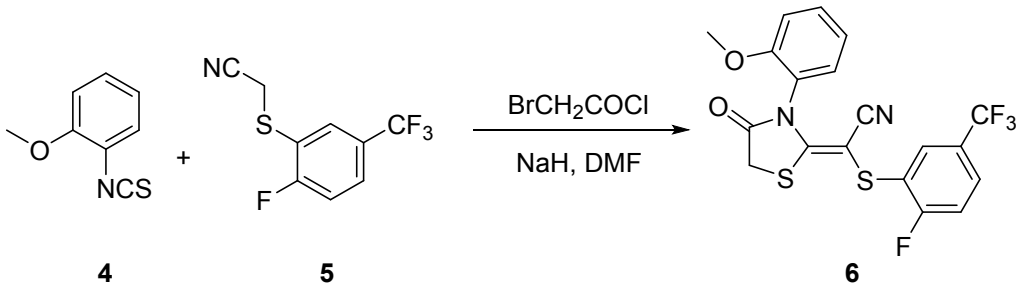
Ii **IIi** **IIIi**

4. Synthesis of compound 6

Starting materials **4** and **5** were obtained according to reported procedures.[1] 2-((2-Fluoro-5-(trifluoromethyl)phenyl)thio)acetonitrile **5** (5 mmol) followed by a solution of 1-isothiocyanato-2-methoxybenzene **4** (5 mmol) in anhydrous DMF (10 mL) were added to a cold suspension of NaH (10 mmol) in dry DMF (10 mL) under Ar_2 atmosphere. The mixture was stirred at room temperature for 0.5 h, then cooled again to 0 °C, added a solution of 2-bromoacetyl chloride (7.5 mmol) in anhydrous

[1] (a) P. Liu, C. Li, J. Zhang and X. Xu, *Synth. Commun*. **2013**, 43, 3342. (b) M. Hayashi, Y. Endo and T. Komura, WO0147902[P].

DMF (5 mL) dropwise and stirred at room temperature overnight. The mixture was poured into ice-cold water, and the resulting precipitate was filtered off, dried, and purified by silica gel chromatography (PE : EA = 3:1) to give compound **6** in yield of 30%.

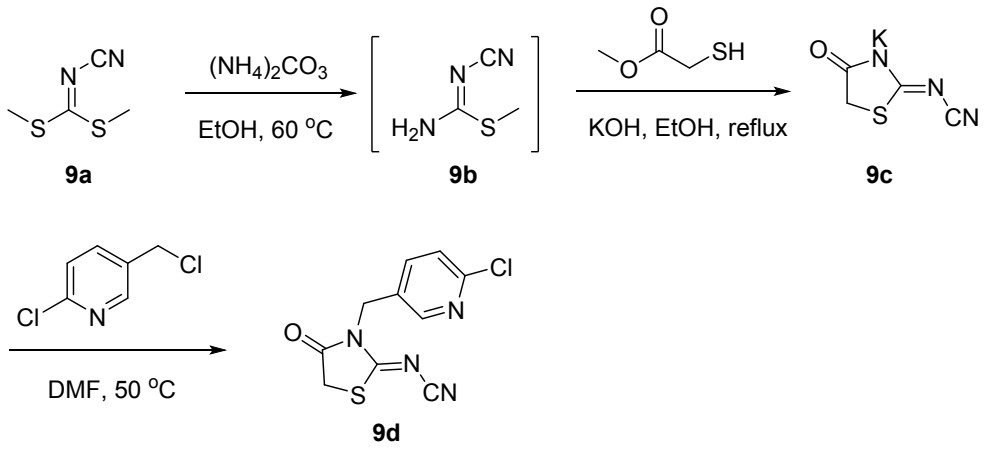


4 **5** **6**

5. Synthesis of (Z)-*N*-(3-((6-chloropyridin-3-yl)methyl)-4-oxothiazolidin-2-ylidene)cyanamide (9d)

In a round-bottomed flask, dimethyl cyanocarbonimidodithioate **9a** (20 mmol) and ammonium carbonate (11 mmol) were stirred in EtOH (30 mL) at 60 °C. After the reaction was complete (monitored by TLC), methyl 2-mercaptoacetate (20 mmol) and 50% KOH solution (2.24g, 20 mmol) were added to the mixture. The reaction mixture was allowed to stir under reflux condition for 5 hours. The mixture was cooled to room temperature and the resulting precipitate was filtered off, washed with cold EtOH to give compound **9c** as faint yellow solid in yield of 73%.

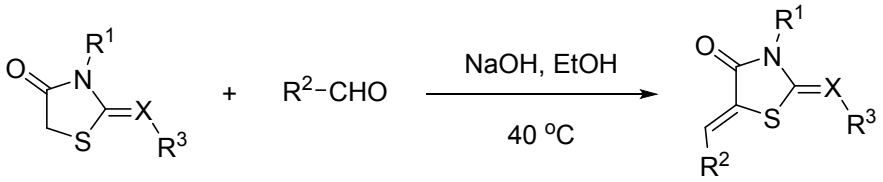
Compound **9c** (12 mmol) was slowly added to a solution of 2-chloro-5-(chloromethyl)pyridine (10 mmol) in DMF (30 mL). The mixture was stirred at 50 °C overnight. The mixture was cooled to room temperature and poured into water. The resulting precipitate was filtered off, dried, and crystallized from EtOH to give compound **9d** in yield of 75%.



9a **9b** **9c** **9d**

6. General procedure for the synthesis of 5- arylidenethiazolidin-4-ones (1a–o, 7, 9)

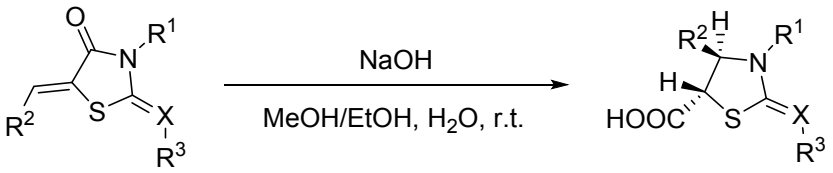
To a solution of appropriate aldehyde (6 mmol) and EtOH (15 mL) was added thiazolidin-4-one **IIIa–i**, **6** or **9d** (5 mmol) and NaOH (0.5 mmol). The mixture was stirred at 40 °C for about 8h (monitored by TLC). The resulting solid was filtered off, washed with EtOH or further crystallized from DCM–MeOH to give target compounds **1a–o, 7, 9** in yield of 80–92%



IIIa-i, 6, 9d **1a-o, 7, 9**

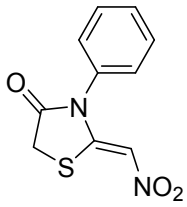
7. General procedure for the synthesis of thiazolidines (2a–o, 8, 10)

To a suspension of 5-arylidenethiazolidin-4-one **1a–h, 1j–o** or **7** (0.5 mmol) in MeOH (2.5 mL) or **1i**, **9** (0.5 mmol) in EtOH (2.5 mL) was added water (3.75 mmol) and NaOH (0.75). The mixture was stirred at room temperature until the reaction was complete as indicated by TLC (typically 0.5–48 h). The mixture was diluted with water (5 mL) and washed with DCM. The obtained water phase was then acidified with 1N HCl and extracted with DCM. The combined DCM extracts were washed with brine (3×2 mL), dried over sodium sulfate, filtered. The filtrate was evaporated under reduced pressure to give compounds **2a–h**, **2j**, and **2l–o.** Compounds **2i**, **2k**, **8** and **10** were further purified by silica gel chromatography (DCM : MeOH = 20:3).

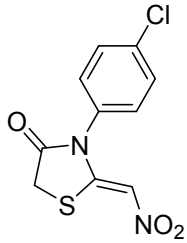


1a-o, 7, 9 **2a-o, 8, 10**

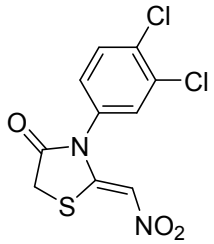
8. Spectroscopic data of starting materials and products



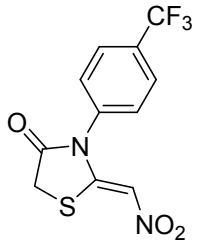
(Z)-2-(nitromethylene)-3-phenylthiazolidin-4-one (IIIa): Pink solid. Yield: 82%. m.p.: 203.4-204.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.64 – 7.54 (m, 3H), 7.42 (d, J = 6.8 Hz, 2H), 6.65 (s, 1H), 4.12 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.58, 164.57, 134.31, 130.19, 130.12, 127.84, 115.90, 32.53.



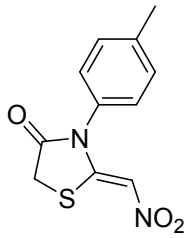
(Z)-3-(4-chlorophenyl)-2-(nitromethylene)thiazolidin-4-one (IIIb): White solid. Yield: 80%. m.p.: 212.3- 213.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.87 (s, 1H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.39, 160.71, 136.96, 132.12, 130.97, 128.90, 118.17, 31.93.



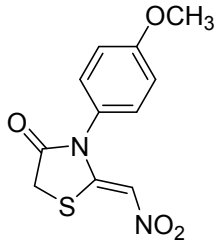
(Z)-3-(3,4-dichlorophenyl)-2-(nitromethylene)thiazolidin-4-one (IIIc): Gray solid. Yield: 76%. m.p.: 216.3- 217.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.13 (dd, J = 8.4, 2.4 Hz, 1H), 6.89 (s, 1H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.15, 160.13, 135.63, 134.89, 132.70, 132.32, 129.74, 126.88, 118.22, 31.86.



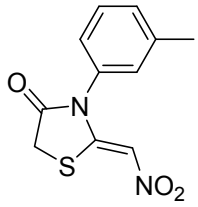
(Z)-2-(nitromethylene)-3-(4-(trifluoromethyl)phenyl)thiazolidin-4-one (IIId): Gray solid. Yield: 75%. m.p.: 238.1-238.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.85 (s, 1H), 3.97 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.00 (s, 3F).



(Z)-2-(nitromethylene)-3-(p-tolyl)thiazolidin-4-one (IIIe): Gray solid. Yield: 85%. m.p.: 176.0-176.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.86 (s, 1H), 3.91 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.83, 161.80, 141.01, 131.22, 131.15, 127.16, 118.08, 32.06, 21.32.

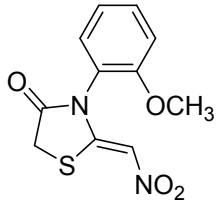


(Z)-3-(4-methoxyphenyl)-2-(nitromethylene)thiazolidin-4-one (IIIf): Gray solid. Yield: 90%. m.p.: 203.7-204.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (dt, J = 8.8, 2.6 Hz, 2H), 7.05 (dt, J = 8.8, 2.6 Hz, 2H), 6.89 (s, 1H), 3.92 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.85, 161.73, 160.95, 128.61, 125.99, 118.21, 115.83, 55.69, 31.97.

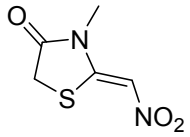


(Z)-2-(nitromethylene)-3-(m-tolyl)thiazolidin-4-one (IIIg): Pink solid. Yield: 85%.

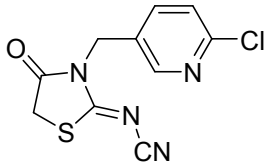
m.p.: 167.5-168.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.03 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 3.93 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.73, 161.56, 141.06, 133.72, 131.46, 130.40, 127.87, 124.35, 118.20, 32.08, 21.32.



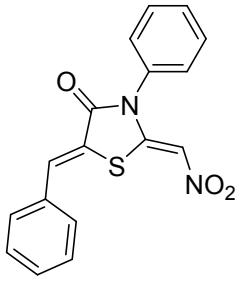
(Z)-3-(2-methoxyphenyl)-2-(nitromethylene)thiazolidin-4-one (IIIh): Pink solid. Yield: 88%. m.p.: 212.6-213.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 – 7.48 (m, 1H), 7.16 (dd, J = 8.0, 1.6 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.81 (s, 1H), 3.92 (d, J = 3.2 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.49, 161.34, 154.43, 132.37, 129.03, 121.85, 121.67, 117.65, 112.80, 55.97, 31.88.



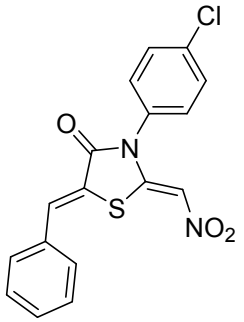
(Z)-3-methyl-2-(nitromethylene)thiazolidin-4-one (IIIi): Gray solid. Yield: 75%. m.p.: 156.2-156.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 3.79 (s, 2H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.87, 160.72, 116.36, 31.76, 30.56.



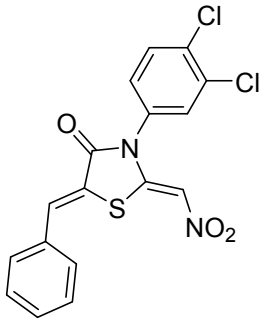
(Z)-N-(3-((6-chloropyridin-3-yl)methyl)-4-oxothiazolidin-2-ylidene)cyanamide (9d): Red solid. Yield: 75%. m.p.: 135.7-136.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.39 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 8.4, 2.4 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 4.84 (s, 2H), 4.38 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 179.15, 172.49, 149.69, 149.54, 139.60, 129.94, 124.12, 113.45, 42.75, 35.88.



(Z)-5-((Z)-benzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one (1a): Yellow solid. Yield: 85%. m.p.: 252.9-253.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.98 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.68 – 7.61 (m, 5H), 7.59 – 7.53 (m, 3H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.43, 156.60, 135.00, 134.20, 133.06, 130.96, 130.49, 130.31, 130.21, 129.61, 127.97, 120.76, 116.06.

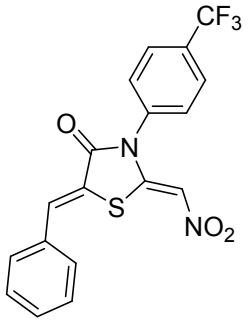


(Z)-5-((Z)-benzylidene)-3-(4-chlorophenyl)-2-(nitromethylene)thiazolidin-4-one (1b): Yellow solid. Yield: 85%. m.p.: 233.6-234.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.61 – 7.48 (m, 5H), 7.26 (dt, J = 8.2, 4.8 Hz, 2H), 6.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.78, 155.12, 136.88, 136.77, 133.00, 132.32, 131.23, 130.93, 130.87, 129.51, 129.00, 119.77, 117.06.

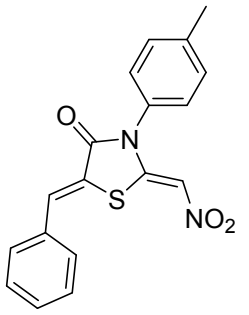


(Z)-5-((Z)-benzylidene)-3-(3,4-dichlorophenyl)-2-(nitromethylene)thiazolidin-4-one (1c): Yellow solid. Yield: 83%. m.p.: 211.5-212.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H), 7.69 (dd, J = 9.6, 7.8 Hz, 3H), 7.59 – 7.49 (m, 3H), 7.46 (d, J = 2.4 Hz, 1H), 7.20 (dd, J = 8.4, 2.4 Hz, 1H), 6.98 (s, 1H). ^{13}C NMR (100 MHz,

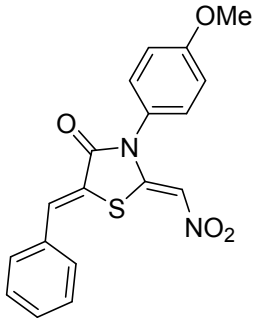
$CDCl_3$) δ: 165.56, 154.65, 137.07, 135.55, 134.83, 132.92, 132.90, 132.28, 131.35, 130.92, 129.84, 129.55, 127.01, 119.42, 117.08.



(Z)-5-((Z)-benzylidene)-2-(nitromethylene)-3-(4-(trifluoromethyl)phenyl)thiazolidin-4-one (1d): Yellow solid. Yield: 82%. m.p.: 240.6-241.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.58 – 7.50 (m, 3H), 7.48 (d, J = 8.4 Hz, 2H), 6.94 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.92 (s, 3F).

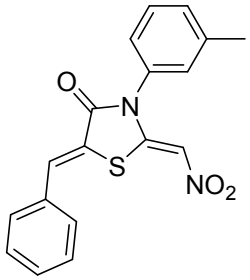


(Z)-5-((Z)-benzylidene)-2-(nitromethylene)-3-(p-tolyl)thiazolidin-4-one (1e): m.p.: Yellow solid. Yield: 87%. 238.5-239.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H), 7.71 – 7.66 (m, 2H), 7.58 – 7.47 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.98 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.05, 155.74, 141.01, 136.36, 133.16, 131.29, 131.21, 131.04, 130.83, 129.46, 127.23, 120.24, 117.13, 21.35.

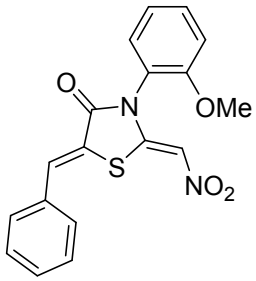


(Z)-5-((Z)-benzylidene)-3-(4-methoxyphenyl)-2-(nitromethylene)thiazolidin-4-

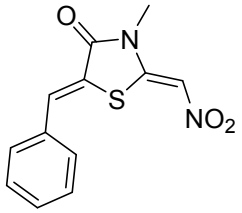
one (1f): Yellow solid. Yield: 92%. m.p.: 221.3-221.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 1H), 7.69 – 7.65 (m, 2H), 7.57 – 7.48 (m, 3H), 7.23 – 7.18 (m, 2H), 7.10 – 7.06 (m, 2H), 6.98 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.16, 160.94, 155.98, 136.35, 133.15, 131.04, 130.83, 129.46, 128.71, 126.19, 120.21, 117.14, 115.79, 55.70.



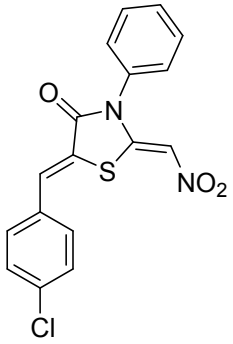
(Z)-5-((Z)-benzylidene)-2-(nitromethylene)-3-(m-tolyl)thiazolidin-4-one (1g): Yellow solid. Yield: 87%. m.p.: 235.1-236.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 1H), 7.70 – 7.65 (m, 2H), 7.57 – 7.45 (m, 4H), 7.37 (d, J = 7.6 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.96 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.99, 155.65, 141.00, 136.35, 133.90, 133.14, 131.43, 131.05, 130.83, 130.36, 129.47, 127.97, 124.46, 120.24, 117.17, 21.35.



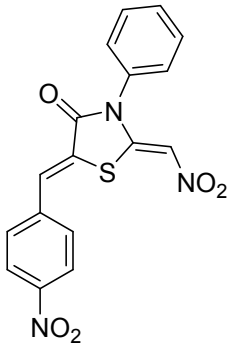
(Z)-5-((Z)-benzylidene)-3-(2-methoxyphenyl)-2-(nitromethylene)thiazolidin-4-one (1h): Yellow solid. Yield: 87%. m.p.: 229.2-230.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 1H), 7.71 – 7.67 (m, 2H), 7.58 – 7.47 (m, 4H), 7.23 (dd, J = 7.8, 1.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.89 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.76, 155.44, 154.61, 136.14, 133.24, 132.35, 130.93, 130.79, 129.43, 129.19, 122.06, 121.68, 120.41, 116.74, 112.82, 55.99.



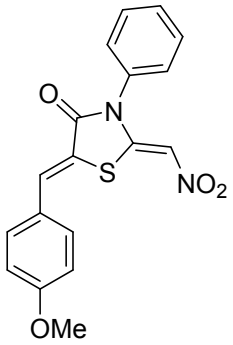
(Z)-5-((Z)-benzylidene)-3-methyl-2-(nitromethylene)thiazolidin-4-one (1i): Yellow solid. Yield: 80%. m.p.: 275.6-276.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.67 – 7.63 (m, 2H), 7.56 – 7.46 (m, 3H), 7.38 (s, 1H), 3.38 (s, 3H).



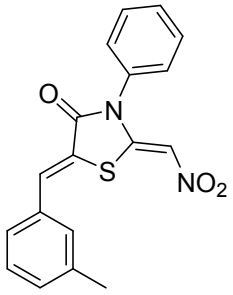
(Z)-5-((Z)-4-chlorobenzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one (1j): Yellow solid. Yield: 87%. m.p.: 250.2-251.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.64 – 7.57 (m, 5H), 7.54 – 7.50 (m, 2H), 7.32 – 7.27 (m, 2H), 6.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.77, 155.04, 137.25, 134.79, 133.90, 131.90, 131.57, 130.69, 130.65, 129.82, 127.53, 120.75, 117.31.



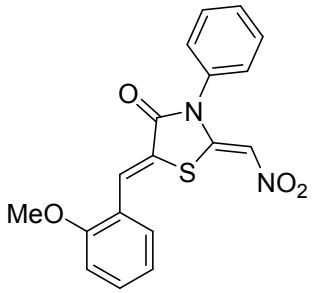
(Z)-5-((Z)-4-nitrobenzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one (1k): Yellow solid. Yield: 80%. m.p.: 234.5-235.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, J = 8.8 Hz, 2H), 7.94 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.67 – 7.58 (m, 3H), 7.31 (dd, J = 7.6, 1.6 Hz, 2H), 6.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.26, 154.00, 148.24, 139.08, 133.65, 132.57, 131.13, 130.88, 130.75, 127.45, 124.85, 124.58, 118.02.



(Z)-5-((Z)-4-methoxybenzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one (1l): Yellow solid. Yield: 85%. m.p.: 260.5-261.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, 1H), 7.67 – 7.63 (m, 2H), 7.62 – 7.56 (m, 3H), 7.32 – 7.28 (m, 2H), 7.08 – 7.04 (m, 2H), 6.96 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.20, 162.02, 155.94, 136.54, 134.14, 133.07, 130.56, 130.53, 127.60, 125.81, 116.95, 116.66, 115.06, 55.61.

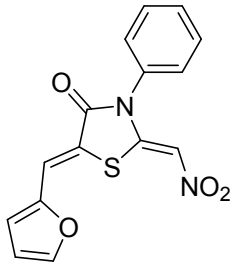


(Z)-5-((Z)-3-methylbenzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one (1m): Yellow solid. Yield: 86%. m.p.: 226.0-226.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, 1H), 7.62 – 7.56 (m, 3H), 7.49 (d, J = 8.0 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 3H), 6.95 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.98, 155.71, 139.33, 136.74, 134.04, 133.08, 132.04, 131.59, 130.59, 129.36, 127.89, 127.59, 119.81, 117.04, 21.49.



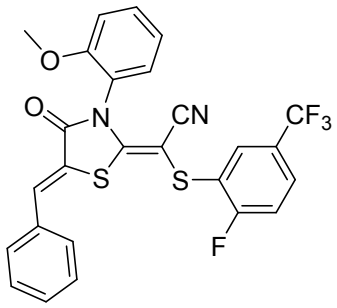
(Z)-5-((Z)-2-methoxybenzylidene)-2-(nitromethylene)-3-phenylthiazolidin-4-one

(1n): Yellow solid. Yield: 83%. m.p.: 291.3-292.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 7.67 (dd, J = 7.6, 1.2 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.50 – 7.45 (m, 1H), 7.30 (dd, J = 7.8, 1.4 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.94 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.08, 158.67, 156.29, 134.18, 132.98, 132.41, 130.54, 130.49, 127.61, 122.29, 121.19, 120.77, 119.95, 116.69, 111.29, 55.58.

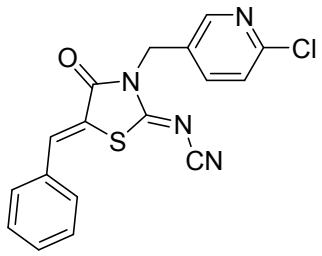


(2Z,5Z)-5-(furan-2-ylmethylene)-2-(nitromethylene)-3-phenylthiazolidin-4-one

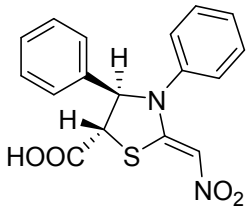
(1o): Yellow solid. Yield: 80%. m.p.: 224.6-225.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J = 2.0 Hz, 1H), 7.67 (s, 1H), 7.62 – 7.56 (m, 3H), 7.31 – 7.27 (m, 2H), 6.95 (s, 1H), 6.91 (d, J = 3.2 Hz, 1H), 6.64 (dd, J = 3.4, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.82, 156.64, 149.99, 147.29, 134.07, 130.55, 127.59, 121.46, 119.11, 118.04, 116.85, 113.58.



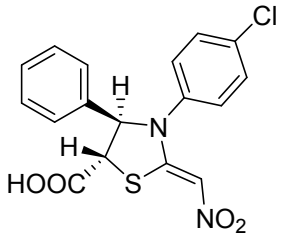
(Z)-2-(5-((Z)-benzylidene)-3-(2-methoxyphenyl)-4-oxothiazolidin-2-ylidene)-2-((2-fluoro-5-(trifluoromethyl)phenyl)thio)acetonitrile (7): Pink solid. Yield: 85%. m.p.: 183.7-184.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.62 – 7.56 (m, 3H), 7.54 – 7.43 (m, 5H), 7.32 (dd, J = 7.6, 1.6 Hz, 1H), 7.23 – 7.10 (m, 3H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -61.85 (s, 3F), -106.09 – -106.18 (m, 1F).



N-((Z)-5-((Z)-benzylidene)-3-((6-chloropyridin-3-yl)methyl)-4-oxothiazolidin-2-ylidene)cyanamide (9): Gray solid. Yield: 80%. m.p.: 204.3-205.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.46 (d, J = 2.0 Hz, 1H), 8.09 (s, 1H), 7.87 (dd, J = 8.4, 2.4 Hz, 1H), 7.71 (dd, J = 8.0, 1.4 Hz, 2H), 7.63 – 7.55 (m, 3H), 7.52 (d, J = 8.4 Hz, 1H), 5.01 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.29, 165.67, 149.74, 149.70, 139.74, 135.47, 132.35, 131.43, 130.49, 129.82, 129.64, 124.17, 119.22, 113.10, 43.22.

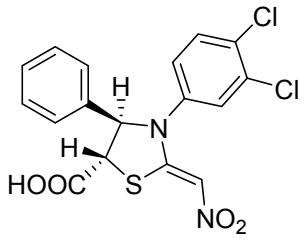


(Z)-2-(nitromethylene)-3,4-diphenylthiazolidine-5-carboxylic acid (2a): Yellow solid. Yield: 95%. m.p.: 211.3-212.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.63 (s, 1H), 7.48 – 7.40 (m, 4H), 7.38 – 7.28 (m, 6H), 6.58 (s, 1H), 5.87 (d, J = 5.2 Hz, 1H), 4.49 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.38, 164.43, 138.45, 136.59, 130.02, 128.81, 128.76, 127.46, 126.50, 109.99, 72.96, 51.71. HRMS (EI) calc. for $C_{17}H_{14}N_2O_4S^+$ 342.0674, found 342.0680.

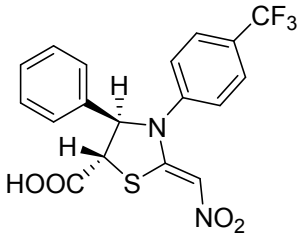


(Z)-3-(4-chlorophenyl)-2-(nitromethylene)-4-phenylthiazolidine-5-carboxylic acid (2b): Yellow solid. Yield: 96%. m.p.: 109.1-109.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.65 (s, 1H), 7.51 – 7.42 (m, 4H), 7.37 – 7.30 (m, 5H), 6.63 (s, 1H), 5.84 (d, J = 5.6 Hz, 1H), 4.50 (d, J = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.21, 164.37, 137.32, 136.37, 133.13, 130.07, 128.84, 128.80, 128.49, 127.58,

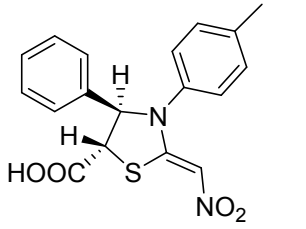
110.38, 72.78, 51.69. HRMS (EI) calc. for $C_{17}H_{13}{}^{35}ClN_2O_4S^+$ 376.0285, found 376.0291; calc. for $C_{17}H_{13}{}^{37}ClN_2O_4S^+$ 378.0255, found 378.0256.



(Z)-3-(3,4-dichlorophenyl)-2-(nitromethylene)-4-phenylthiazolidine-5-carboxylic acid (2c): Yellow solid. Yield: 95%. m.p.: 124.9-125.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.52 (s, 1H), 7.68 – 7.65 (m, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.38 – 7.28 (m, 4H), 6.78 (s, 1H), 5.89 (d, J = 6.4 Hz, 1H), 4.53 (d, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 169.97, 164.35, 138.29, 136.16, 132.16, 131.77, 131.36, 128.90, 128.80, 128.77, 127.74, 127.26, 111.01, 72.58, 51.81. HRMS (EI) calc. for $C_{17}H_{12}{}^{35}Cl_2N_2O_4S^+$ 409.9895, found 409.9900; calc. for $C_{17}H_{12}{}^{35}Cl^{37}ClN_2O_4S^+$ 411.9865, found 411.9864.

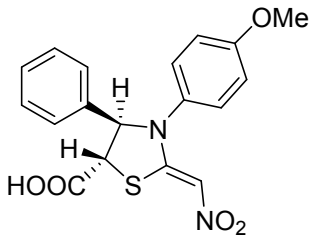


(Z)-2-(nitromethylene)-4-phenyl-3-(4-(trifluoromethyl)phenyl)thiazolidine-5-carboxylic acid (2d): Yellow solid. Yield: 96%. m.p.: 103.2-103.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.79 (s, 1H), 5.94 (d, J = 5.2 Hz, 1H), 4.47 (d, J = 5.2 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ: -61.21 (s, 3F). HRMS (EI) calc. for $C_{18}H_{13}F_3N_2O_4S^+$ 410.0548, found 410.0544.

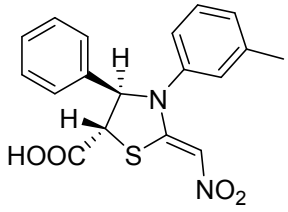


(Z)-2-(nitromethylene)-4-phenyl-3-(p-tolyl)thiazolidine-5-carboxylic acid (2e): Yellow solid. Yield: 97%. m.p.: 239.3-240.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ:

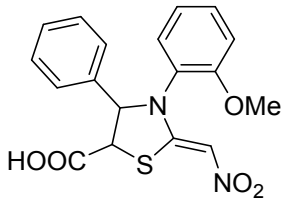
13.62 (s, 1H), 7.46 – 7.43 (m, 2H), 7.37 – 7.30 (m, 3H), 7.22 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.54 (s, 1H), 5.82 (t, J = 5.2 Hz, 1H), 4.47 (d, J = 5.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.41, 164.53, 138.54, 136.66, 135.82, 130.47, 128.76, 127.46, 126.31, 109.84, 73.02, 51.65, 20.59. HRMS (EI) calc. for $C_{18}H_{16}N_2O_4S^+$ 356.0831, found 356.0832.



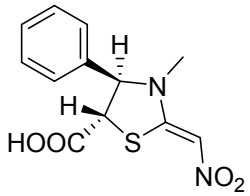
(Z)-3-(4-methoxyphenyl)-2-(nitromethylene)-4-phenylthiazolidine-5-carboxylic acid (2f): Yellow solid. Yield: 96%. m.p.: 150.6-151.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.42 – 7.37 (m, 2H), 7.35 – 7.25 (m, 3H), 7.19 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.45 (s, 1H), 5.76 (d, J = 5.6 Hz, 1H), 4.27 (d, J = 5.6 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.21, 165.86, 158.89, 137.50, 131.11, 128.67, 128.49, 128.00, 127.53, 115.03, 109.36, 73.93, 55.30, 53.34. HRMS (ES+) calc. for $C_{18}H_{17}N_2O_5S$ $(M+H)^+$, 373.0858; found, 373.0857.



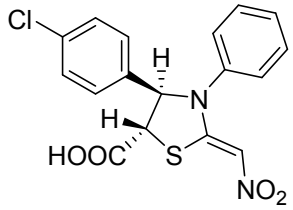
(Z)-2-(nitromethylene)-4-phenyl-3-(m-tolyl)thiazolidine-5-carboxylic acid (2g): Yellow solid. Yield: 95%. m.p.: 130.4-131.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.57 (s, 1H), 7.47 – 7.43 (m, 2H), 7.38 – 7.27 (m, 4H), 7.16 (d, J = 8.4 Hz, 1H), 7.14 (s, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.58 (s, 1H), 5.84 (d, J = 4.8 Hz, 1H), 4.46 (d, J = 4.8 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.44, 164.40, 139.77, 138.39, 136.66, 129.72, 129.53, 128.77, 127.38, 126.74, 123.53, 109.95, 72.98, 51.70, 20.73. HRMS (EI) calc. for $C_{18}H_{16}N_2O_4S^+$ 356.0831, found 356.0834.



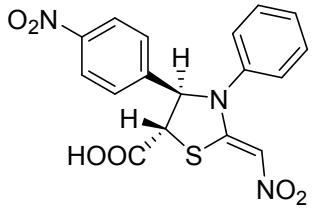
(Z)-3-(2-methoxyphenyl)-2-(nitromethylene)-4-phenylthiazolidine-5-carboxylic acid (2h): Yellow solid. Yield: 97%. m.p.: 111.9-112.8 °C. The diastereomeric ratio was 1.7:1 determined by ^{1}H NMR spectroscopic analysis. ^{1}H NMR (400 MHz, DMSO-d_6, stereoisomeric mixture) δ: 13.70 (s, 1H×1.7 + s, 1H), 7.49 (dd, J = 7.6, 1.6 Hz, 1H), 7.42 – 7.36 (m, 6H), 7.34 – 7.25 (m, 6H×1.7), 7.13 (dd, J = 8.4, 0.8 Hz, 1H×1.7), 7.04 – 6.97 (m, 2H + m, 1H×1.7), 6.84 (td, J = 7.6, 1.2 Hz, 1H×1.7), 6.34 (s, 1H×1.7), 6.27 (s, 1H), 5.83 (d, J = 7.2 Hz, 1H), 5.67 (d, J = 8.0 Hz, 1H×1.7), 4.73 (d, J = 8.4 Hz, 1H×1.7), 4.65 (d, J = 7.2 Hz, 1H), 3.85 (s, 3H×1.7), 3.62 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.09, 169.45, 165.57, 163.36, 154.22, 154.12, 136.34, 136.13, 130.88, 130.68, 129.76, 128.91, 128.74, 128.69, 128.16, 127.98, 127.86, 127.08, 126.10, 125.48, 121.39, 120.81, 113.14, 113.09, 109.95, 109.61, 73.42, 71.75, 55.98, 55.64, 52.22, 51.14. HRMS (EI) calc. for $C_{18}H_{16}N_2O_5S^+$ 372.0780, found 372.0789.



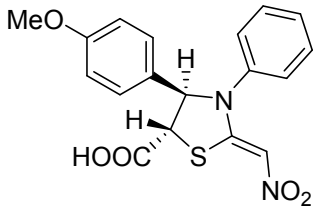
(Z)-3-methyl-2-(nitromethylene)-4-phenylthiazolidine-5-carboxylic acid (2i): Light red solid. Yield: 61%. m.p.: 159.7-160.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.40 (s, 1H), 7.46 – 7.39 (m, 3H), 7.33 – 7.30 (m, 2H), 7.25 (s, 1H), 5.50 (d, J = 3.6 Hz, 1H), 4.20 (d, J = 3.6 Hz, 1H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.76, 163.93, 137.07, 129.08, 128.78, 126.55, 108.40, 72.19, 51.35, 35.04. HRMS (EI) calc. for $C_{12}H_{12}N_2O_4S^+$ 280.0518, found 280.0521.



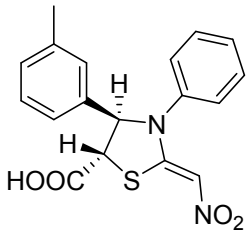
(Z)-4-(4-chlorophenyl)-2-(nitromethylene)-3-phenylthiazolidine-5-carboxylic acid (2j): Yellow solid. Yield: 96%. m.p.: 111.2-112.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.64 (s, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 – 7.28 (m, 2H), 6.55 (s, 1H), 5.89 (d, J = 5.4 Hz, 1H), 4.51 (d, J = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 170.21, 164.38, 138.33, 135.57, 133.39, 130.09, 129.56, 128.91, 128.74, 126.52, 110.14, 72.10, 51.49. HRMS (EI) calc. for $C_{17}H_{13}{}^{35}ClN_2O_4S^+$ 376.0285, found 376.0283; calc. for $C_{17}H_{13}{}^{37}ClN_2O_4S^+$ 378.0255, found 378.0258.



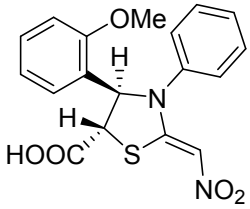
(Z)-2-(nitromethylene)-4-(4-nitrophenyl)-3-phenylthiazolidine-5-carboxylic acid (2k): Gray solid. Yield: 70%. m.p.: 234.4-235.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.11 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 6.46 (s, 1H), 6.01 (d, J = 7.8 Hz, 1H), 4.15 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ: 168.73, 166.98, 147.11, 145.97, 138.86, 129.98, 129.40, 128.60, 126.64, 123.47, 109.51, 73.61, 55.73. HRMS (ES+) calc. for $C_{17}H_{13}N_3O_6NaS$ $(M+Na)^+$, 410.0423; found, 410.0422.



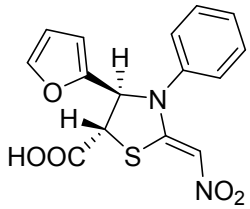
(Z)-4-(4-methoxyphenyl)-2-(nitromethylene)-3-phenylthiazolidine-5-carboxylic acid (2l): Yellow solid. Yield: 93%. m.p.: 93.0-93.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.61 (s, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.26 (d, J = 7.2 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.51 (s, 1H), 5.79 (d, J = 5.6 Hz, 1H), 4.46 (d, J = 5.6 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.27, 164.97, 159.28, 138.64, 129.95, 128.90, 128.78, 128.71, 126.63, 114.01, 109.60, 73.16, 55.01, 52.73. HRMS (ES+) calc. for $C_{18}H_{17}N_2O_5S$ $(M+H)^+$ 373.0858, found 373.0859.



(Z)-2-(nitromethylene)-3-phenyl-4-(m-tolyl)thiazolidine-5-carboxylic acid (2m): Yellow solid. Yield: 95%. m.p.: 143.4-144.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.56 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 7.14 – 7.10 (m, 1H), 6.57 (s, 1H), 5.81 (d, J = 4.6 Hz, 1H), 4.44 (d, J = 4.6 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.45, 164.44, 138.49, 138.09, 136.62, 130.03, 129.44, 128.83, 128.66, 127.84, 126.49, 124.39, 109.95, 73.03, 51.75, 20.92. HRMS (EI) calc. for $C_{18}H_{16}N_2O_4S^+$ 356.0831, found 356.0832.

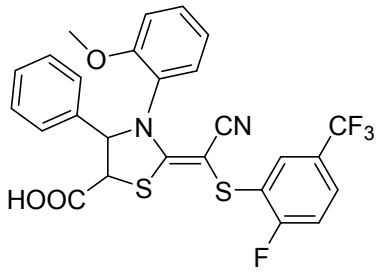


(Z)-4-(2-methoxyphenyl)-2-(nitromethylene)-3-phenylthiazolidine-5-carboxylic acid (2n): Light yellow solid. Yield: 95%. m.p.: 132.5-133.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.57 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 – 7.31 (m, 5H), 7.03 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.66 (s, 1H), 6.02 (d, J = 3.6 Hz, 1H), 4.37 (d, J = 3.6 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 171.00, 164.30, 156.25, 138.47, 130.22, 130.06, 128.85, 127.61, 126.18, 123.67, 120.45, 111.57, 109.87, 68.93, 55.71, 50.21. HRMS (EI) calc. for $C_{18}H_{16}N_2O_5S^+$ 372.0780, found 372.0784.

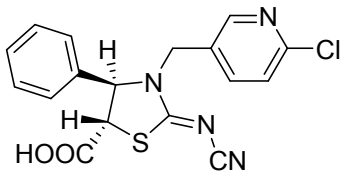


(Z)-4-(furan-2-yl)-2-(nitromethylene)-3-phenylthiazolidine-5-carboxylic acid (2o): Gray solid. Yield: 82%. m.p.: 237.8-238.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ:

13.68 (s, 1H), 7.69 (dd, J = 1.6, 0.8 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.20 – 7.16 (m, 2H), 6.52 (d, J = 3.6 Hz, 1H), 6.43 (s, 1H), 6.41 (dd, J = 3.4, 1.8 Hz, 1H), 5.89 (d, J = 4.4 Hz, 1H), 4.70 (d, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.20, 164.01, 148.63, 144.02, 137.97, 130.16, 129.28, 126.67, 110.71, 110.43, 109.91, 66.70, 48.46. HRMS (EI) calc. for $C_{15}H_{12}N_2O_5S^+$ 332.0467, found 332.0469.



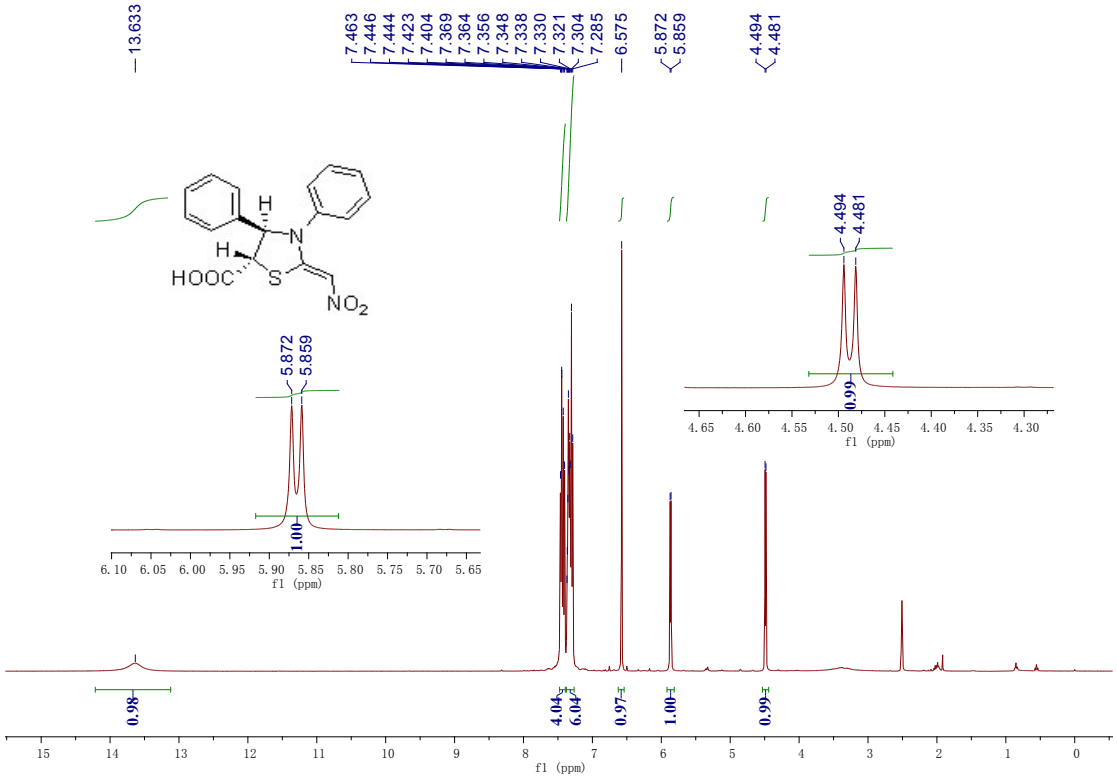
(Z)-2-(cyano((2-fluoro-5-(trifluoromethyl)phenyl)thio)methylene)-3-(2-methoxyphenyl)-4-phenylthiazolidine-5-carboxylic acid (8): Yellow solid. Yield: 82%. m.p.: 199.3-200.1 °C. The diastereomeric ratio was 1.17:1 determined by ^{1}H NMR spectroscopic analysis. ^{1}H NMR (400 MHz, DMSO-d_6, stereoisomeric mixture) δ: 7.76 – 7.64 (m, 4H), 7.56 – 7.45 (m, 4H×1.17), 7.35 – 7.19 (m, 6H + m, 6H×1.17), 7.04 (d, J = 8.0 Hz, 1H×1.17), 6.92 – 6.84 (m, 1H + m, 1H×1.17), 6.70 (t, J = 7.6 Hz, 1H), 5.88 (d, J = 6.4 Hz, 1H), 5.68 (d, J = 9.2 Hz, 1H×1.17), 4.39 (d, J = 9.2 Hz, 1H×1.17), 4.05 (d, J = 6.4 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H×1.17). ^{19}F NMR (376 MHz, DMSO-d_6, stereoisomeric mixture) δ: -60.48 (s, 3F), -60.58 (s, 3F×1.17), -108.93 – -108.99 (m, 1F×1.17), -109.10 – -109.17 (m, 1F). HRMS (EI) calc. for $C_{26}H_{18}F_4N_2O_3S_2^+$ 546.0695, found 546.0698.



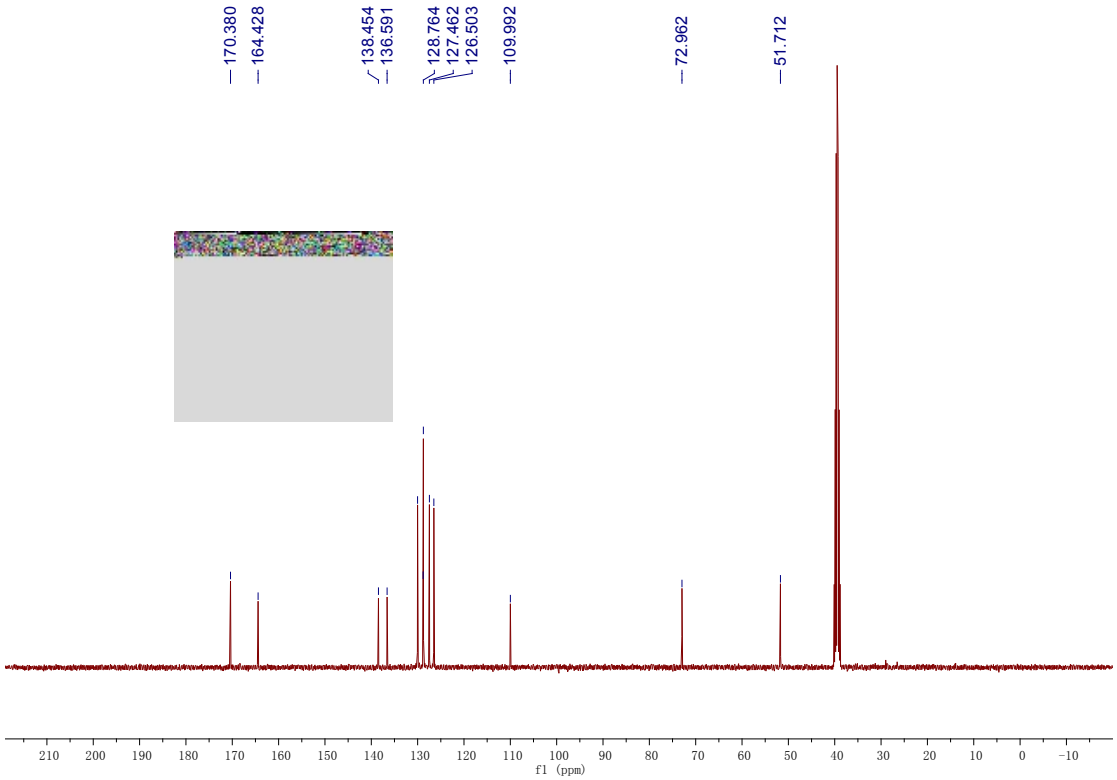
(Z)-3-((6-chloropyridin-3-yl)methyl)-2-(cyanoimino)-4-phenylthiazolidine-5-carboxylic acid (10): Gray solid. Yield: 81%. m.p.: 89.6-90.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.17 (s, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.32 (d, J = 6.4 Hz, 2H), 5.59 (d, J = 2.0 Hz, 1H), 4.77 (d, J = 15.6 Hz, 1H), 4.32 (d, J = 2.0 Hz, 1H), 4.20 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 169.68, 149.21, 139.31, 136.95, 135.14, 130.43, 129.11, 129.05, 128.90, 128.89, 126.95,

123.99, 69.60, 53.10, 45.54. HRMS (ES+) calc. for $C_{17}H_{14}{}^{35}ClN_4O_2S$ $(M+H)^+$, 373.0526; found, 373.0525; calc. for $C_{17}H_{14}{}^{37}ClN_4O_2S$ $(M+H)^+$, 375.0496; found, 375.0497.

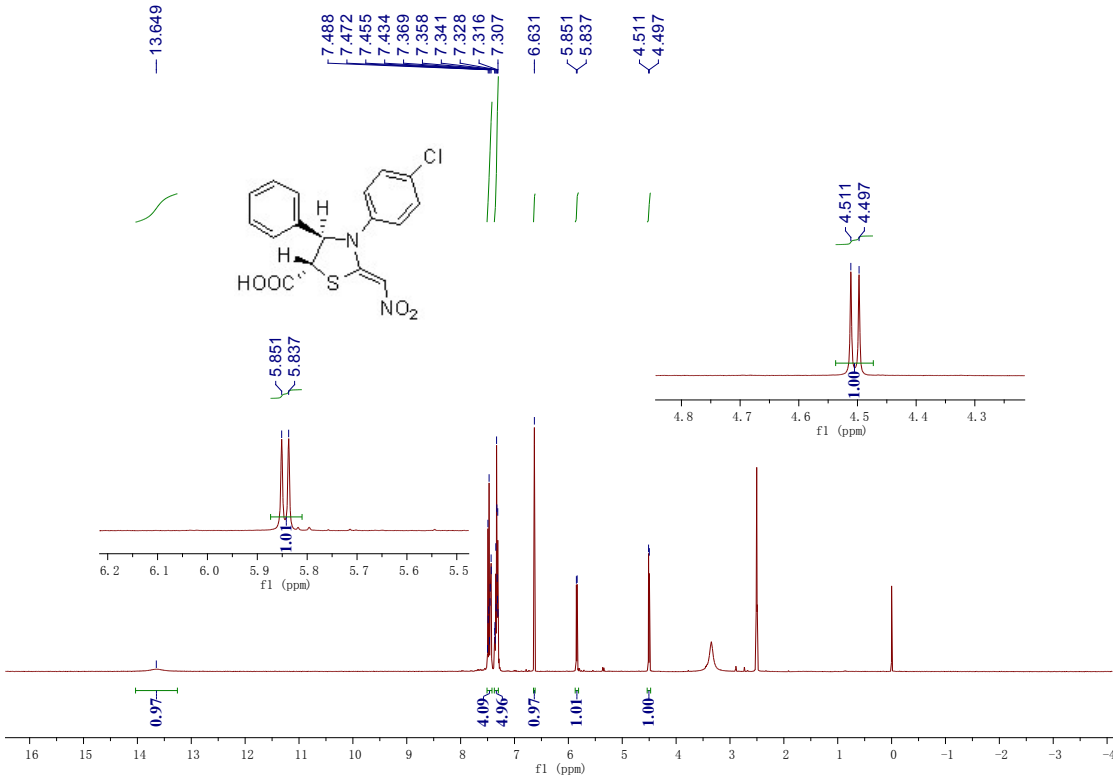
9. ^{1}H, ^{19}F and ^{13}C NMR spectra of compounds 2a–o, 8, 10



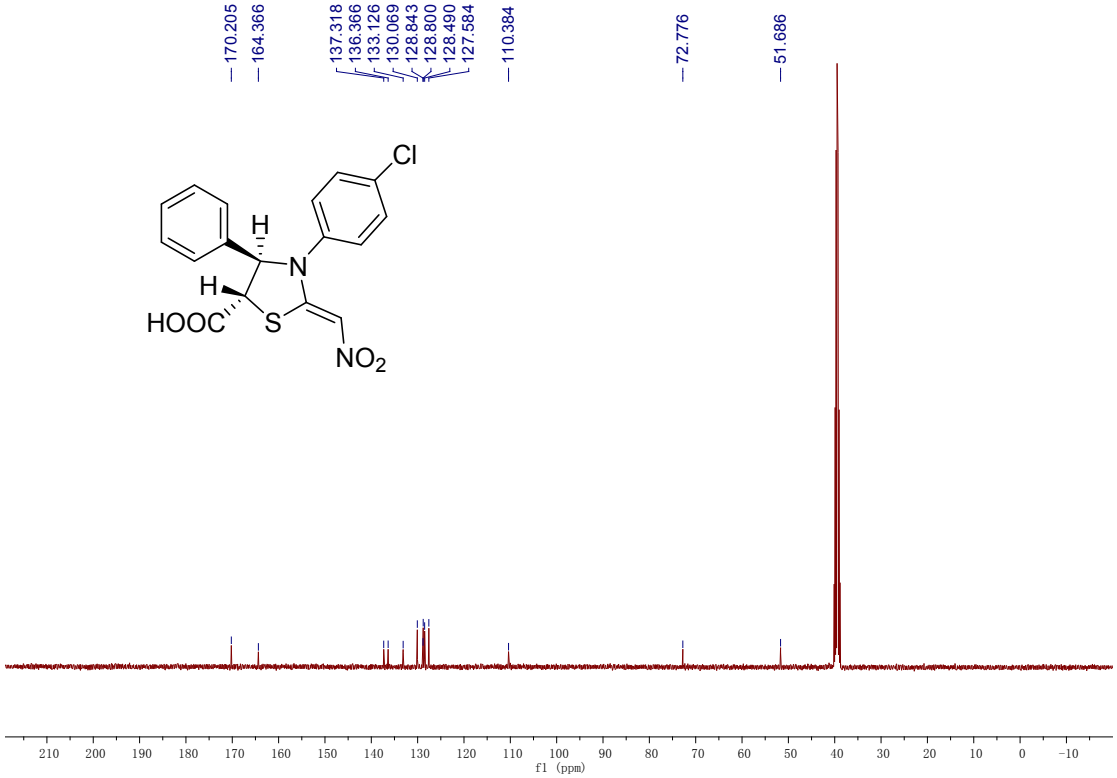
^{1}H NMR spectrum of compound **2a**



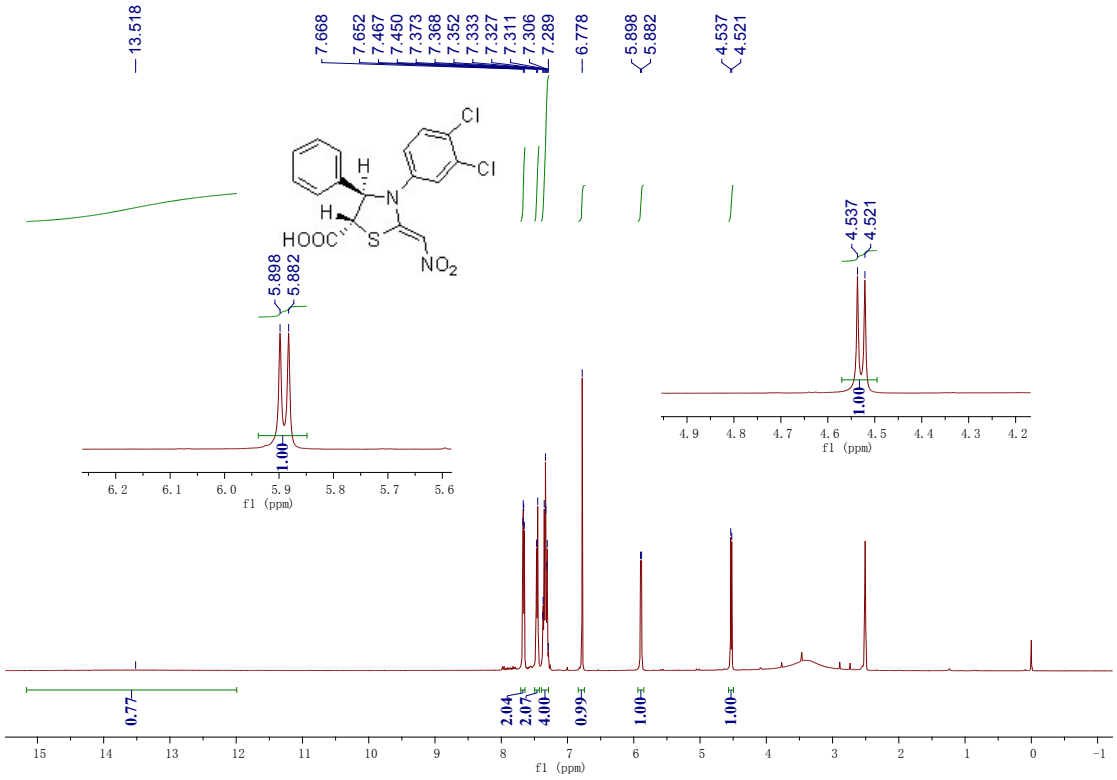
^{13}CNMR spectrum of compound **2a**



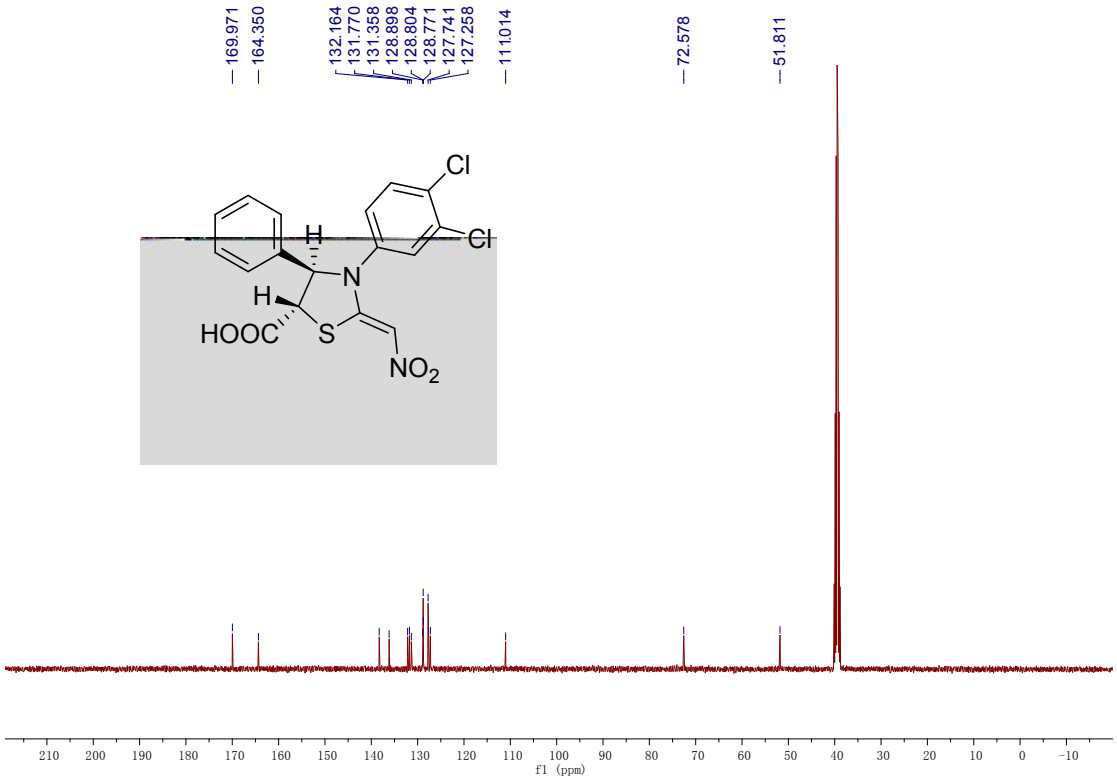
^{1}H NMR spectrum of compound **2b**



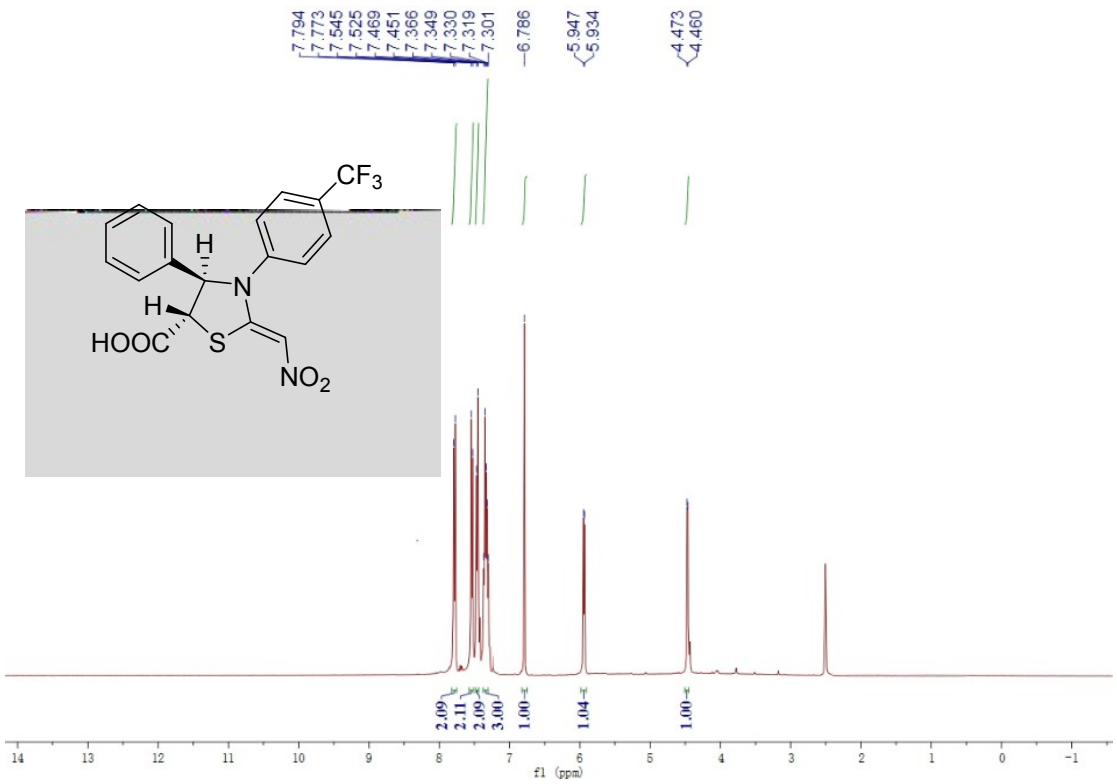
^{13}CNMR spectrum of compound **2b**



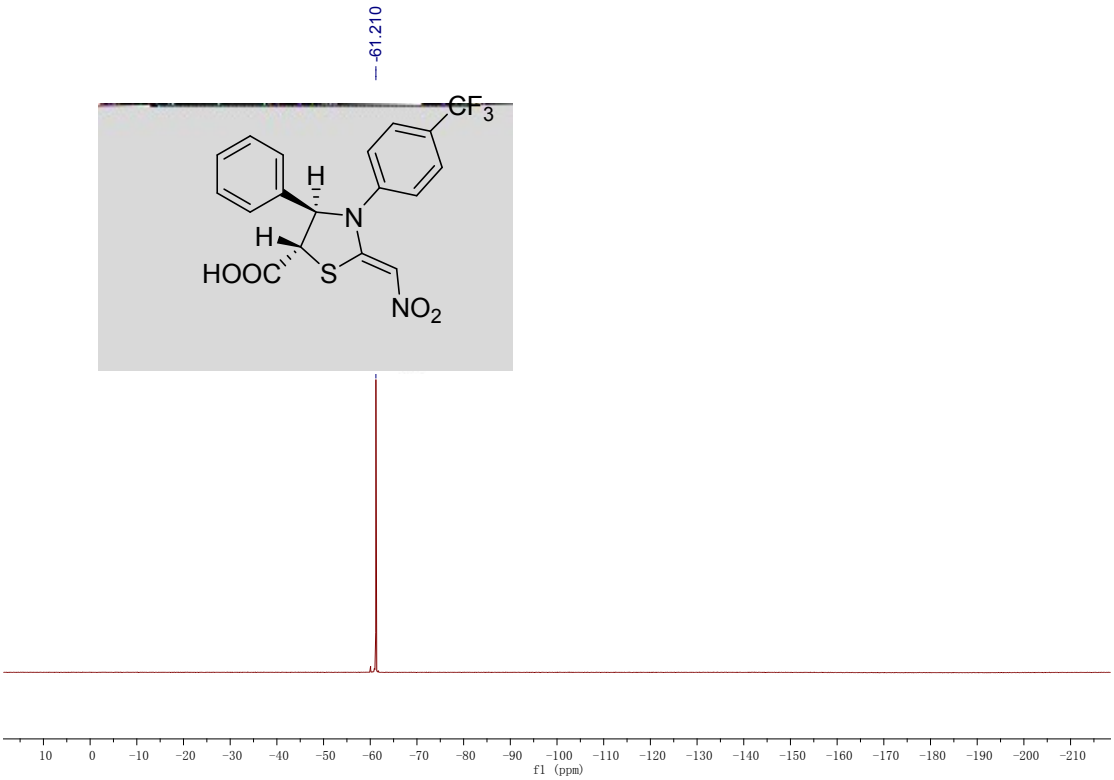
^{1}H NMR spectrum of compound **2c**



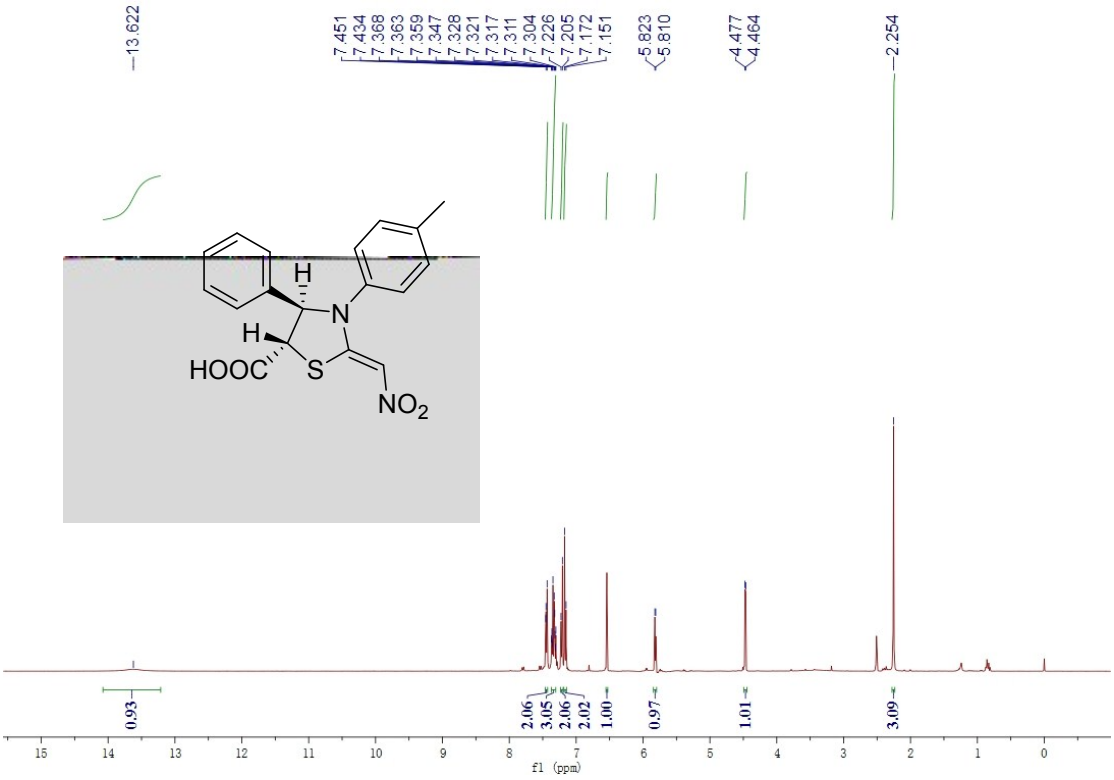
^{13}CNMR spectrum of compound **2c**



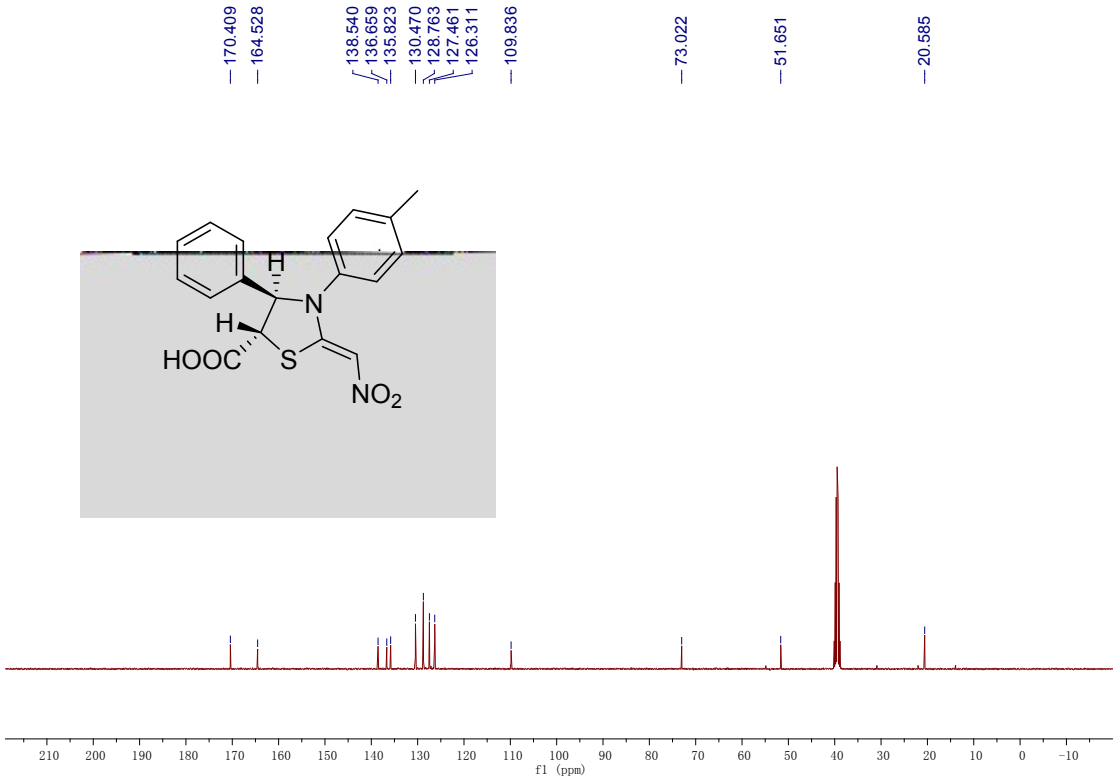
^{1}H NMR spectrum of compound **2d**



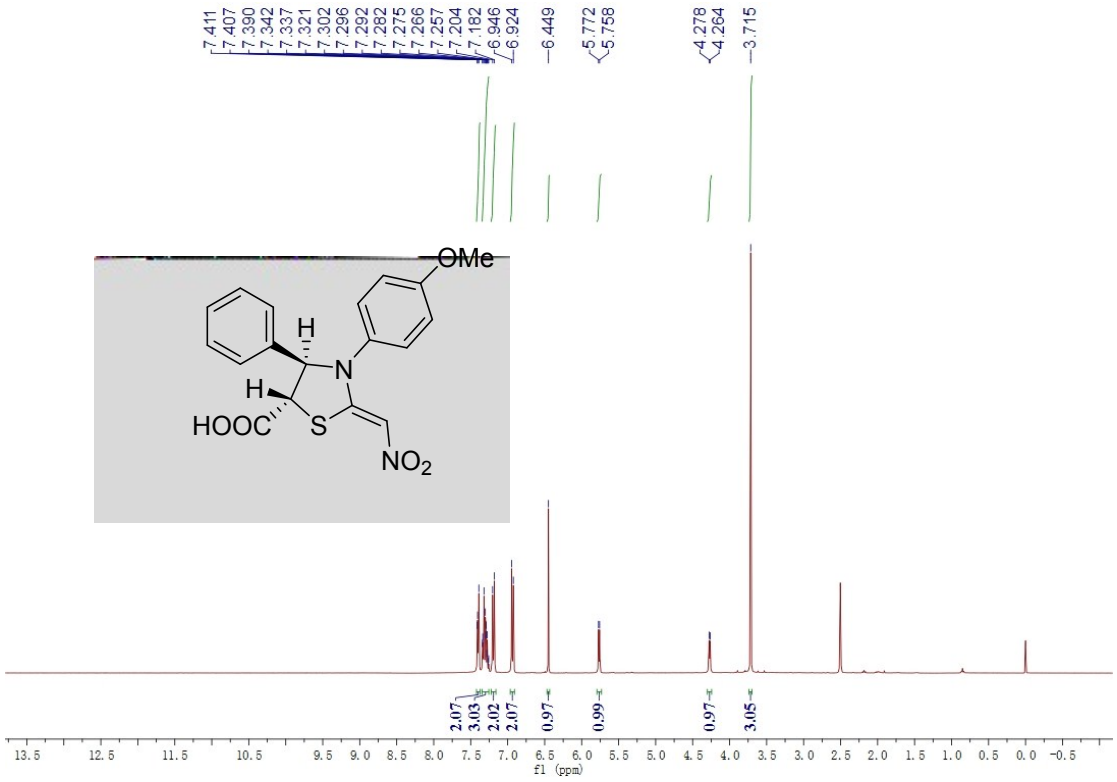
^{19}F NMR spectrum of compound **2d**



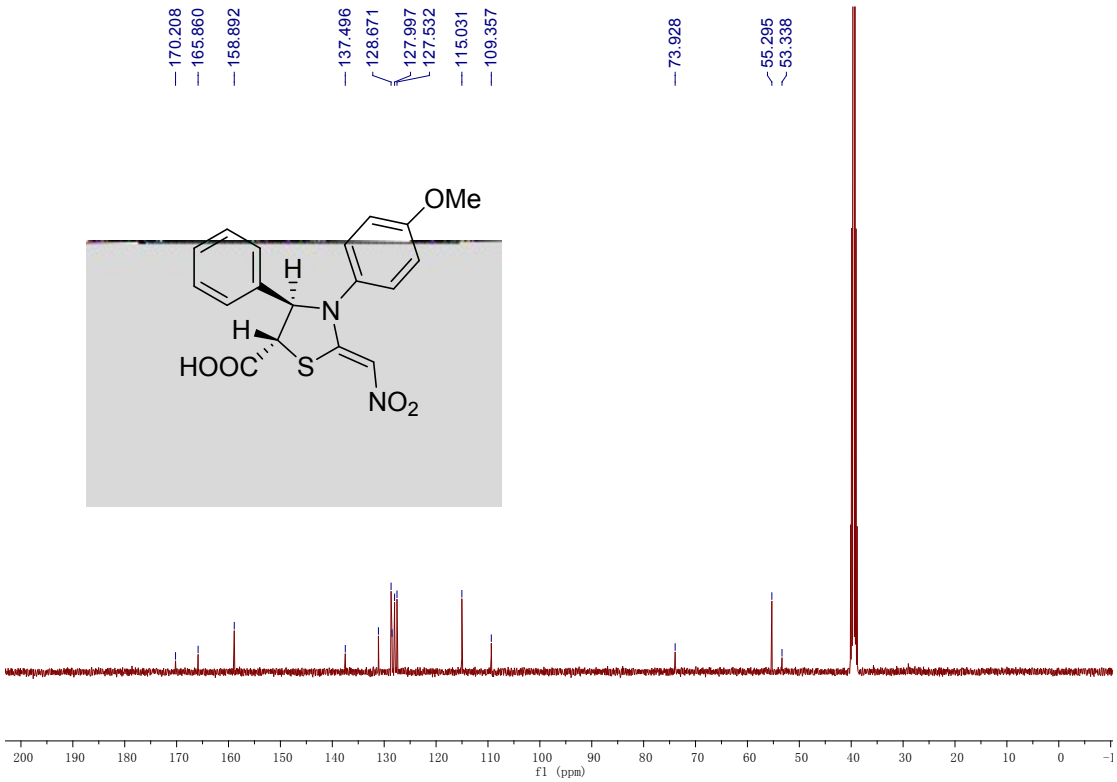
^{1}H NMR spectrum of compound **2e**



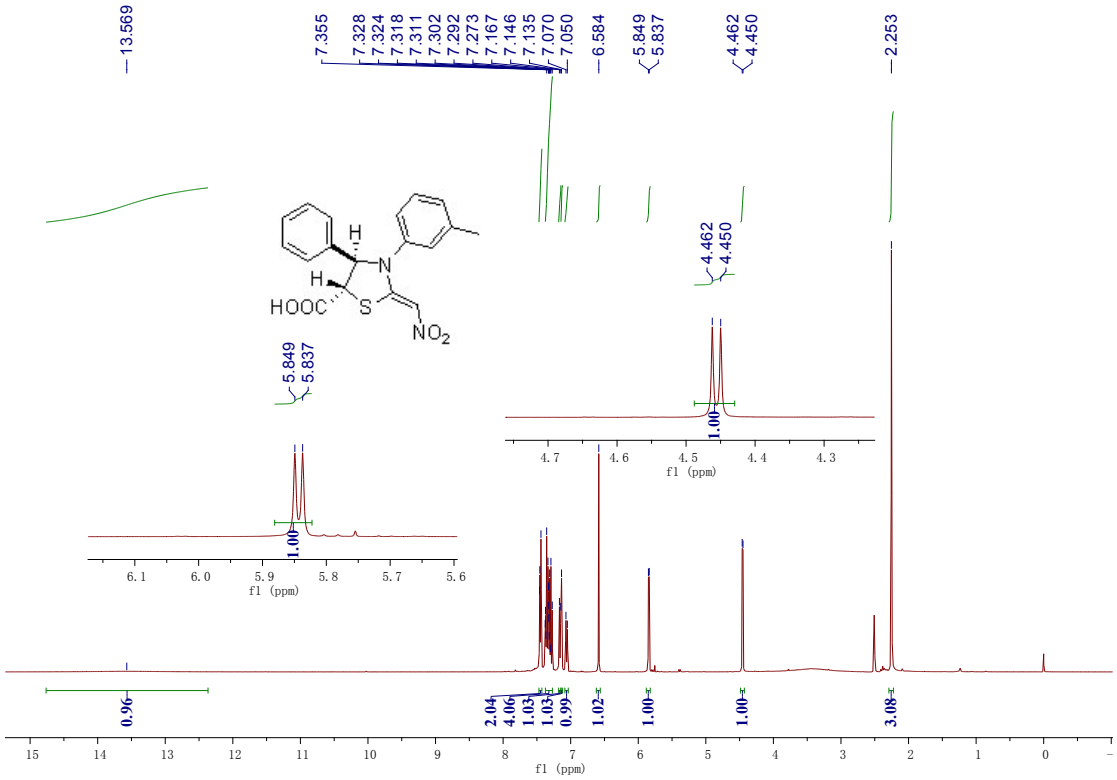
^{13}CNMR spectrum of compound **2e**



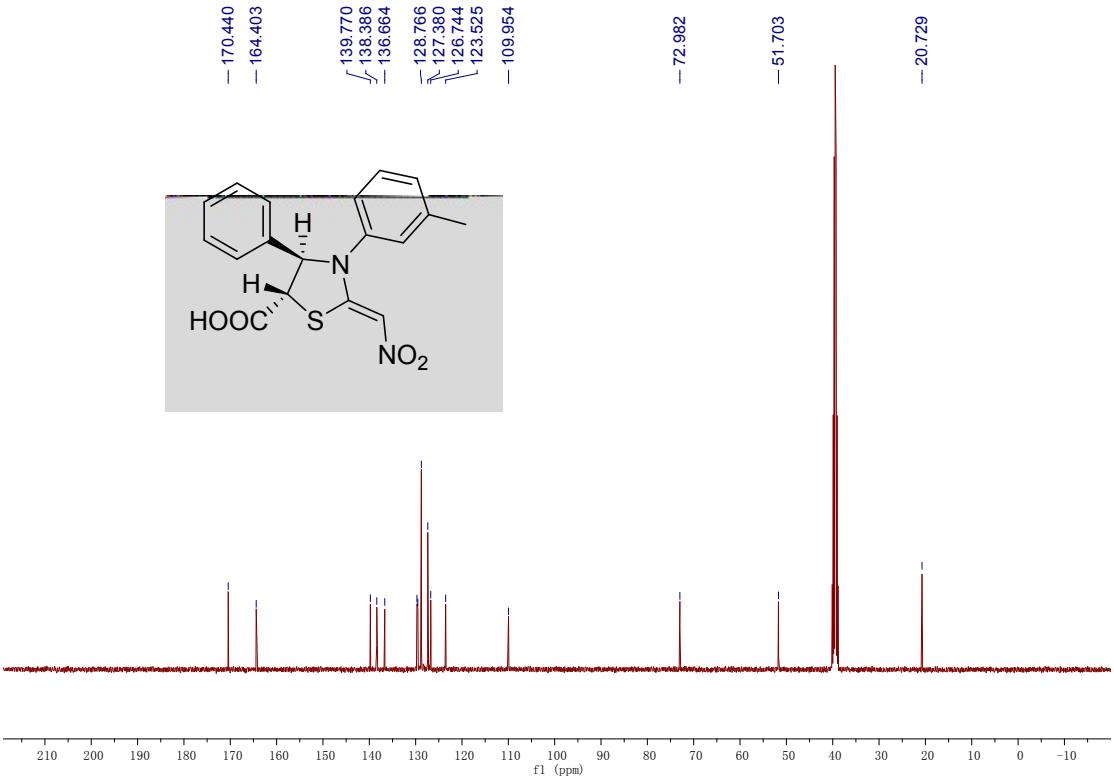
^{1}H NMR spectrum of compound **2f**



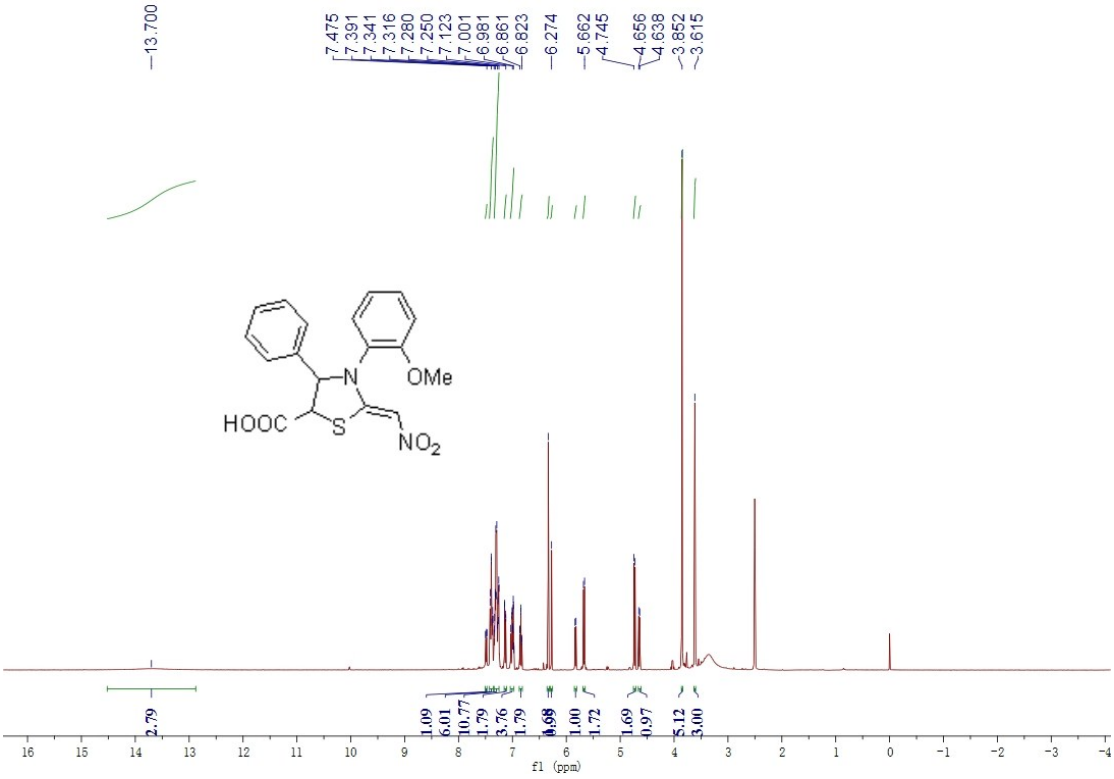
^{13}CNMR spectrum of compound **2f**



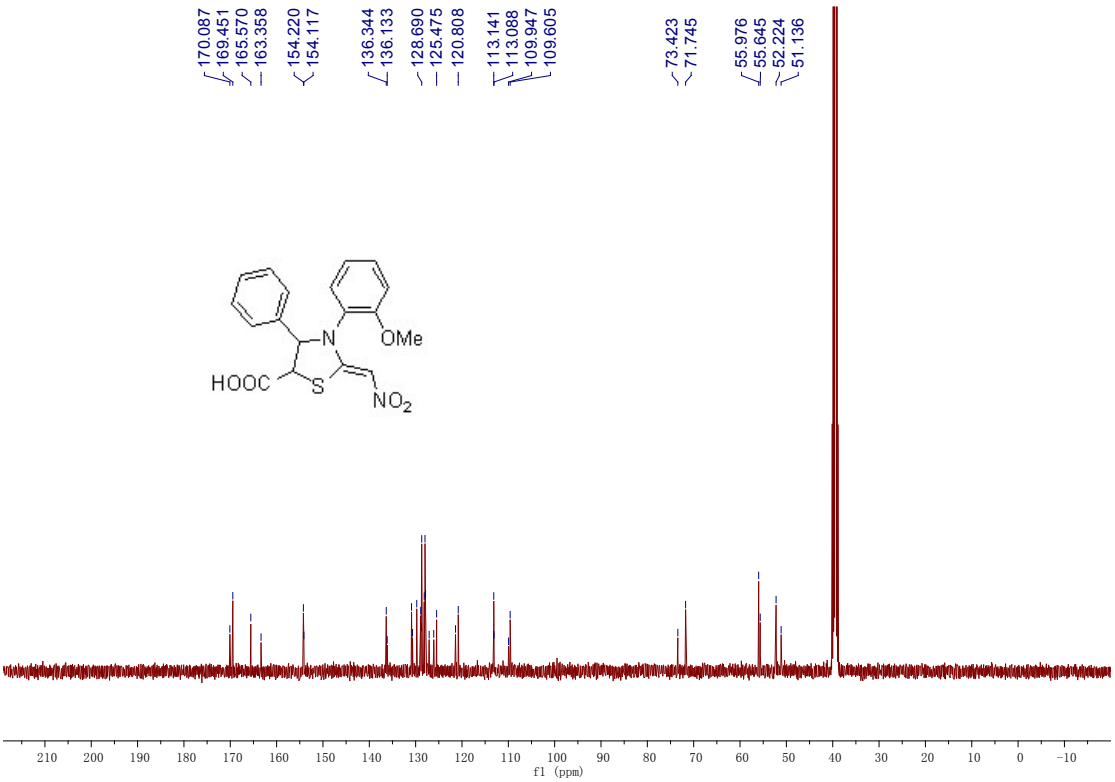
^{1}H NMR spectrum of compound **2g**



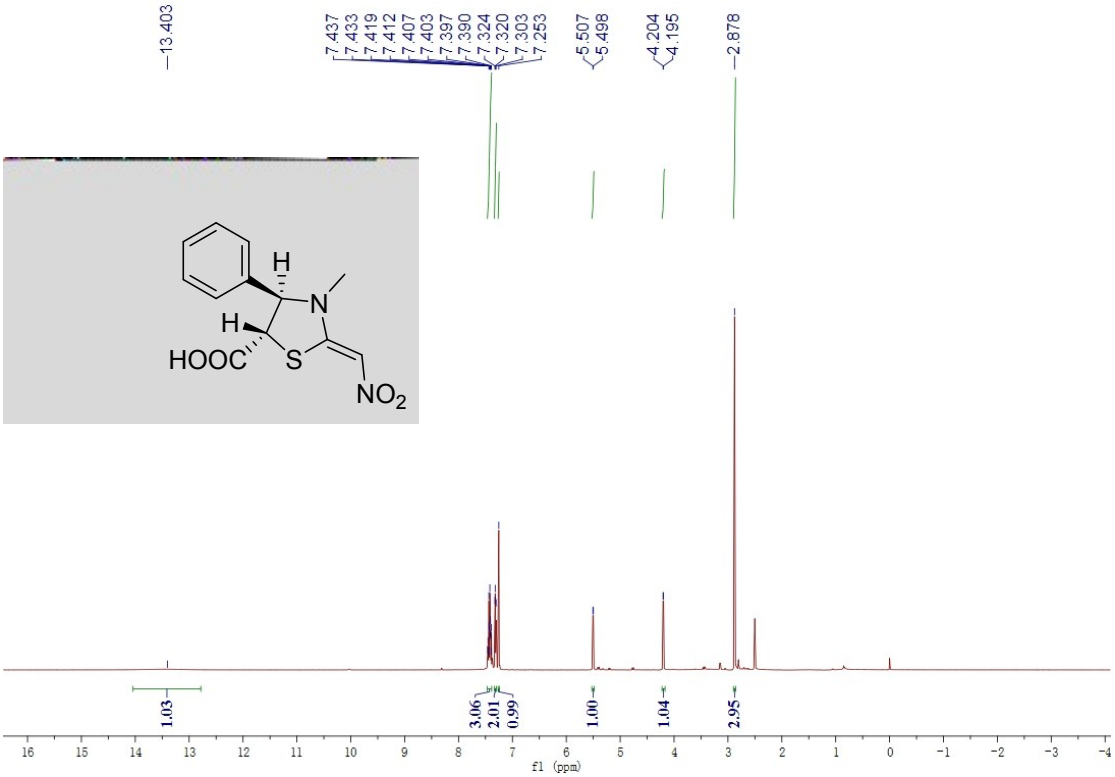
^{13}CNMR spectrum of compound **2g**



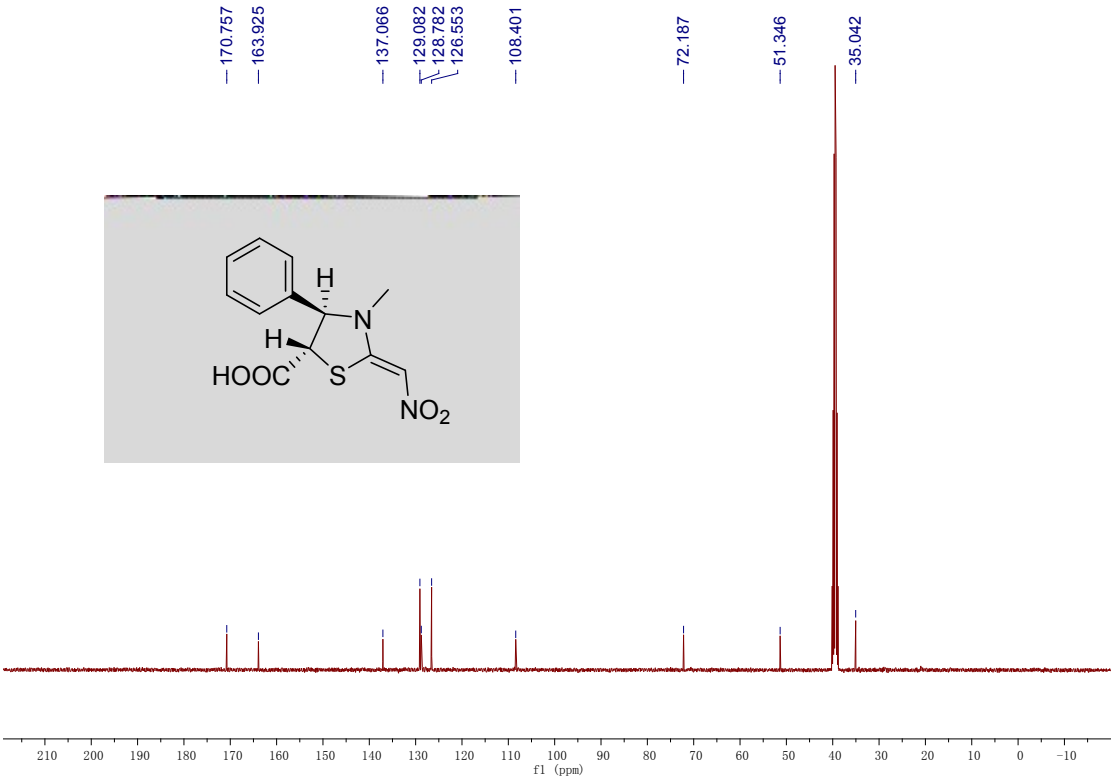
^{1}H NMR spectrum of compound **2h**



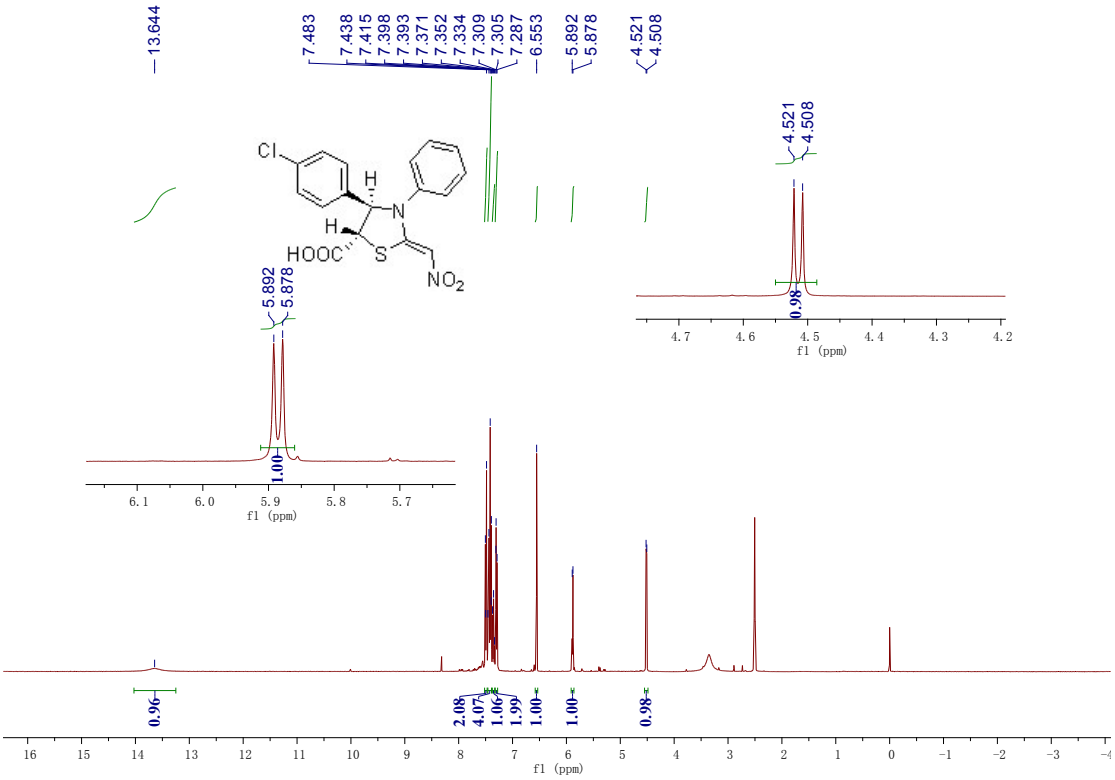
^{13}CNMR spectrum of compound **2h**



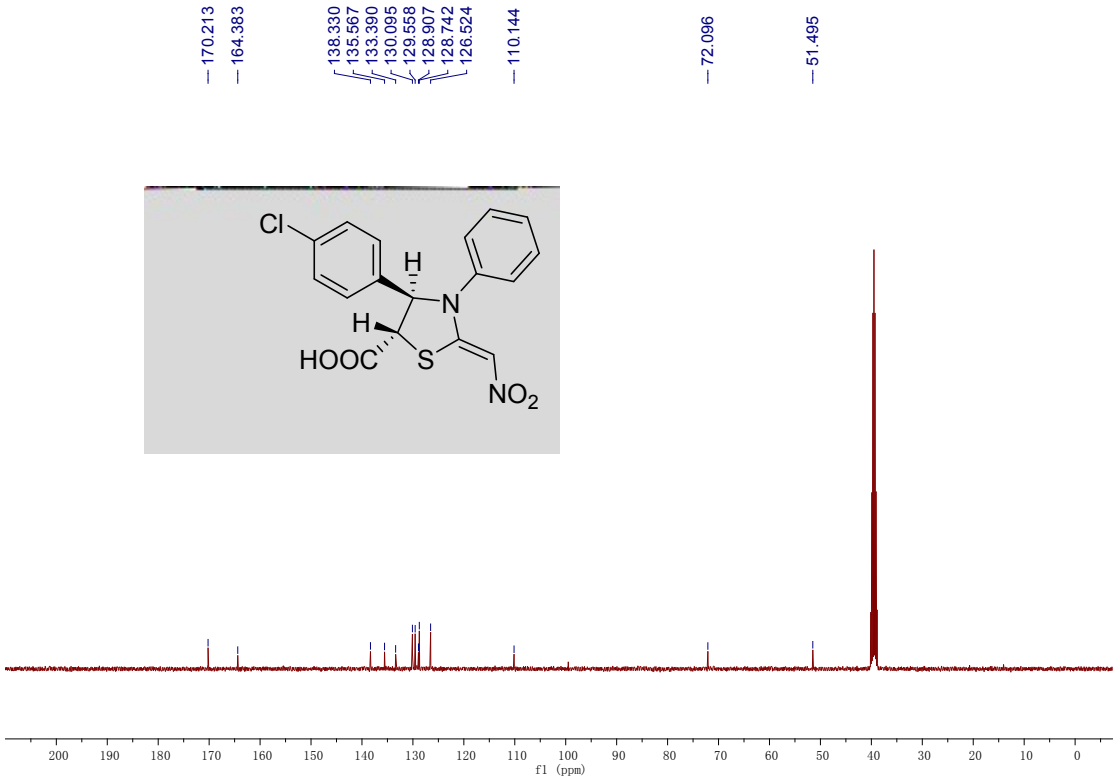
^{1}H NMR spectrum of compound **2i**



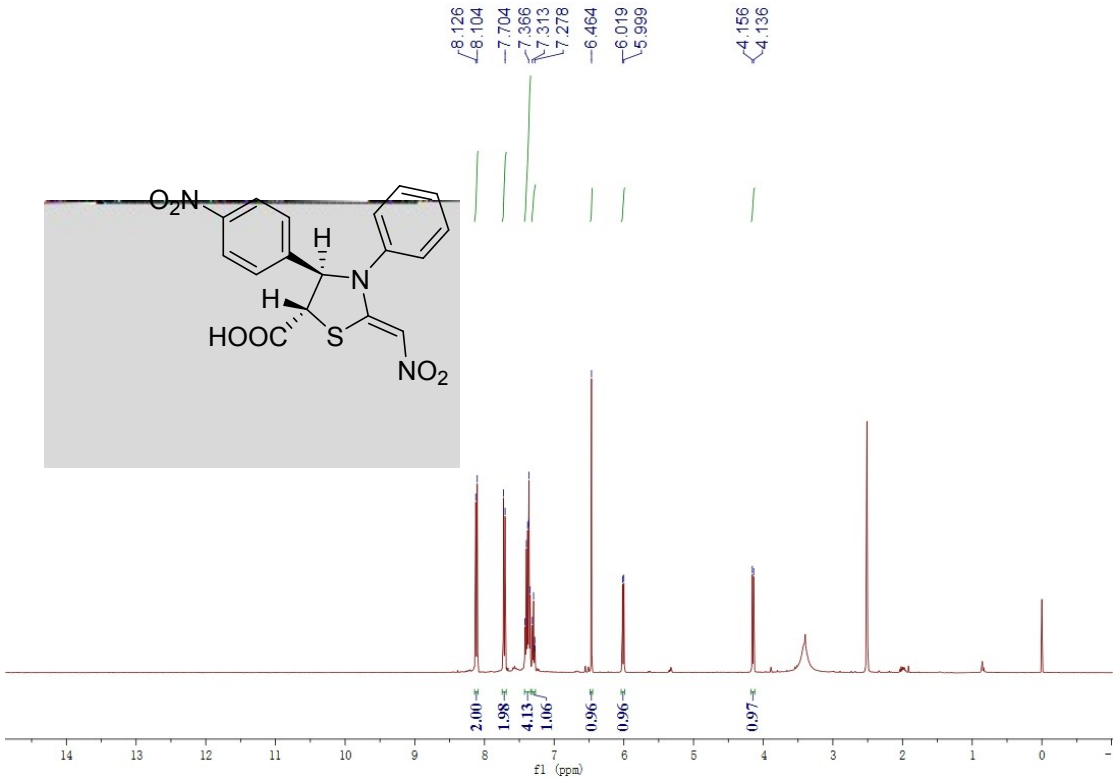
^{13}CNMR spectrum of compound **2i**



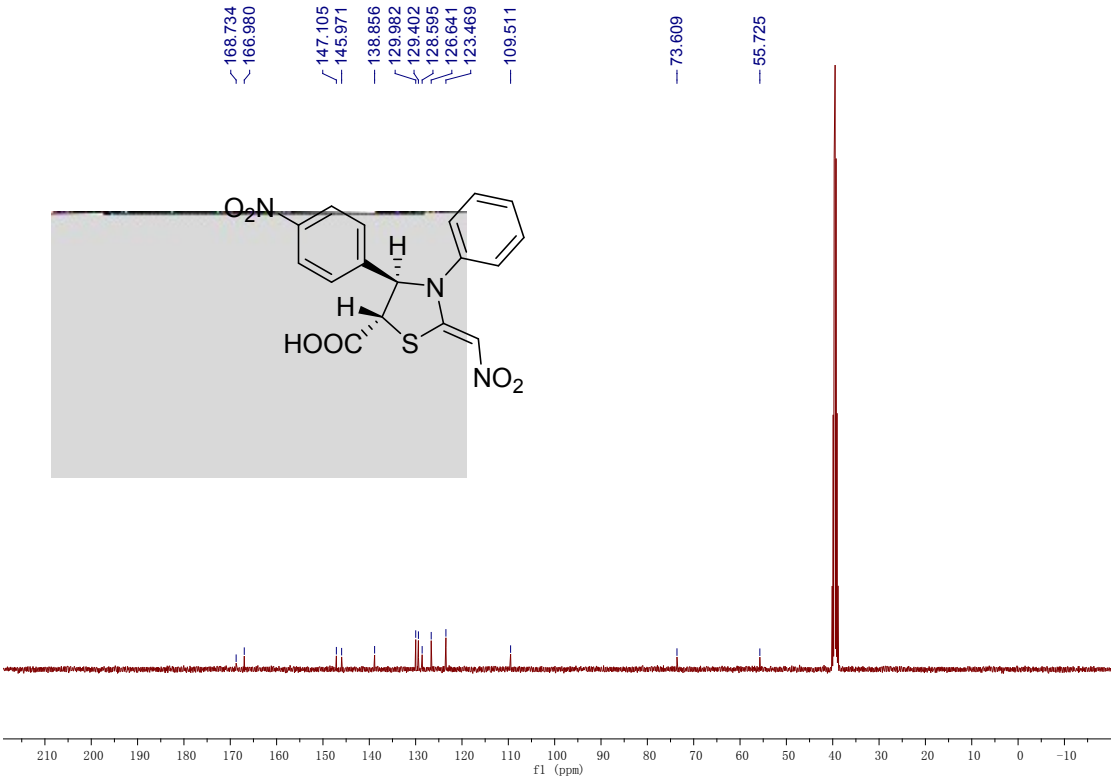
^{1}H NMR spectrum of compound **2j**



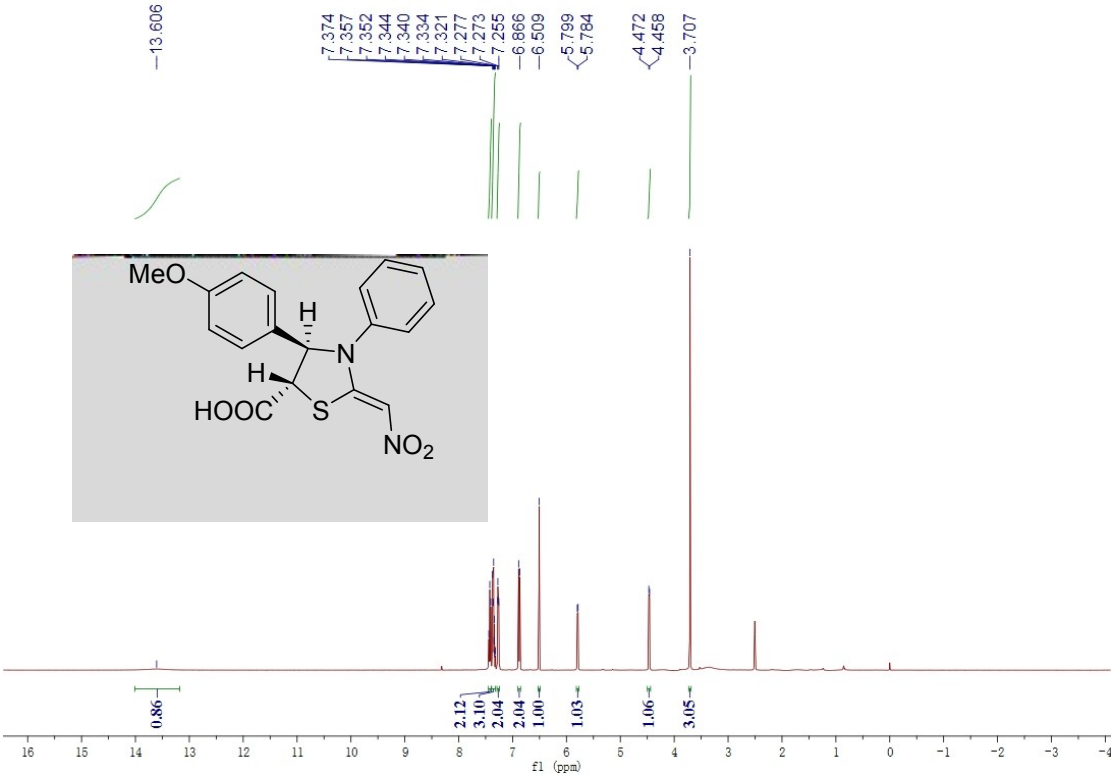
^{13}CNMR spectrum of compound **2j**



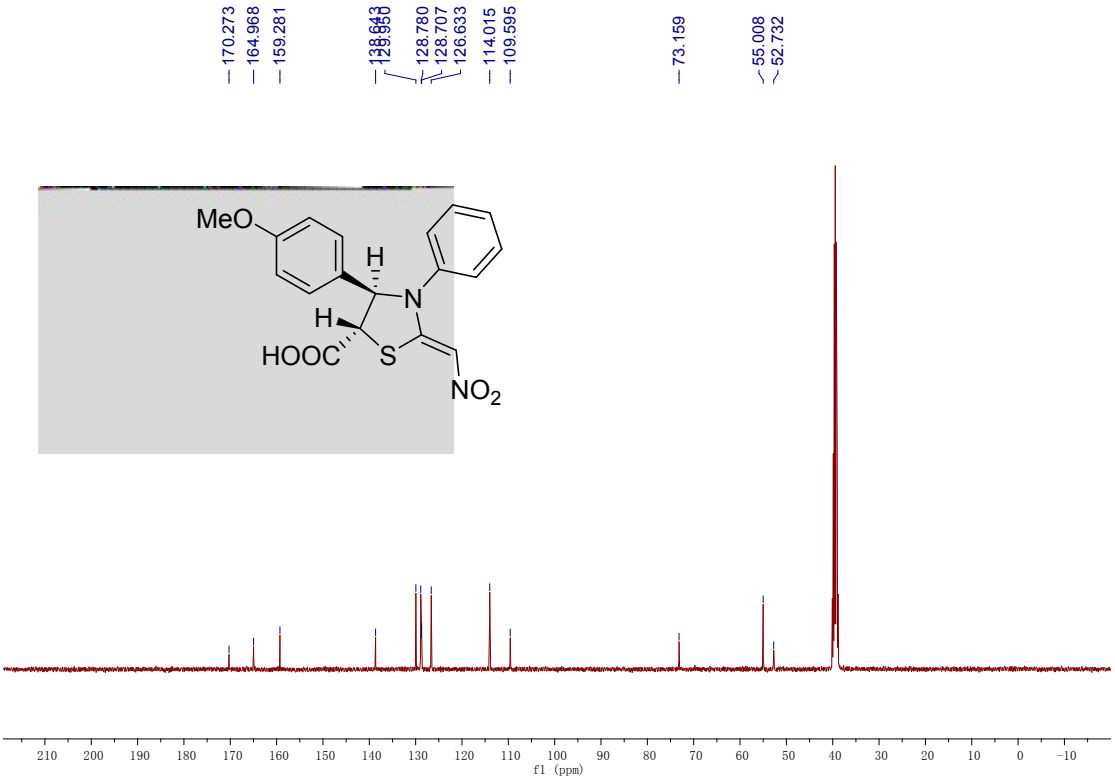
^{1}H NMR spectrum of compound **2k**



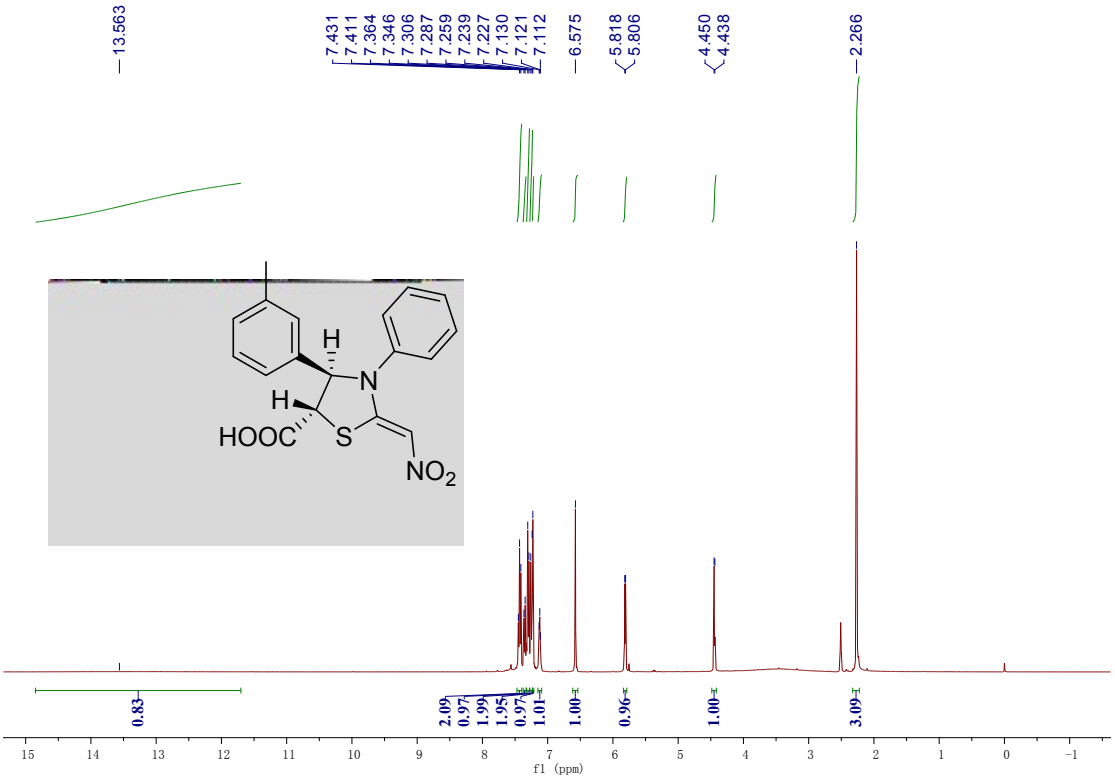
^{13}CNMR spectrum of compound **2k**



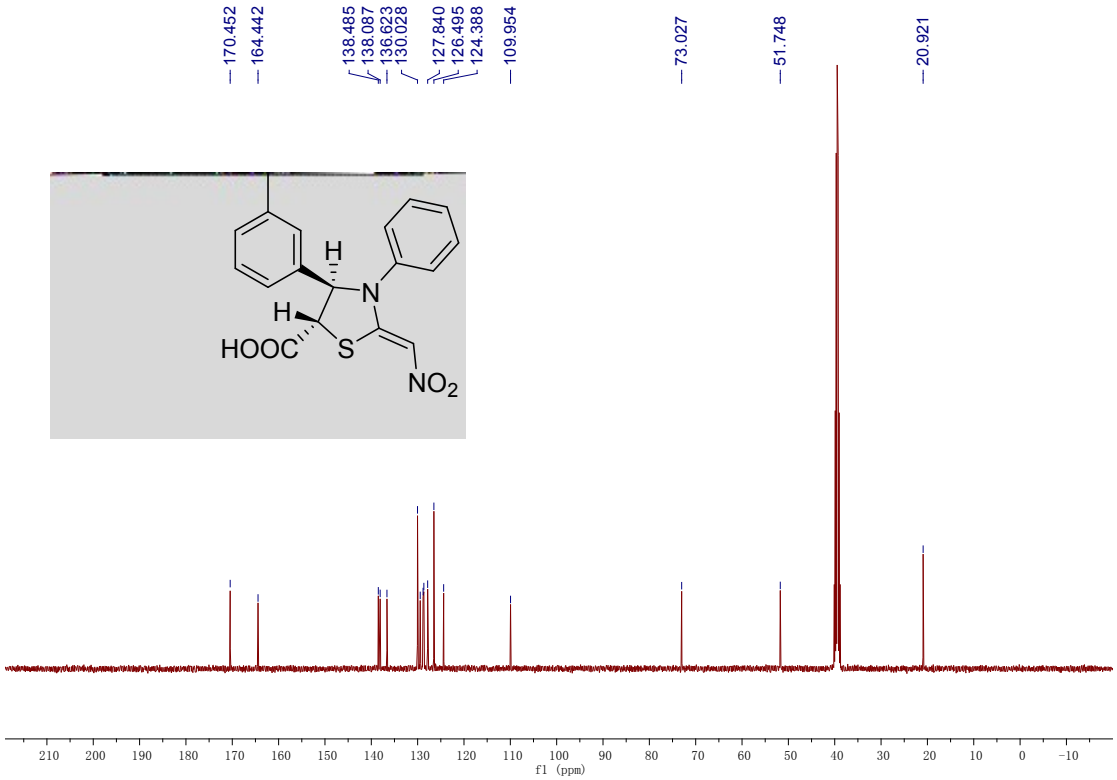
^{1}H NMR spectrum of compound **2l**



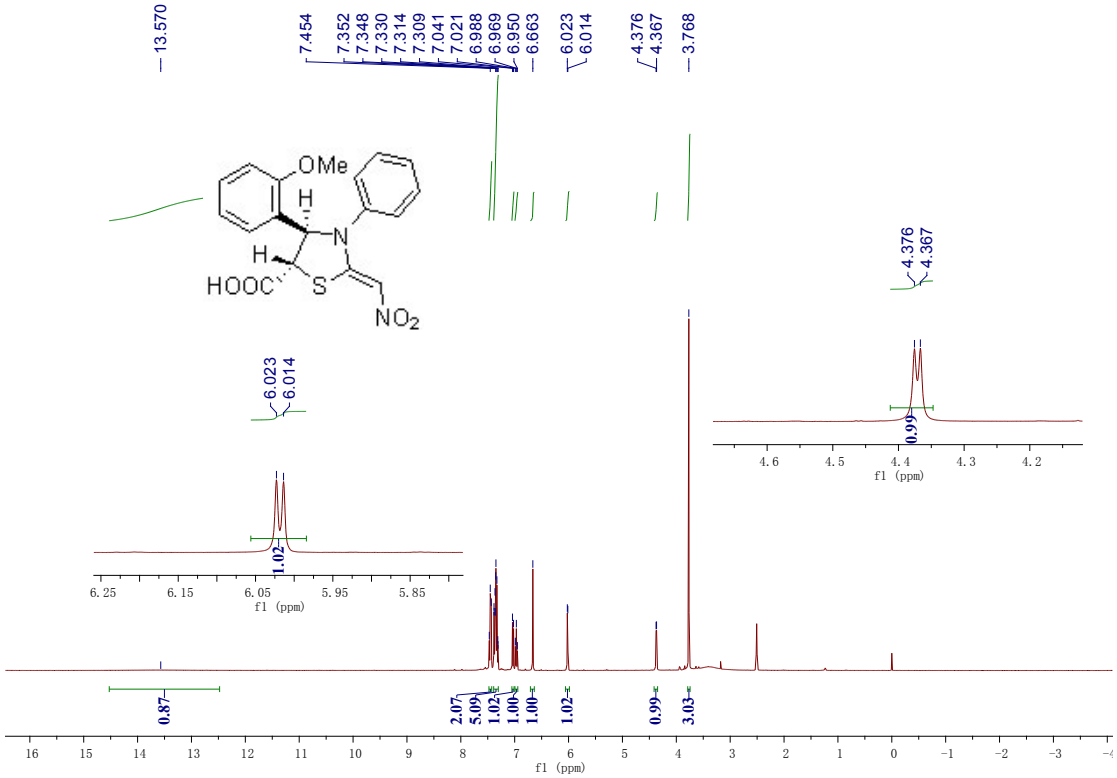
^{13}CNMR spectrum of compound **2l**



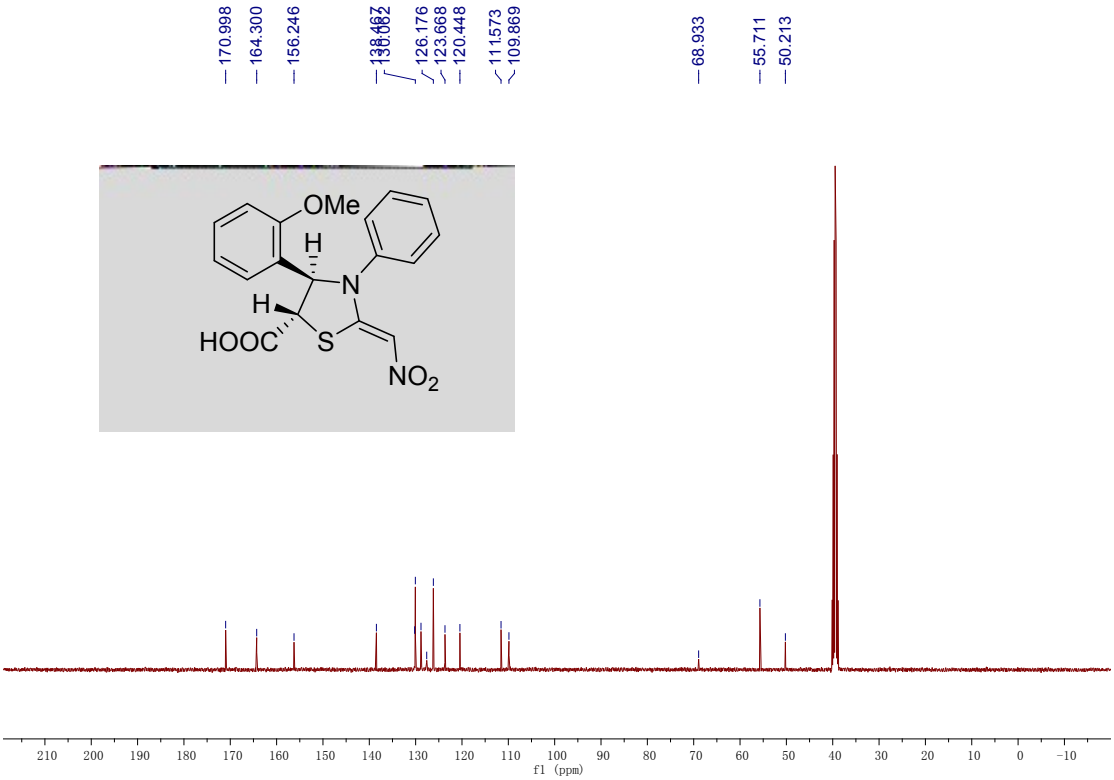
^{1}H NMR spectrum of compound **2m**



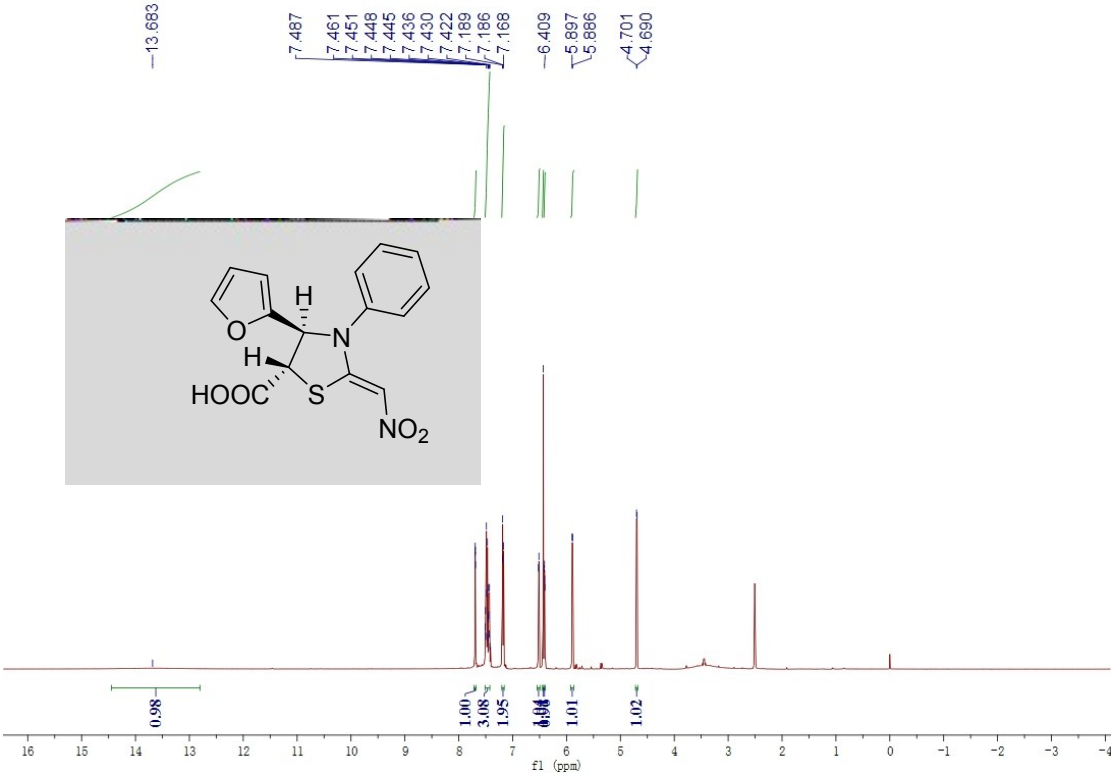
^{13}CNMR spectrum of compound **2m**



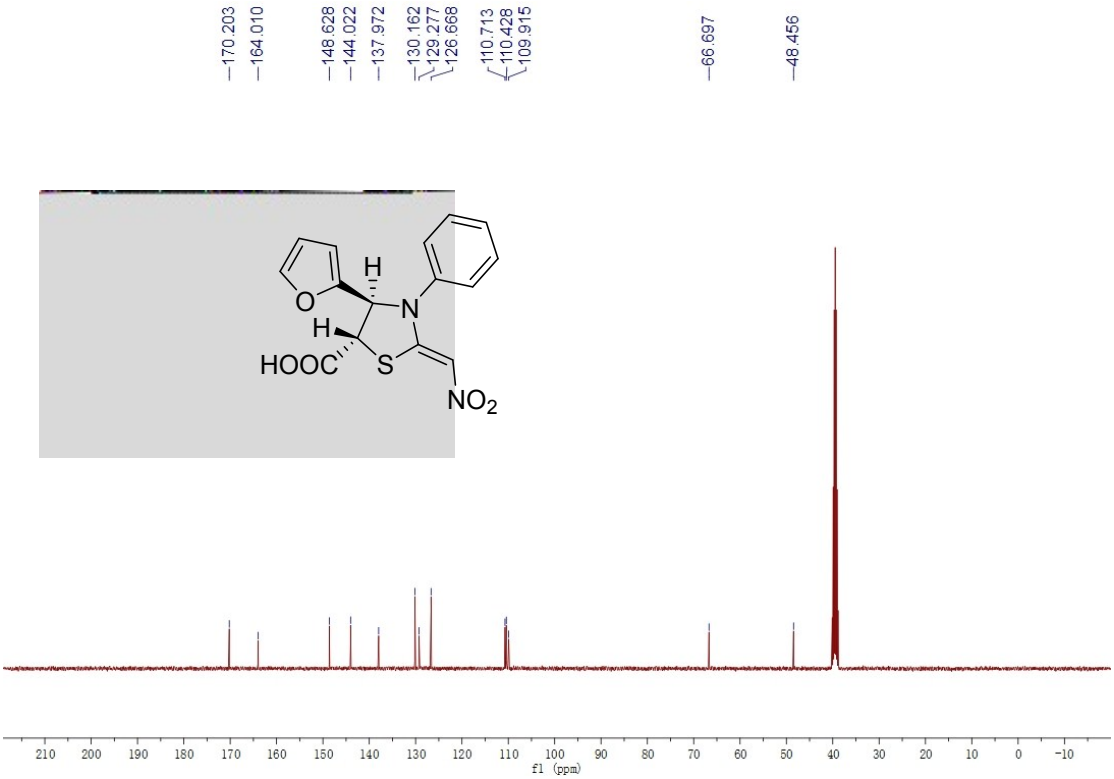
^{1}H NMR spectrum of compound **2n**



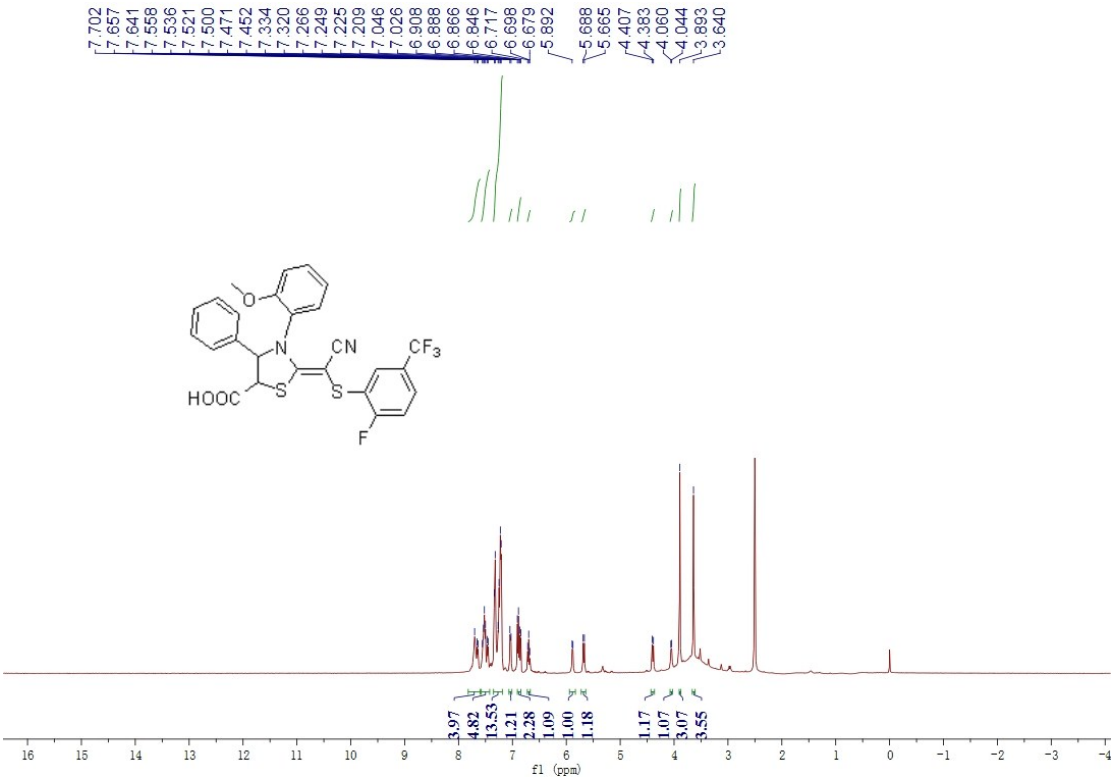
^{13}CNMR spectrum of compound **2n**



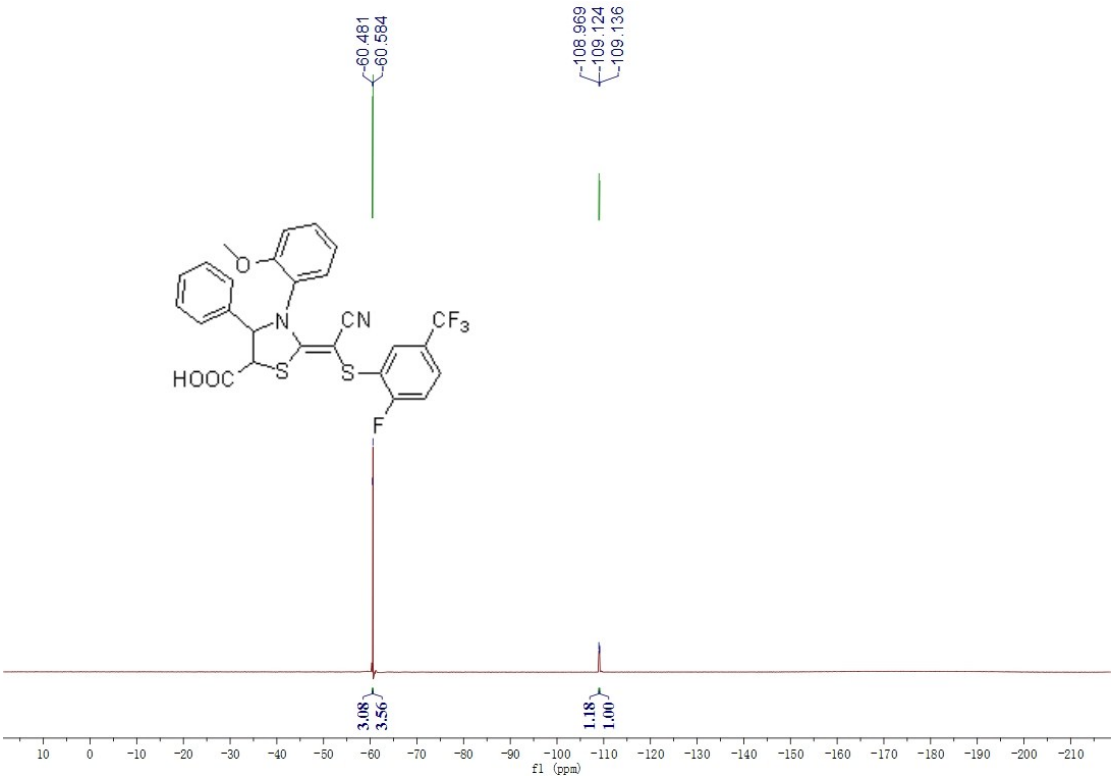
^{1}H NMR spectrum of compound **2o**



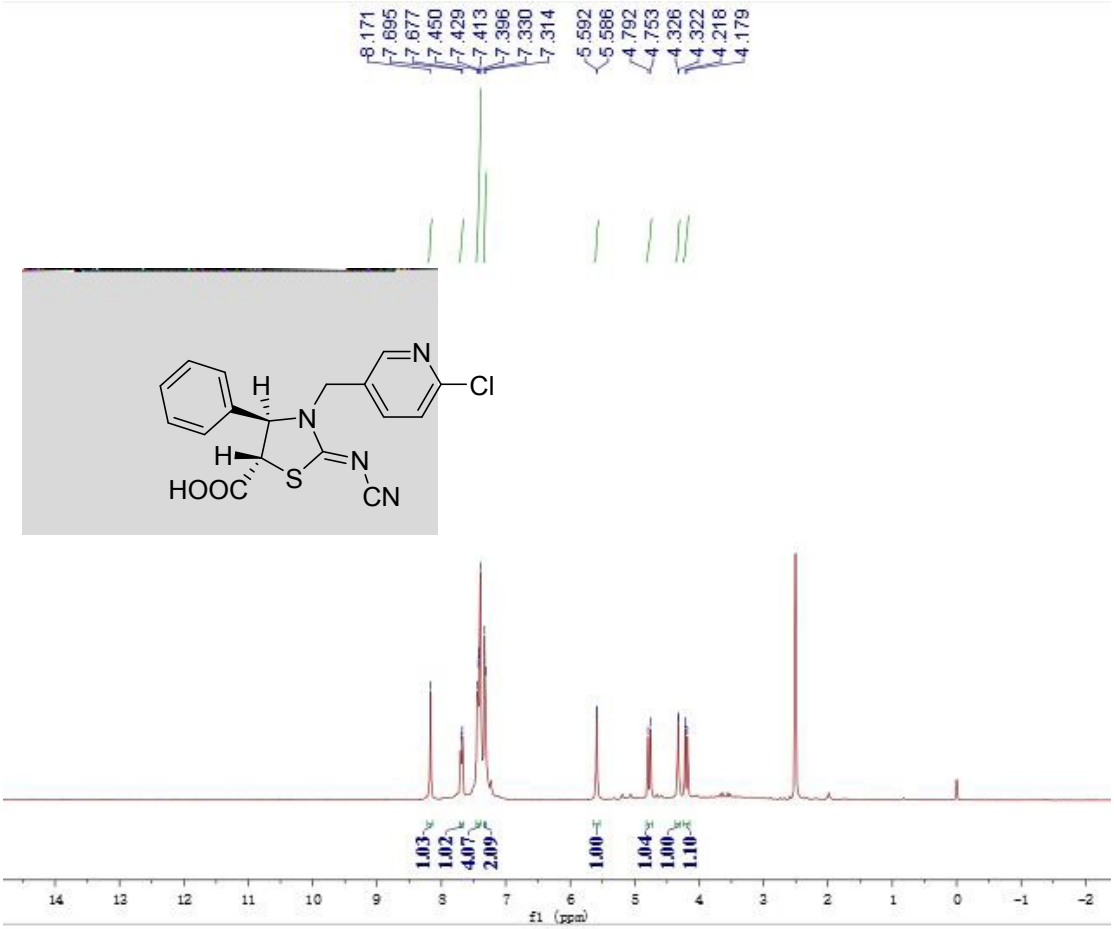
^{13}CNMR spectrum of compound **2o**



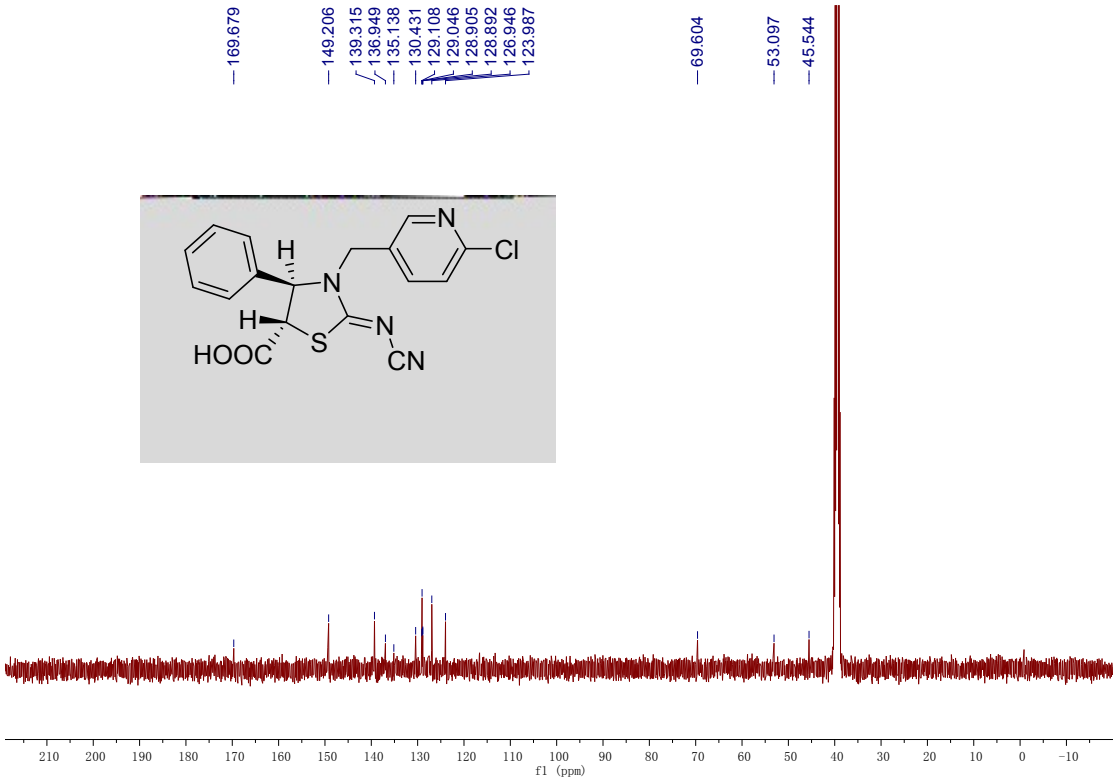
^{1}H NMR spectrum of compound **8**



^{19}F NMR spectrum of compound **8**



^{1}H NMR spectrum of compound **10**



^{13}CNMR spectrum of compound **10**