Supplementary Information

Radical-mediated sulfonylation relay of alkyl alkynes/alkenes and electron-deficient alkenes to access vinyl and alkyl sulfones

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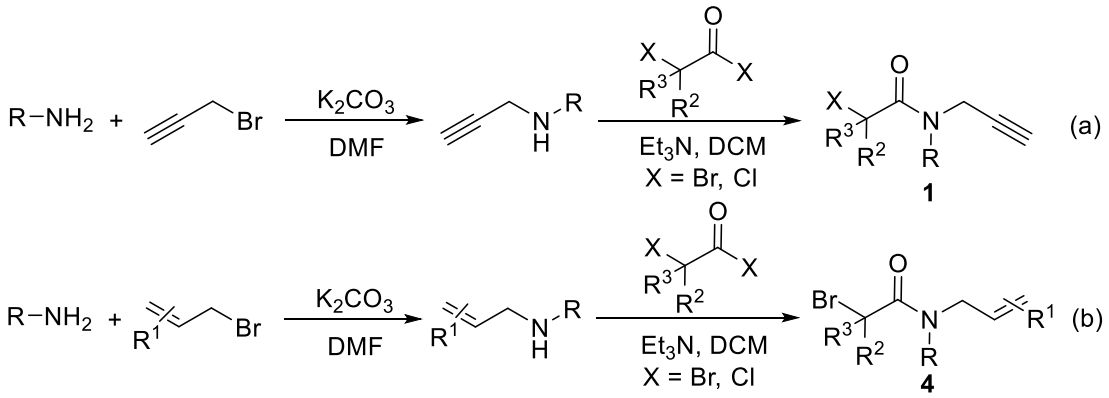
(A) General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. All products were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. Unless otherwise specified, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Reaction progress was monitored by thin-layer chromatography (TLC) or GC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was carried out on silica gel (200-300 mesh). Chemical yields refer to pure isolated substances.

(B) Experimental section

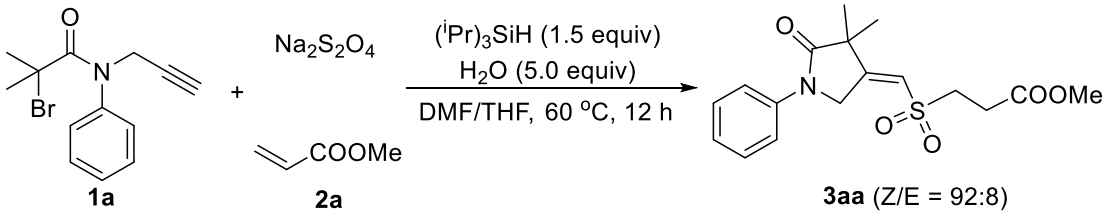
(a) Preparation of substrates

(1) Substrates **1 and 4** were prepared according to the literatures.[1,2]



(2) All of the electron-deficient alkenes (**2**) were purchased from ChemicalMalland used directly without further purification unless specified. **2j-2l** were prepared according to the literatures.[3]

(b) Typical experimental procedure for the synthesis of compound 3aa:

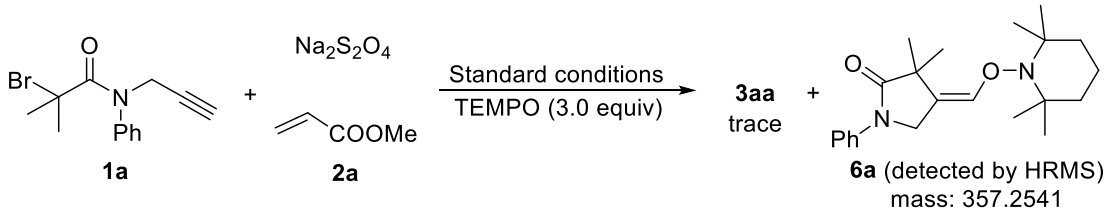


To a Schlenk tube were added **1a** (0.2 mmol), **2a** (1.2 equiv, 0.24 mmol), $Na_2S_2O_4$ (2.0 equiv, 0.4 mmol), $(^iPr)_3SiH$ (1.5 equiv, 0.3 mmol), H_2O (5.0 equiv, 1 mmol) and DMF/THF (2.0 mL, 1 : 1). Then the tube was stirred at 60 ^oC (oil bath temperature) under a N_2 atmosphere for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered. Then removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1 : 1) to provide the desired product **3aa** in 85% yield.

(c) General procedure for the 5.0 mmol scale synthesis of 3aa:

To a Schlenk tube were added **1a** (1.401 g, 5.0 mmol), **2a** (0.516 g, 6.0 mmol), $Na_2S_2O_4$ (1.741 g, 10.0 mmol), $(^iPr)_3SiH$ (1.187 g, 7.5 mmol), H_2O (5.0 equiv, 25.0 mmol) and DMF/THF (20.0 mL, 1 : 1). Then the tube was stirred at 60 ^oC (oil bath temperature) under a N_2 atmosphere for 24 h until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the reaction mixture was filtered. Then removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1 : 1) to provide the desired product **3aa** in 80% yield.

(d) Radical trapping experiments with TEMPO



To a Schlenk tube were added **1a** (0.2 mmol), **2a** (1.2 equiv, 0.24 mmol), $Na_2S_2O_4$ (2.0 equiv, 0.4 mmol), $(^iPr)_3SiH$ (1.5 equiv, 0.3 mmol), H_2O (5.0 equiv, 1 mmol) and DMF/THF (2 mL, 1 : 1), TEMPO (3.0 equiv, 0.6 mmol). Then the tube was stirred at 60 ^oC (oil bath temperature) under a N_2 atmosphere for 12 h until complete consumption of starting material as monitored by TLC. The desired product **3aa** was not obtained. In addition, the product **6a** of vinyl radical coupling with TEMPO was detected by HMRS (Figure S1).

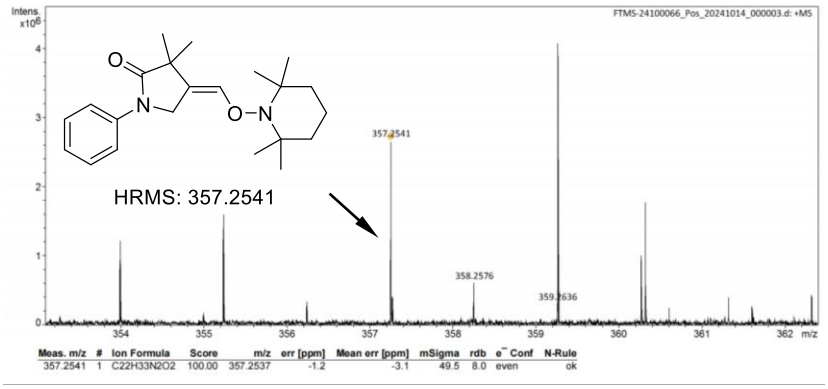
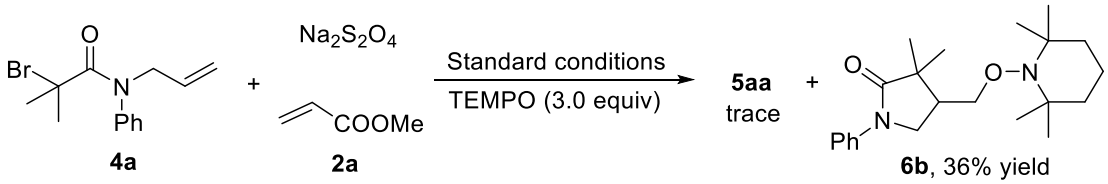


Figure S1 HMRS of 6a



To a Schlenk tube were added **4a** (0.2 mmol), **2a** (1.2 equiv, 0.24 mmol), $Na_2S_2O_4$ (2.0 equiv, 0.4 mmol), $(^iPr)_3SiH$ (1.5 equiv, 0.3 mmol), H_2O (5.0 equiv, 1.0 mmol) and DMF/THF (2.0 mL, 1 : 1), TEMPO (3.0 equiv, 0.6 mmol). Then the tube was stirred at 60 ^oC (oil bath temperature) under a N_2 atmosphere for 12 h until complete consumption of starting material as monitored by TLC. The desired product **5aa** was not detected, and product **6b** was obtained with a yield of 36%.

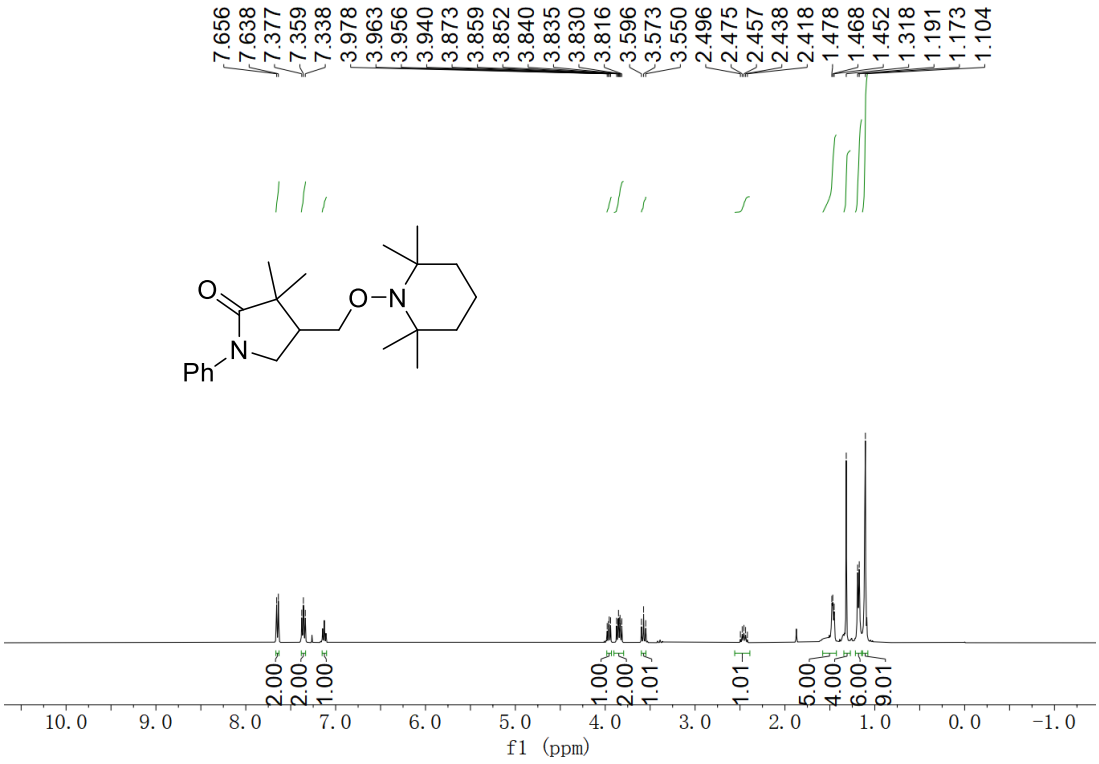


Figure S2 ^{1}H NMR of 6b

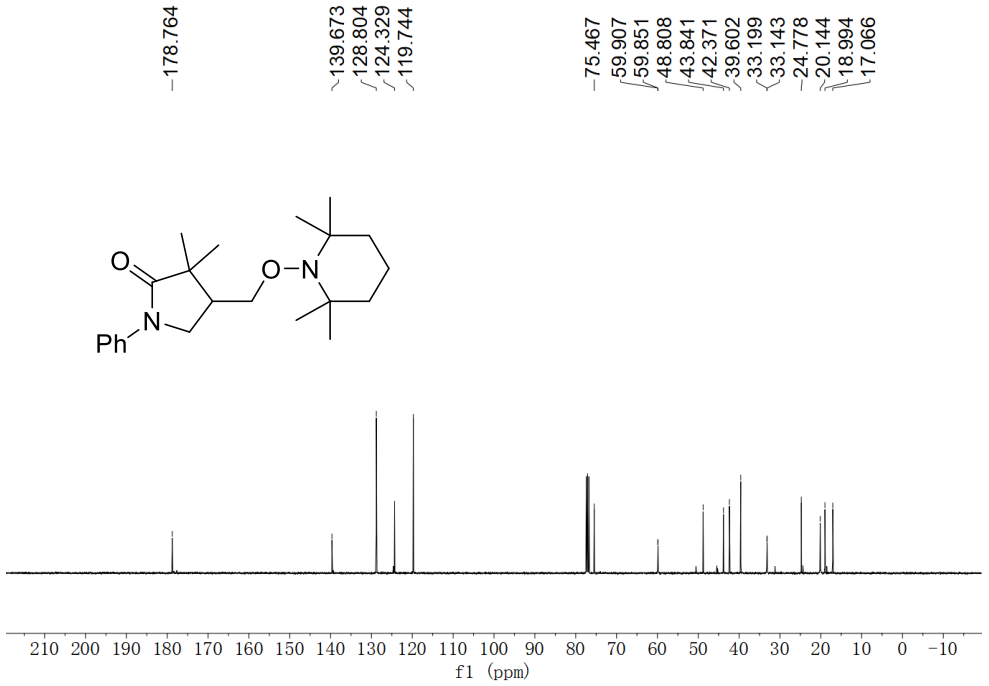


Figure S3 ^{13}C NMR of 6b

(e) Proton capture experiments

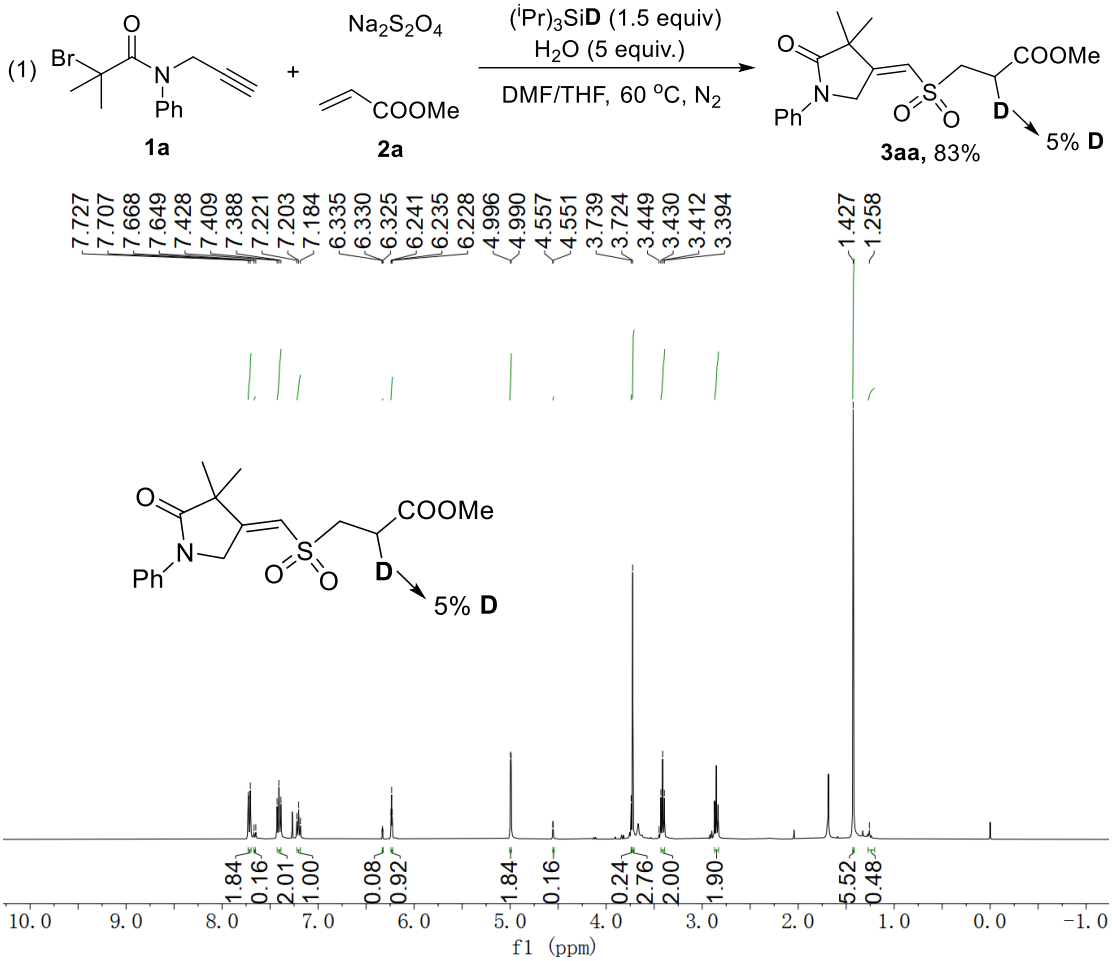


Figure S4 ^{1}H NMR of 3aa (5% D)

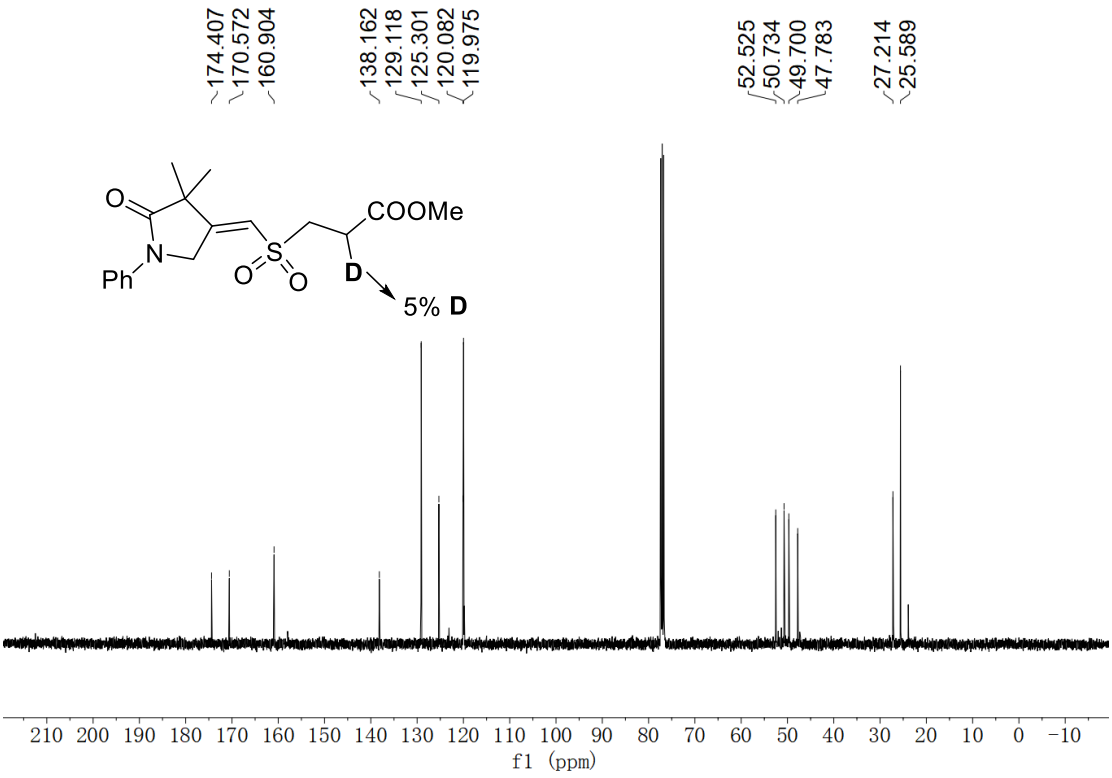


Figure S5 ^{13}C NMR of 3aa(5% D)

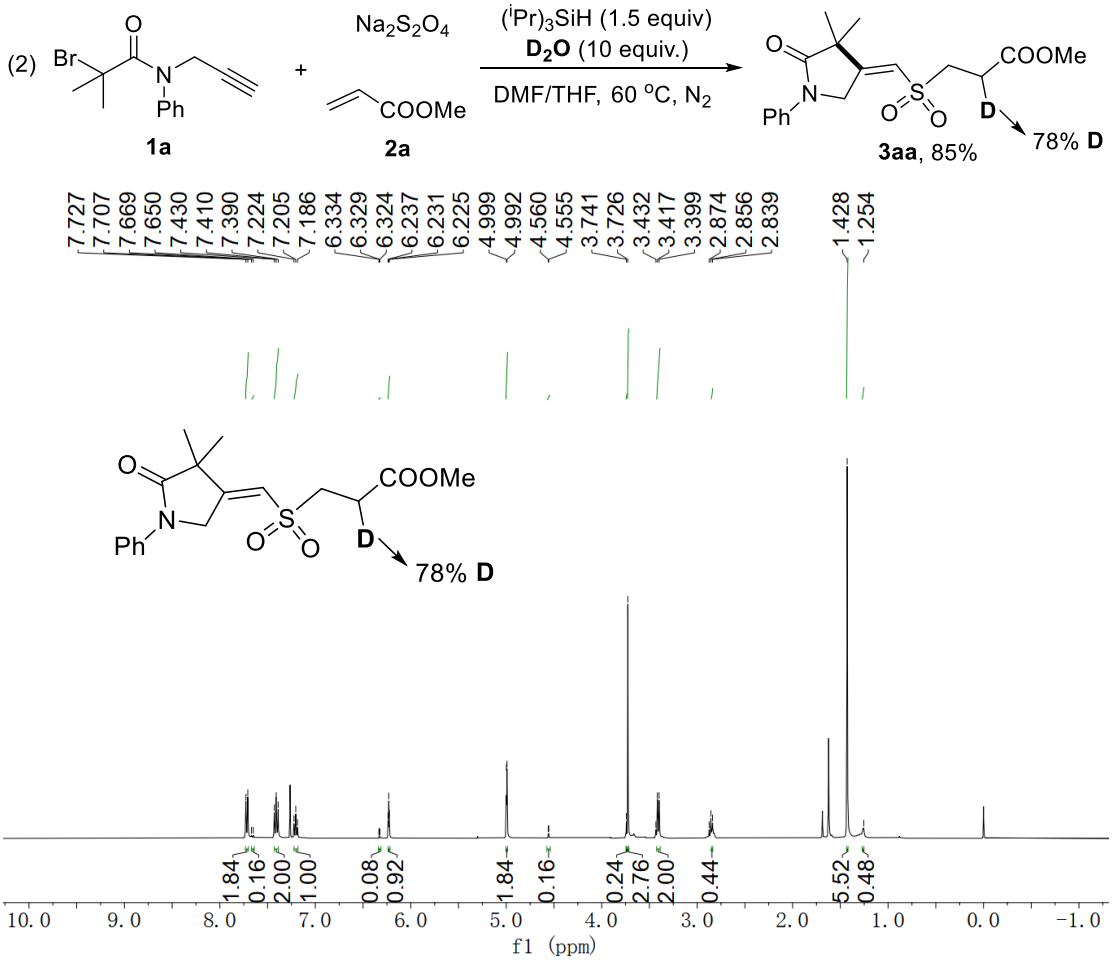


Figure S6 ^{1}H NMR of 3aa(78%D)

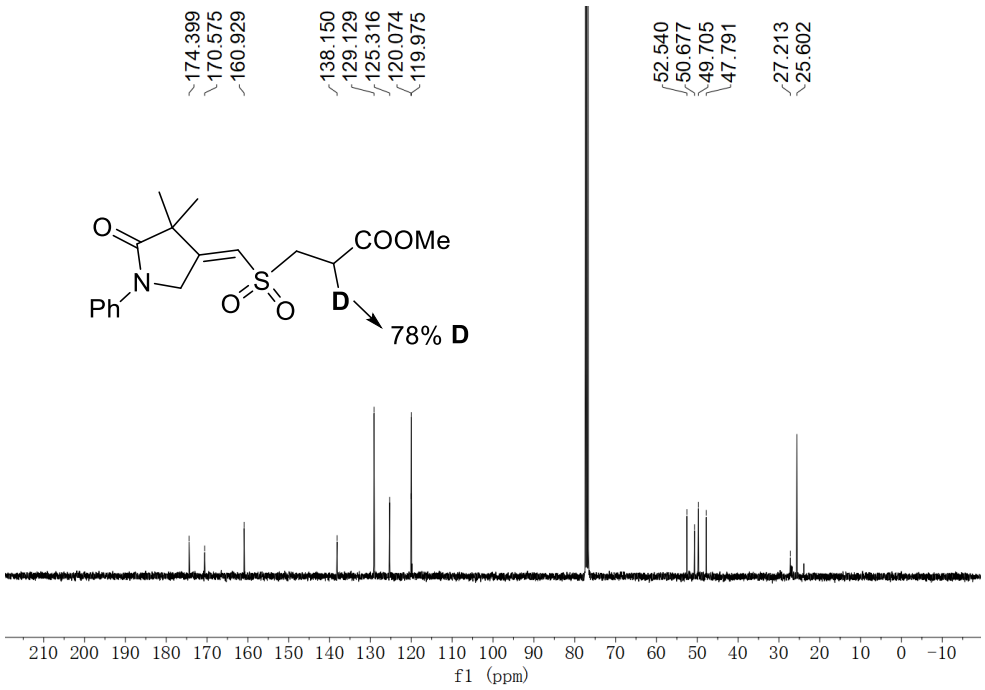
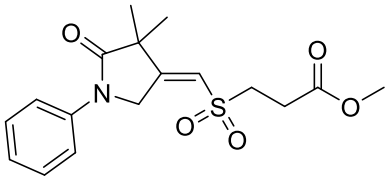


Figure S7 ^{13}C NMR of 3aa(78%D)

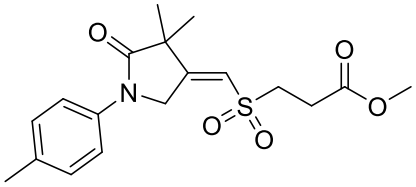
(C) Analytical data

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3aa, Z/E = 92 : 8):



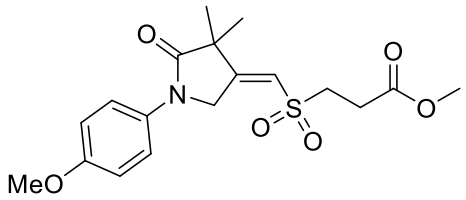
59.7 mg, 85%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.0 Hz, 1.84H), 7.66 (d, *J* = 8.4 Hz, 0.16H), 7.50 (d, *J* = 7.6 Hz, 0.16H), 7.41 (t, *J* = 7.6 Hz, 1.84H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.33 (t, *J* = 2.4 Hz, 0.08H), 6.24 (d, *J* = 2.4 Hz, 0.92H), 4.99 (d, *J* = 2.0 Hz, 1.84H), 4.55 (d, *J* = 2.0 Hz, 0.16H), 3.74 (s, 3H), 3.45-3.39 (m, 2H), 2.95-2.83 (m, 2H), 1.43 (s, 5.52H)), 1.33 (s, 0.48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 170.6, 160.9, 138.2, 129.1, 125.3, 120.1, 120.0, 52.5, 50.7, 49.7, 47.8, 27.2, 25.6, 23.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{22}NO_5S$ ($[M+H]^+$) 352.1213, found 352.1206.

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(p-tolyl)pyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ba, Z/E = 95 : 5):



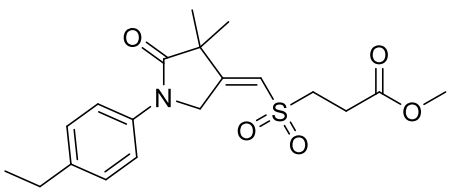
56.9 mg, 78%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.4 Hz, 1.9H), 7.52 (d, *J* = 8.4 Hz, 0.1H), 7.36 (d, *J* = 8.0 Hz, 0.1H), 7.20 (d, *J* = 8.0 Hz, 1.9H), 6.31 (s, 0.05H), 6.22 (s, 0.95H), 4.96 (s, 1.9H), 4.52 (s, 0.1H), 4.15-4.09 (m, 0.15H), 3.75-3.68 (m, 2.85H), 3.43-3.34 (m, 2H), 2.95-2.83 (m, 2H), 2.34 (s, 2.85H), 2.04 (s, 0.15H), 1.42 (s, 5.7H), 1.32 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 170.6, 161.2, 135.7, 135.1, 129.6, 120.0, 120.0, 52.5, 50.7, 49.8, 47.7, 27.2, 25.6, 20.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S$ ($[M+H]^+$) 366.1370, found 366.1366.

methyl (Z)-3-(((1-(4-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ca, Z/E = 90 : 10):



57.9 mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 9.2 Hz, 1.8H), 7.54 (d, *J* = 9.2 Hz, 0.2H), 7.38 (d, *J* = 8.8 Hz, 0.2H), 6.93 (d, *J* = 9.2 Hz, 1.8H), 6.31 (t, *J* = 2.0 Hz, 0.1H), 6.23 (t, *J* = 2.0 Hz, 0.9H), 4.95 (d, *J* = 2.8 Hz, 1.8H), 4.51 (d, *J* = 2.0 Hz, 0.2H), 3.81 (s, 2.7H), 3.75 (s, 0.3H), 3.74 (s, 0.3H), 3.72 (s, 2.7H), 3.44-3.39 (m, 2H), 2.94-2.83 (m, 2H), 1.42 (s, 5.4H), 1.31 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.0, 170.6, 161.2, 157.1, 131.3, 121.8, 120.0, 114.3, 55.5, 52.5, 50.7, 50.1, 47.5, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_6S$ ($[M+H]^+$) 382.1319, found 382.1315.

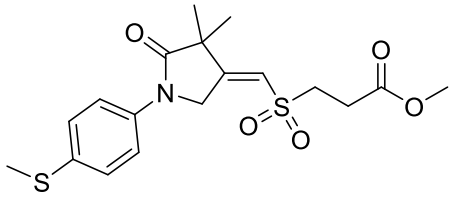
methyl (Z)-3-(((1-(4-ethylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3da, Z/E > 99 : 1):



60.6 mg, 80%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.24 (t, *J* = 2.4 Hz,

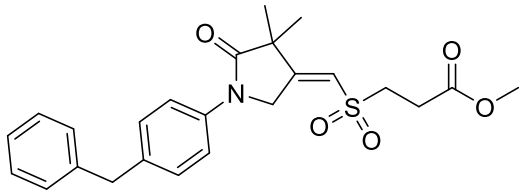
1H), 4.97 (d, *J* = 2.4 Hz, 2H), 3.71 (s, 3H), 3.40 (t, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.41 (s, 6H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 170.6, 161.1, 141.5, 135.8, 128.4, 120.1, 120.0, 52.5, 50.7, 49.8, 47.7, 28.3, 27.2, 25.5, 15.6; HRMS *m/z* (ESI) calcd for $C_{19}H_{26}NO_5S$ ($[M+H]^+$) 380.1526, found 380.1525.

methyl (Z)-3-(((4,4-dimethyl-1-(4-(methylthio)phenyl)-5-oxopyrrolidin-3-ylidene) methyl)sulfonyl)propanoate (3ea, Z/E = 99 : 1):



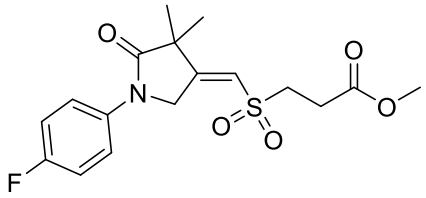
63.5 mg, 80%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.8 Hz, 1.98H), 7.59 (d, *J* = 8.8 Hz, 0.02H), 7.50 (d, *J* = 8.8 Hz, 0.02H), 7.29 (d, *J* = 8.8 Hz, 1.98H), 6.32 (t, *J* = 2.0 Hz, 0.01H), 6.24 (t, *J* = 2.4 Hz, 0.99H), 4.96 (d, *J* = 2.8 Hz, 1.98H), 4.52 (d, *J* = 2.4 Hz, 0.02H), 3.92-3.91(m, 0,03), 3.74-3.72 (m, 2.97H), 3.43-3.34 (m, 2.0H), 2.91-2.83 (m, 2.0H), 2.66 (s, 0.03H), 2.49 (s, 2.97H), 1.42 (s, 5.94H), 1.26 (s, 0.06H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:174.3, 170.6, 160.7, 135.6, 135.1, 127.5, 120.4, 120.1, 52.5, 50.7, 49.7, 47.7, 27.2, 25.6, 16.3; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S_2$ ($[M+H]^+$) 398.1091, found 398.1088.

methyl (Z)-3-(((1-(4-benzylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)meth yl)sulfonyl)propanoate (3fa, Z/E = 95 : 5):



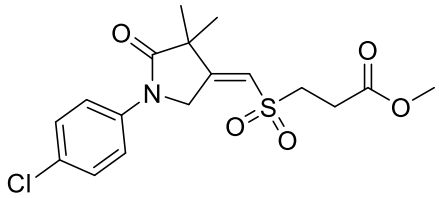
72.3 mg, 82%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.4 Hz, 1.9H), 7.41 (d, *J* = 8.4 Hz, 0.1H), 7.30-7.16 (m, 7H), 6.22 (t, *J* = 2.4 Hz, 1H), 4.96 (d, *J* = 2.4 Hz, 2.0H), 3.98 (s, 1.9H), 3.89 (s, 0.1H), 3.75 (s, 0.15H), 3.72 (s, 2.85H), 3.42-3.83 (m, 2.0H), 2.93 (t, *J* = 7.2 Hz, 0.1H), 2.84 (t, *J* = 7.2 Hz, 1.9H), 1.41 (s, 5.7H), 1.31 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 170.6, 161.0, 140.9, 138.3, 136.3, 129.6, 128.9, 128.5, 126.2, 120.2, 120.0, 52.5, 50.7, 49.8, 47.7, 41.3, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{24}H_{28}NO_5S_2$ ($[M+H]^+$) 442.1683, found 442.1682.

methyl (Z)-3-(((1-(4-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ga, Z/E = 95 : 5):



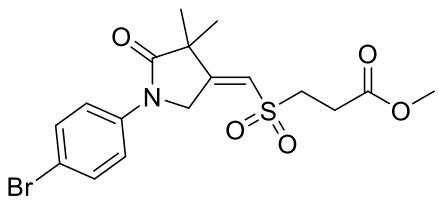
54.6 mg, 74%; yellow oil; eluent: petroleum ether/ethyl acetate = 2:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.61 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 0.1H), 7.10 (t, *J* = 8.8 Hz, 1.9H), 6.33 (t, *J* = 2.0 Hz, 0.05H), 6.24 (t, *J* = 2.4 Hz, 0.95H), 4.97 (d, *J* = 2.8 Hz, 1.9H), 4.53 (d, *J* = 2.0 Hz, 0.1H), 3.74 (s, 0.15H), 3.73(s, 2.85), 3.49-3.40 (m, 2H), 3.92-3.84 (m, 2H), 1.43 (s, 5.7H), 1.26(s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 170.6, 160.5, 159.9 (d, *J* = 243.9 Hz), 134.2 (d, *J* = 2.9 Hz), 121.8 (d, *J* = 7.8 Hz), 120.2, 115.8 (d, *J* = 22.3 Hz), 52.5, 50.7, 49.9, 47.6, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}FNO_5S$ ($[M+H]^+$) 370.1119, found 370.1115.

methyl (Z)-3-(((1-(4-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ha, Z/E = 90 : 10):



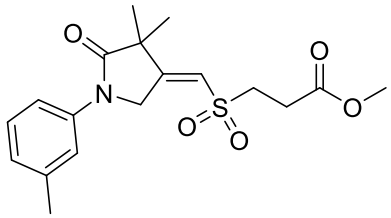
58.5mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 9.2 Hz, 1.8H), 7.63 (d, *J* = 8.8 Hz, 0.2H), 7.39-7.36 (m, 2H), 6.34 (t, *J* = 2.4 Hz, 0.1H), 6.24 (t, *J* = 2.8 Hz, 0.9H), 4.96 (d, *J* = 2.4 Hz, 1.8H), 4.53 (d, *J* = 2.4 Hz, 0.2H), 3.74 (s, 0.3H), 3.73(s, 2.7), 3.45-3.40 (m, 2H), 2.92-2.84 (m, 2H), 1.42 (s, 5.4H), 1.26 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 170.6, 160.2, 136.8, 130.4, 129.1, 121.0, 120.3, 52.5, 50.8, 49.6, 47.7, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}ClNO_5S$ ($[M+H]^+$) 386.0824, found 386.0825.

methyl (Z)-3-(((1-(4-bromophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)sulfonyl)propanoate (3ia, Z/E = 98 : 2):



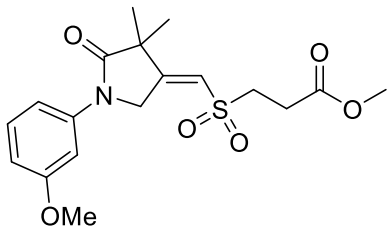
68.8 mg, 80%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65-7.62 (m, 2H), 7.53-7.50 (m, 2H), 6.34 (t, *J* = 2.4 Hz, 0.02H), 6.25 (t, *J* = 2.8 Hz, 0.98H), 4.96 (d, *J* = 2.8 Hz, 1.96H), 4.52 (d, *J* = 2.8 Hz, 0.04H), 3.74 (s, 0.06), 3.72 (s, 2.94H), 3.43-3.34 (m, 2H), 2.91-2.83 (m, 2H), 1.42 (s, 5.88H), 1.26 (s, 0.12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 170.6, 160.2, 137.3, 132.1, 121.3, 120.3, 118.1, 52.5, 50.7, 49.5, 47.8, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}BrNO_5S$ ($[M+H]^+$) 430.0319, found 430.0314.

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(m-tolyl)pyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ja, Z/E = 95 : 5):



52.5 mg, 72%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.49 (m, 2H), 7.31-7.27 (m, 1H), 7.03-7.01 (m, 1H), 6.32 (t, *J* = 2.0 Hz, 0.05H), 6.23 (t, *J* = 2.4 Hz, 0.95H), 4.98 (d, *J* = 2.4 Hz, 1.9H), 4.54 (d, *J* = 2.0 Hz, 0.1H), 3.74 (s, 0.15), 3.73 (s, 2.85H), 3.45-3.40 (m, 2H), 2.92-2.84 (m, 2H), 2.38 (s, 3H), 1.42 (s, 5.7H), 1.42 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 170.6, 161.1, 139.1, 138.1, 128.9, 126.2, 120.7, 120.0, 117.2, 52.5, 50.7, 49.8, 47.8, 27.2, 25.6, 21.6; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S$ ($[M+H]^+$) 366.1370, found 366.1368.

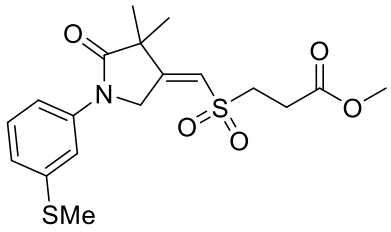
methyl (Z)-3-(((1-(3-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ka, Z/E = 95 : 5):



54.9 mg, 72%; yellow oil; eluent: petroleum ether/ethyl acetate = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (t, *J* = 2.0 Hz, 0.95H), 7.47 (t, *J* = 2.4 Hz, 0.05H), 7.32-7.28 (m, 1H), 7.20-7.08 (m, 1H), 6.79-6.74 (m, 1H), 6.29-6.23 (m, 1H), 4.97 (d, *J* = 2.4 Hz, 1.9H), 4.53 (d, *J* = 2.0 Hz, 0.1H), 3.91 (s, 0.15H), 3.83 (s, 2.85H), 3.74 (s, 0.15), 3.73 (s, 2.85H), 3.44-3.39 (m, 2H), 2.94-2.83 (m, 2H), 1.42 (s, 5.7H), 1.32 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 170.6, 160.7, 160.1, 139.4, 129.8, 120.1, 111.8,

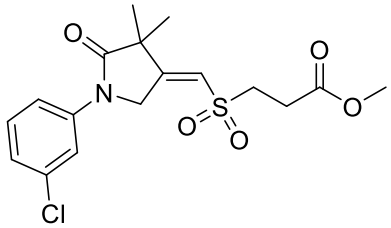
111.1, 105.9, 55.4, 52.5, 50.7, 49.8, 47.9, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_6S$ ($[M+H]^+$) 382.1319, found 382.1316.

methyl (Z)-3-(((4,4-dimethyl-1-(3-(methylthio)phenyl)-5-oxopyrrolidin-3-ylidene) methyl)sulfonyl)propanoate (3la, Z/E = 95 : 5):



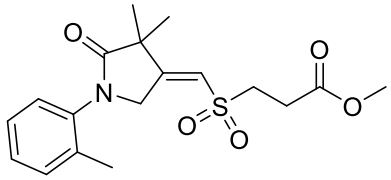
55.6 mg, 70%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (t, *J* = 1.6 Hz, 0.05H), 7.78 (t, *J* = 1.6 Hz, 0.95H), 7.41-7.36 (m, 1H), 7.32-7.28 (m, 1H), 7.09-7.05 (m, 1H), 6.33 (t, *J* = 1.6 Hz, 0.05H), 6.24 (t, *J* = 2.0 Hz, 0.95H), 4.98 (d, *J* = 2.0 Hz, 2H), 3.76-3.72 (m, 3H), 3.43-3.34 (m, 2H), 3.89-3.84 (m, 2H), 2.51 (s, 3H), 1.42 (s, 5.7H), 1.32 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 170.6, 160.6, 140.0, 138.7, 129.3, 123.2, 120.2, 117.8, 116.2, 52.6, 50.8, 49.7, 47.9, 27.2, 25.6, 15.7; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S_2$ ($[M+H]^+$) 398.1091, found 398.1087.

methyl (Z)-3-(((1-(3-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)meth-yl)sulfonyl)propanoate (3ma, Z/E = 96 : 4):



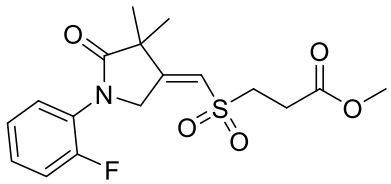
53.1 mg, 69%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (t, *J* = 2.4 Hz, 0.96H), 7.75 (t, *J* = 2.0 Hz, 0.04H), 7.61-7.55 (m, 1H), 7.38-7.31 (m, 1H), 7.21-7.16 (m, 1H), 6.35 (t, *J* = 2.0 Hz, 0.04H), 6.25 (t, *J* = 2.8 Hz, 0.96H), 4.97 (d, *J* = 2.8 Hz, 1.92H), 4.53 (d, *J* = 2.0 Hz, 0.08H), 3.76 (s, 0.12H), 3.73 (s, 2.88H), 3.45-3.40 (m, 2H), 2.95-2.84 (m, 2H), 1.43 (s, 5.76H), 1.32 (s, 0.24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 170.6, 160.1, 139.3, 134.9, 130.1, 125.2, 120.4, 119.9, 117.7, 52.6, 50.7, 49.5, 47.8, 27.2, 25.6; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}ClNO_5S$ ($[M+H]^+$) 386.0824, found 386.0819.

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(o-tolyl)pyrrolidin-3-ylidene)methyl)sulfony l)sulfonyl)propanoate (3na, Z/E = 90 : 10):



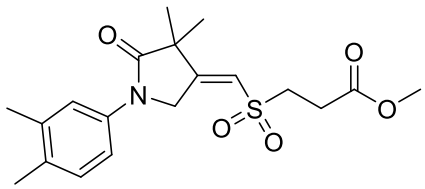
33.6 mg, 46%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.23 (m, 3H), 7.18-7.13 (m, 1H), 6.32 (t, *J* = 2.0 Hz, 0.1H), 6.25 (t, *J* = 2.8 Hz, 0.9H), 4.88 (d, *J* = 2.8 Hz, 0.2H), 4.83 (d, *J* = 2.4 Hz, 1.8H), 3.73 (s, 3H), 3.40 (t, *J* = 7.2 Hz, 1.8H), 3.22 (t, *J* = 7.2 Hz, 0.2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.21 (s, 3H), 1.44 (s, 5.4H), 1.39 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 170.6, 162.2, 135.8, 135.7, 131.3, 128.6, 127.1, 126.8, 120.1, 52.5, 51.7, 50.6, 46.5, 27.2, 25.6, 17.8; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S$ ($[M+H]^+$) 366.1370, found 366.1368.

methyl (Z)-3-(((1-(2-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3oa, Z/E = 95 : 5):



36.2 mg, 49%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.38 (m, 1H), 7.35-7.29 (m, 1H), 7.22-7.15 (m, 2H), 6.24 (t, *J* = 2.8 Hz, 1H), 4.97 (d, *J* = 2.8 Hz, 0.1H), 4.93 (d, *J* = 2.4 Hz, 1.9H), 3.74 (s, 2.85H), 3.67 (s, 0.15H), 3.40 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 1.44 (s, 5.7H), 1.26 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.0, 170.6, 161.7, 157.4 (d, *J* = 249.2 Hz), 129.4 (d, *J* = 8Hz), 128.2 (d, *J* = 6.0 Hz), 124.8 (d, *J* = 11.8 Hz), 124.7 (d, *J* = 3.7 Hz), 120.1, 116.8 (d, *J* = 19.7 Hz), 52.5, 51.0 (d, *J* = 4.4 Hz), 50.7, 46.4, 27.2, 25.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{21}FNO_5S$ ($[M+H]^+$) 370.1119, found 370.1118.

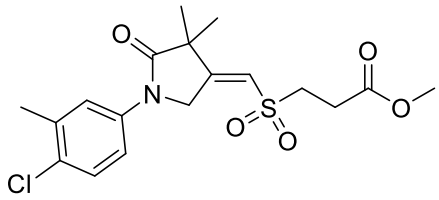
methyl (Z)-3-(((1-(3,4-dimethylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3pa, Z/E = 97 : 3):



59.1 mg, 78%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 2.4 Hz, 1H), 7.40-7.33 (m, 1H), 7.18-7.13 (m, 1H), 6.23 (t, *J* = 2.8 Hz, 1H), 5.00-4.95 (m, 2H), 3.90 (s, 0.09H), 3.72 (s, 2.91H), 3.40 (t, *J* = 7.6

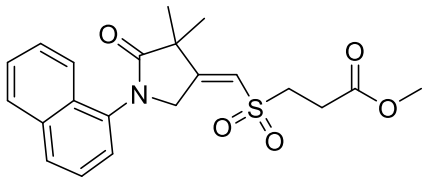
Hz, 2H), 2.94-2.82 (m, 2H), 2.28 (s, 3H), 2.24 (s, 3H) 1.41 (s, 5.82H), 1.31 (s, 0.18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 170.6, 161.3, 137.4, 135.9, 133.9, 130.1, 121.4, 119.9, 117.6, 52.5, 50.7, 49.9, 47.7, 27.2, 25.6, 20.0, 19.3; HRMS *m/z* (ESI) calcd for $C_{19}H_{26}NO_5S$ ($[M+H]^+$) 380.1526, found 380.1522.

methyl (Z)-3-(((1-(4-chloro-3-methylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3qa, Z/E = 90 : 10):



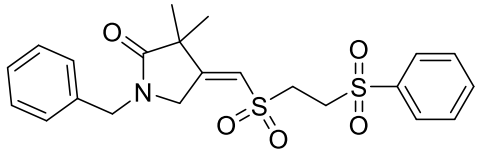
61.4 mg, 77%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 2.4 Hz, 0.9H), 7.70 (d, *J* = 2.0 Hz, 0.1H), 7.51-7.47 (m, 1H), 7.29-7.23 (m, 1H), 6.33 (t, *J* = 2.0 Hz, 0.1H), 6.24 (t, *J* = 2.4 Hz, 0.9H), 4.95 (d, *J* = 2.8 Hz, 1.8H), 4.51 (d, *J* = 2.0 Hz, 0.2H), 3.74 (s, 0.3H), 3.73 (s, 2.7H), 3.45-3.40 (m, 2H), 2.92-2.84 (m, 2H), 2.36 (s, 3H), 1.42 (s, 5.4H), 1.26 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 170.6, 160.4, 136.9, 134.7, 133.0, 131.1, 120.4, 120.3, 118.0, 52.6, 50.8, 49.6, 47.7, 27.2, 25.6, 19.5; HRMS *m/z* (ESI) calcd for $C_{18}H_{23}ClNO_5S$ ($[M+H]^+$) 400.0980, found 400.0978.

methyl (Z)-3-(((4,4-dimethyl-1-(naphthalen-1-yl)-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ra, Z/E > 99 : 1):



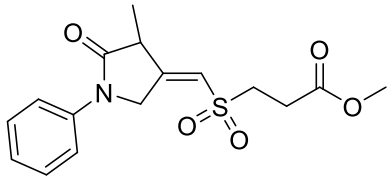
44.1 mg, 55%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93-7.88 (m, 2H), 7.62-7.60 (m, 1H), 7.56-7.50 (m, 3H), 7.43-7.41 (m, 1H), 6.30 (t, *J* = 2.4 Hz, 1H), 5.0 (d, *J* = 2.4 Hz, 2H), 3.74 (s, 3H), 3.41 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 1.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 170.6, 162.2, 134.6, 133.7, 129.5, 129.2, 128.8, 127.2, 126.6, 125.6, 125.2, 122.0, 120.3, 52.8, 52.6, 50.7, 46.7, 27.2, 25.9; HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_5S$ ($[M+H]^+$) 402.1370, found 402.1365.

(Z)-1-benzyl-3,3-dimethyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methylene)pyrrolidin-2-one (3si, Z/E = 99 : 1):



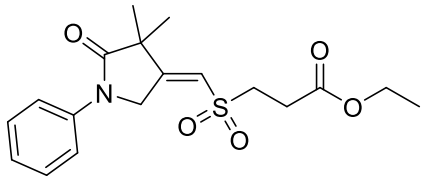
70.6 mg, 79%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.89 (m, 2H), 7.83 (t, *J* = 12.4 Hz, 0.01H), 7.73 (t, *J* = 7.2 Hz, 0.99H), 7.64-7.54 (m, 3H), 7.36-7.30 (m, 4H), 7.22-7.14 (m, 2H), 6.19 (t, *J* = 2.4 Hz, 0.99H), 6.13 (t, *J* = 2.0 Hz, 0.01H), 4.65 (s, 0.02H), 4.51 (s, 1.98H), 4.35 (d, *J* = 2.4 Hz, 1.98H), 4.21 (d, *J* = 4.8 Hz, 0.02H), 3.60-3.36 (m, 2H), 1.35 (s, 5.94H), 1.23 (s, 0.06H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.0, 163.9, 138.0, 135.3, 134.7, 129.8, 129.8, 129.0, 128.1, 128.1, 119.5, 48.8, 48.4, 48.3, 46.7, 46.3, 25.5; HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_5S_2$ ($[M+H]^+$) 448.1247, found 448.1244.

methyl (Z)-3-(((4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ta, Z/E > 99 : 1):



30.3 mg, 45%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 4.52 (d, *J* = 2.0 Hz, 2H), 4.19 (s, 2H), 3.76 (s, 3.0H), 3.38 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8, 169.2, 138.9, 138.5, 134.3, 129.2, 124.4, 118.7, 53.3, 53.0, 52.6, 48.6, 26.8, 9.6; HRMS *m/z* (ESI) calcd for $C_{16}H_{20}NO_5S$ ($[M+H]^+$) 338.1057, found 338.1052.

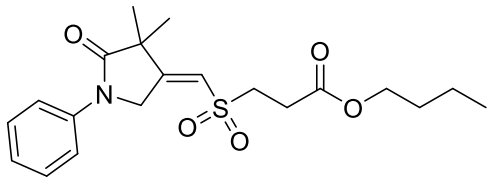
ethyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ab, Z/E = 90 : 10):



52.6 mg, 72%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.0 Hz, 1.8H), 7.66 (d, *J* = 7.6 Hz, 0.2H), 7.51 (t, *J* = 7.2 Hz, 0.2H), 7.41 (t, *J* = 8.0 Hz, 1.8H), 7.22-7.16 (m, 1H), 6.27 (t, *J* = 2.4 Hz, 0.1H), 6.23 (t, *J* = 2.8 Hz, 0.9H), 5.04 (d, *J* = 2.4 Hz, 0.2H), 5.00 (d, *J* = 2.4 Hz, 1.8H), 4.22-4.15 (m, 2H), 3.43-3.33 (m, 2H), 2.90-2.82 (m, 2H), 1.43 (s, 5.4H), 1.30 (s, 0.6H),

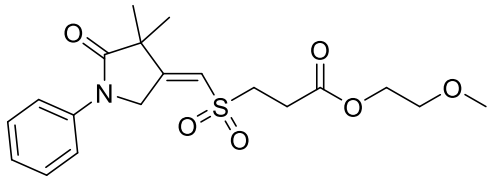
1.28-1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:174.4, 170.1, 160.8, 138.2, 129.1, 125.3, 120.1, 120.0, 61.6, 50.8, 49.7, 48.7, 47.8, 27.5, 27.0, 25.6, 14.1; HRMS *m/z* (ESI) calcd for $C_{18}H_{24}NO_5S$ ($[M+H]^+$) 366.1370, found 366.1368.

butyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) propanoate (3ac, Z/E = 95 : 5):



58.2 mg, 74%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 6.8 Hz, 1.9H), 7.66 (d, *J* = 6.0 Hz, 0.1H), 7.45-7.39 (m, 2H), 7.22-7.17 (m, 1H), 6.33 (t, *J* = 1.6 Hz, 0.05H), 6.23 (t, *J* = 2.0 Hz, 0.95H), 5.00 (d, *J* = 2.0 Hz, 1.9H), 4.56 (d, *J* = 1.6 Hz, 0.1H), 4.15-4.10 (m, 2H), 3.41 (t, *J* = 6.0 Hz, 1.9H), 3.35 (t, *J* = 6.0 Hz, 0.1H), 2.90-2.83 (m, 2H), 1.63-1.56 (m, 4H), 1.43 (s, 5.7H), 1.38-1.33 (m, 0.15H), 1.25 (s, 0.3H), 0.95-0.80 (m, 2.85H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:174.5, 170.3, 160.9, 138.2, 129.2, 125.4, 120.1, 120.0, 65.6, 50.8, 49.8, 47.8, 30.5, 27.5, 25.7, 19.1, 13.7; HRMS *m/z* (ESI) calcd for $C_{20}H_{28}NO_5S$ ($[M+H]^+$) 394.1683, found 394.1682.

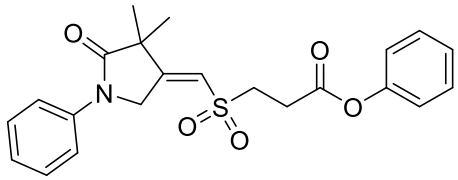
2-methoxyethyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl) Propanoate (3ad, Z/E = 95 : 5):



60.1 mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.6 Hz, 1.9H), 7.66 (d, *J* = 8.4 Hz, 0.1H), 7.53-7.39 (m, 2H), 7.22-7.12 (m, 1H), 6.32 (t, *J* = 2.0 Hz, 0.05H), 6.24 (t, *J* = 2.4 Hz, 0.95H), 4.99 (d, *J* = 2.4 Hz, 1.9H), 4.55 (d, *J* = 2.0 Hz, 0.1H), 4.27 (t, *J* = 4.4 Hz, 1.9H), 4.11 (t, *J* = 7.2 Hz, 0.1H), 3.61-3.56 (m, 2H), 3.45-3.40 (m, 2H), 3.37 (s, 0.15H), 3.35 (s, 2.85H), 2.95-2.87 (m, 2H), 1.42 (s, 5.7H), 1.26 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 170.2, 160.9, 138.2, 129.1, 125.3, 120.1, 120.0, 70.1, 64.5, 59.0, 50.7, 49.7, 47.8, 27.4, 25.6; HRMS *m/z* (ESI) calcd for $C_{19}H_{26}NO_6S$($[M+H]^+$) 396.1480, found 396.1476.

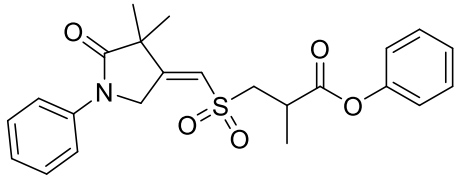
phenyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)

propanoate (3ae, Z/E = 90 : 10):



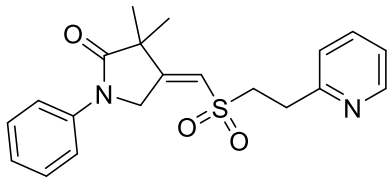
65.3 mg, 79%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.6 Hz, 1.8H), 7.63 (d, *J* = 8.0 Hz, 0.2H), 7.38-7.32 (m, 4H), 7.23-7.13 (m, 2H), 7.08-7.06 (m, 2H), 6.32 (t, *J* = 2.0 Hz, 0.1H), 6.28 (t, *J* = 2.4 Hz, 0.9H), 4.97 (d, *J* = 2.4 Hz, 1.8H), 4.42 (d, *J* = 2.0 Hz, 0.2H), 4.48-3.42 (m, 2H), 3.10-3.01 (m, 2H), 1.35 (s, 5.4H), 1.28 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 169.0, 161.1, 150.4, 138.3, 129.6, 129.6, 129.1, 126.3, 125.3, 121.3, 120.0, 50.6, 49.7, 47.8, 27.7, 25.5; HRMS *m/z* (ESI) calcd for $C_{22}H_{24}NO_5S$ ($[M+H]^+$) 414.1370, found 414.1368.

phenyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) -2-methylpropanoate (3af, Z/E = 95 : 5):



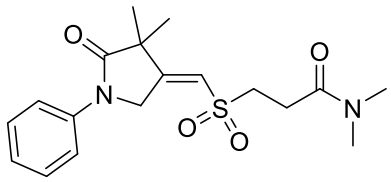
66.6 mg, 78%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.0 Hz, 0.1H), 7.67 (d, *J* = 7.6 Hz, 1.9H), 7.39-7.33 (m, 4H), 7.28-7.23 (m, 1H), 7.21-7.15 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1.9H), 6.97 (d, *J* = 7.6 Hz, 0.1H), 6.30-6.26 (m, 1H), 5.04-5.00 (m, 2H), 4.14-4.08 (m, 0.05H), 3.78-3.73 (m, 0.95H), 3.36-3.27 (m, 1H), 3.20-3.15 (m, 0.95H), 2.96-2.93 (m, 0.05H), 1.70 (d, *J* = 4.8 Hz, 0.15H), 1.52 (d, *J* = 7.2 Hz, 2.85H), 1.42-1.39 (m, 3H), 1.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 172.4, 160.8, 150.5, 138.2, 129.6, 129.1, 126.3, 125.2, 121.2, 120.7, 119.9, 58.1, 49.7, 47.8, 34.9, 25.7, 25.5, 17.9; HRMS *m/z* (ESI) calcd for $C_{23}H_{26}NO_5S$($[M+H]^+$) 428.1526, found 428.1520.

(Z)-3,3-dimethyl-1-phenyl-4-(((2-(pyridin-2-yl)ethyl)sulfonyl)methylene)pyrrolidi n-2-one (3ag, Z/E = 95 : 5):



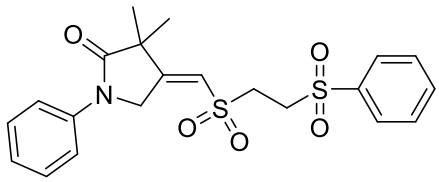
56.3 mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54-8.50 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1.9H), 7.67 (d, *J* = 1.6 Hz, 0.1H), 7.65-7.59 (m, 0.95H), 7.53-7.49 (m, 0.05H), 7.42-7.34 (m, 2.0 H), 7.25-7.16 (m, 3.0 H), 6.25 (t, *J* = 2.4 Hz, 0.05H), 6.12 (t, *J* = 2.4 Hz, 0.95H), 4.97 (d, *J* = 2.8 Hz, 1.9H), 4.45 (d, *J* = 1.6 Hz, 0.1H), 3.67-3.62 (m, 2H), 3.39 -3.30 (m, 2H), 1.31 (s, 5.7H), 1.26 (s, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 159.7, 156.9, 149.5, 138.2, 136.9, 129.1, 125.2, 123.4, 122.3, 120.6, 119.9, 54.3, 49.7, 47.6, 30.5, 25.5; HRMS *m/z* (ESI) calcd for $C_{20}H_{23}N_2O_3S$ ($[M+H]^+$) 371.1424, found 371.1426.

(Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)-N,N-dimethylpropanamide (3ah, Z/E > 99 : 1):



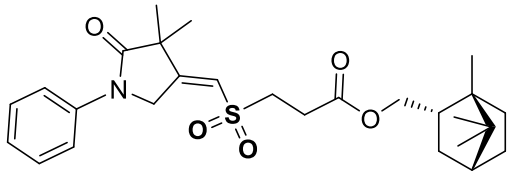
45.1 mg, 62%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 5.46-5.42 (m, 1H), 4.48 (d, *J* = 2.4 Hz, 2H), 3.02 (s, 3H), 2.96 (s, 3H), 2.43-2.42 (m, 4H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.2, 172.0, 139.3, 139.1, 128.9, 124.5, 121.1, 119.8, 49.2, 45.6, 37.3, 35.5, 32.6, 26.0, 23.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{25}N_2O_4S$ ($[M+H]^+$) 365.1530, found 365.1525.

(Z)-3,3-dimethyl-1-phenyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methylene)pyrrolidin-2-one (3ai, Z/E = 92 : 8):



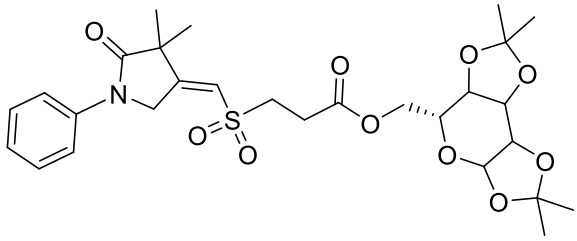
73.6 mg, 85%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94-7.91 (m, 2H), 7.75-7.68 (m, 3H), 7.65-7.56 (m, 2H), 7.48-7.39 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.34 (t, *J* = 2.0 Hz, 0.08H), 6.26 (t, *J* = 2.8 Hz, 0.92H), 4.96 (d, *J* = 2.8 Hz, 1.84H), 4.57 (d, *J* = 2.0 Hz, 0.16H), 3.58-3.44 (m, 4H), 1.44 (s, 5.52H), 1.26 (s, 0.48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 162.7, 138.1, 138.0, 134.7, 129.8, 129.2, 128.1, 125.4, 120.0, 119.6, 49.7, 48.9, 48.5, 48.0, 25.7; HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_5S_2$ ($[M+H]^+$) 434.1091, found 434.1088.

(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(((Z)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3aj, Z/E > 99 : 1):



74.1 mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.25 (t, *J* = 2.4 Hz, 1.0H), 4.99 (d, *J* = 2.8 Hz, 2.0H), 4.93-4.90 (m, 1H), 4.40 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 2.38-2.30 (m, 1H), 1.91-1.66 (m, 2H), 1.43 (s, 6.0H), 0.89 (s, 3H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 170.6, 169.9, 160.9, 138.2, 129.1, 125.3, 120.0, 80.6, 61.1, 50.6, 49.7, 48.8, 47.8, 47.8, 44.8, 36.7, 33.9, 28.04, 27.3, 27.1, 25.6, 19.7, 18.8, 13.5; HRMS *m/z* (ESI) calcd for $C_{26}H_{36}NO_5S$ ($[M+H]^+$) 474.2309, found 474.2306.

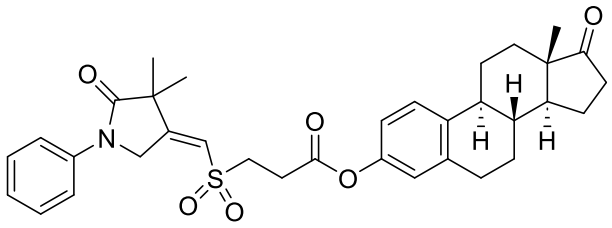
((5R)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 3-(((E)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ak, Z/E = 97 : 3):



76.5 mg, 66%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73-7.67 (m, 2H), 7.46-7.39 (m, 2H), 7.25-7.19 (t, *J* = 6.0 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 0.03H), 6.24 (t, *J* = 2.0 Hz, 0.97H), 5.67 (d, *J* = 4.0 Hz, 0.03H), 5.49 (d, *J* = 3.6 Hz, 0.97H), 5.04 (d, *J* = 2.0 Hz, 0.06H), 5.00 (d, *J* = 2.0 Hz, 1.94H), 4.63-4.60 (m, 0.97H), 4.57-4.55 (m, 0.03H), 4.33-4.27 (m, 2.91H), 4.25-4.24 (m, 0.09H), 4.22-4.20 (m, 0.97H), 4.14-4.10 (m, 0.03H), 4.02-4.00 (m, 0.97H), 3.93-3.90 (m, 0.03H), 3.41 (t, *J* = 5.6 Hz, 1.94H), 3.27 (t, *J* = 5.6 Hz, 0.06H), 2.95-2.88 (m, 2.0H), 1.80 (s, 0.09H), 1.72-1.68 (m, 0.27H), 1.50 (s, 2.91H), 1.44-1.43 (s, 8.74H), 1.32 (d, *J* = 9.2 Hz, 5.82H), 1.25 (d, *J* = 5.6 Hz, 0.18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 170.1, 160.9, 138.2, 129.1, 125.3, 120.1, 109.8, 108.9, 96.3, 71.0, 70.7, 70.3,

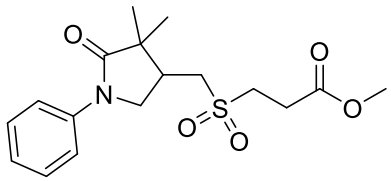
65.9, 64.5, 50.8, 49.8, 47.8, 27.5, 26.1, 26.0, 25.7, 25.6, 24.9, 24.5; HRMS *m/z* (ESI) calcd for $C_{28}H_{38}NO_{10}S$ ([M+H]$^+$) 580.2211, found 580.2208.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3-(((Z)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3al, Z/E = 90 : 10):



74.2 mg, 63%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 6.0 Hz, 1.8H), 7.65 (d, *J* = 6.0 Hz, 0.2H), 7.45-7.38 (m, 2H), 7.31-7.27 (m, 1H), 7.20 (d, *J* = 5.6 Hz, 0.9H), 7.05 (t, *J* = 2.4 Hz, 0.1H), 6.90-6.84 (m, 1H), 6.80-6.79 (m, 1H), 6.36 (t, *J* = 2.0 Hz, 0.1H), 6.28 (t, *J* = 2.0 Hz, 0.9H), 5.03 (d, *J* = 2.0 Hz, 1.8H), 4.54 (d, *J* = 1.6 Hz, 0.2H), 3.55-3.50 (m, 2H), 3.16-3.08 (m, 2H), 2.96-2.87 (m, 2H), 2.54-2.48 (m, 1H), 2.42-2.35 (m, 1H), 2.31-2.21 (m, 1.0H), 2.20-2.11(m, 1.0H), 2.09-1.95(m, 4.0H), 1.68-1.42 (m, 9.9H), 1.32-1.25 (m, 1.1H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 220.8, 174.4, 169.2, 161.2, 148.2, 138.4, 138.2, 138.0, 129.2, 126.6, 125.4, 121.2, 120.1, 120.0, 118.4, 50.8, 50.4, 49.8, 48.0, 47.9, 44.2, 38.0, 35.9, 31.6, 29.4, 27.7, 26.3, 25.8, 25.7, 21.6, 13.9; HRMS *m/z* (ESI) calcd for $C_{34}H_{40}NO_6S$ ([M+H]$^+$) 590.2571, found 590.2567.

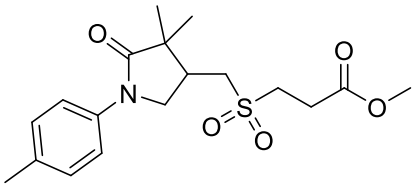
methyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5aa):



65.0 mg, 92%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.15 (t, *J* = 9.2 Hz, 1H), 3.76-3.71 (m, 4H), 3.47-3.35 (m, 2H), 3.26 (d, *J* = 13.2 Hz, 1H), 3.11 (t, *J* = 12.4 Hz, 1H), 2.93 (t, *J* = 14.4 Hz, 2H), 2.85-2.78 (m, 1H), 1.31 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 170.9, 139.0, 128.9, 124.8, 119.9, 52.7, 52.6, 50.2, 49.4, 44.5, 36.9, 26.9, 23.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{24}NO_5S$ ([M+H]$^+$) 354.1370, found 354.1372.

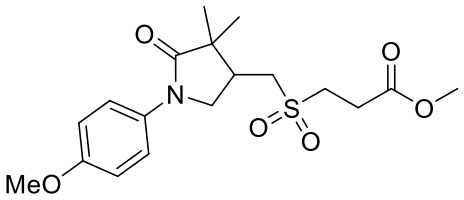
methyl 3-(((4,4-dimethyl-5-oxo-1-(p-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propa-

noate (5ba):



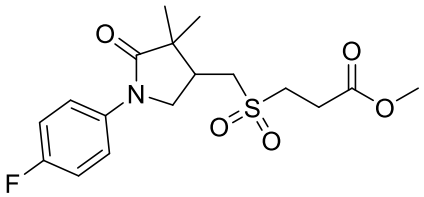
68.3 mg, 93%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.11 (t, *J* = 8.4 Hz, 1H), 3.76-3.68 (m, 4H), 3.47-3.35 (m, 2H), 3.25 (d, *J* = 13.6 Hz, 1H), 3.11 (t, *J* = 12.0 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.84-2.76 (m, 1H), 2.32 (s, 3H), 1.30 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 170.9, 136.5, 134.5, 129.4, 119.9, 52.7, 52.6, 50.3, 49.4, 44.4, 36.9, 26.9, 23.5, 20.9, 18.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_5S([M+H]^+)$ 367.1526, found 367.1527.

methyl 3-(((1-(4-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ca)



70.5 mg, 92%; yellow oil; eluent: petroleum ether/ethyl acetate = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 9.2 Hz, 2H), 6.88 (t, *J* = 9.6 Hz, 2H), 4.04 (t, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 3.72-3.65 (m, 4H), 3.46-3.34 (m, 2H), 3.27 (t, *J* = 13.6 Hz, 1H), 3.13 (t, *J* = 12.0 Hz, 1H), 2.88 (t, *J* = 14.0 Hz, 2H), 2.80-2.73 (m, 1H), 1.26 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 170.9, 156.6, 132.2, 121.7, 114.0, 55.4, 52.4, 52.3, 50.6, 49.1, 44.2, 36.8, 26.7, 23.3, 18.8; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_6S([M+H]^+)$ 384.1476, found 384.1473.

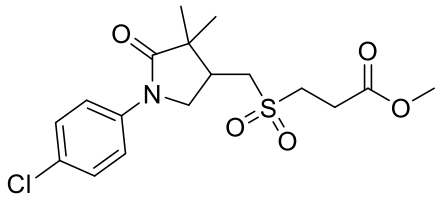
methyl 3-(((1-(4-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5da):



63.8 mg, 86%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.57 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 4.11 (t, *J* = 9.6 Hz, 1H), 3.7-3.67 (m, 4H), 3.44-3.39 (m, 2H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.11 (t, *J* = 12.4 Hz,

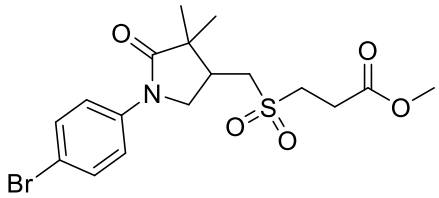
1H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.85-2.79 (m, 1H), 1.31 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.6, 170.9, 159.6 (d, *J* = 242.9 Hz), 135.1 (d, *J* = 2.9 Hz), 121.6 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 22.3 Hz), 52.6, 50.4, 49.5, 44.4, 36.9, 26.9, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{23}FNO_5S([M+H]^+)$ 372.1276, found 372.1271.

methyl 3-(((1-(4-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ea):



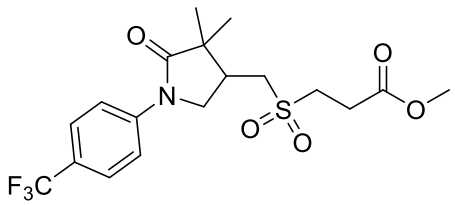
68.9 mg, 89%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 4.11 (t, *J* = 9.6 Hz, 1H), 3.76-3.68 (m, 4H), 3.48-3.34 (m, 2H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.11 (t, *J* = 25.2 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.85-2.78 (m, 1H), 1.30 (s, 3H),1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 170.9, 137.6, 129.8, 128.9, 120.9, 52.6, 52.6, 50.1, 49.4, 44.5, 36.7, 26.9, 23.4, 19.0; HRMS *m/z* (ESI) calcd for $C_{17}H_{23}ClNO_5S([M+H]^+)$ 388.0980, found 388.0976.

methyl 3-(((1-(4-bromophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5fa):



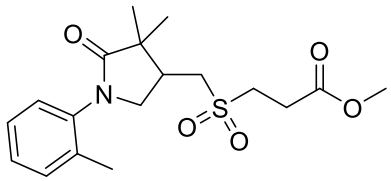
75.0 mg, 87%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 9.2 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 1H), 3.75-3.67 (m, 4H), 3.48-3.36 (m, 2H), 3.27 (d, *J* = 13.6 Hz, 1H), 3.12 (t, *J* = 11.6 Hz, 1H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.84-2.77 (m, 1H), 1.29 (s, 3H),1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 170.9, 138.1, 131.8, 121.3, 117.5, 52.6, 52.5, 50.0, 49.4, 44.5, 36.7, 26.9, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{23}BrNO_5S([M+H]^+)$ 432.0475, found 432.0472.

methyl 3-(((4,4-dimethyl-5-oxo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ga):



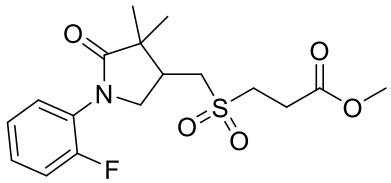
71.6 mg, 85%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 4.19 (t, *J* = 9.2 Hz, 1H), 3.77 (s, 4H), 3.48-3.37 (m, 2H), 3.28 (d, *J* = 13.2 Hz, 1H), 3.13 (t, *J* = 12.4 Hz, 1H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.88-2.81 (m, 1H), 1.33 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.2, 170.9, 141.9, 126.1 (q, *J* = 4.1 Hz), 126.5, 124.0 (d, *J* = 269.8 Hz), 119.3, 52.6, 52.6, 49.9, 49.5, 44.6, 36.7, 26.9, 23.4, 19.0; HRMS *m/z* (ESI) calcd for $C_{18}H_{23}F_3NO_5S([M+H]^+)$ 422.1244, found 422.1240.

methyl 3-(((4,4-dimethyl-5-oxo-1-(o-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ha):



50.7 mg, 69%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.20 (m, 3H), 7.11-7.09 (m, 1H), 3.93-3.89 (m, 1H), 3.73 (s, 3H), 3.64 (t, *J* = 10.0 Hz, 1H), 3.39-3.35 (m, 2H), 3.27-3.22 (m, 1H), 3.12 (t, *J* = 12.0 Hz, 1H), 2.88 (t, *J* = 7.2 Hz, 3H), 2.19 (s, 3H), 1.28 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 170.9, 136.9, 135.5, 131.1, 128.1, 126.9, 126.7, 52.5, 52.3, 49.4, 43.4, 38.0, 26.8, 23.3, 18.9, 17.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_5S([M+H]^+)$ 368.1526, found 368.1520.

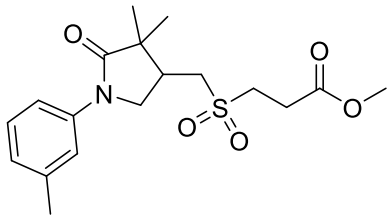
methyl 3-(((1-(2-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ia):



45.3 mg, 61%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (t, *J* = 8.0 Hz, 1H), 7.28-7.23 (m, 1H), 7.18-7.11 (m, 2H), 4.02 (t, *J* = 9.6 Hz, 1H), 3.78-3.74 (m, 4H), 3.46-3,34 (m, 2H), 3.25 (d, *J* = 13.2 Hz, 1H), 3.12 (t, *J* = 12.0 Hz, 1H), 2.92 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 3H), 1.12 (s, 3H); ^{13}C NMR

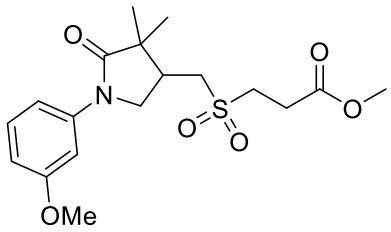
(100 MHz, $CDCl_3$) δ: 177.3, 170.9, 158.7 (d, *J* = 248.6 Hz), 128.7 (d, *J* = 7.9 Hz), 128.0 (d, *J* = 1.8 Hz), 125.9 (d, *J* = 11.9 Hz), 124.5 (d, *J* = 3.7 Hz), 116.6 (d, *J* = 19.7 Hz), 52.6 (d, *J* = 19.7 Hz), 51.8 (d, *J* = 3.9 Hz), 49.4, 43.3, 37.9, 26.9, 23.2, 18.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{23}FNO_5S([M+H]^+)$ 372.1276, found 372.1273.

methyl 3-(((4,4-dimethyl-5-oxo-1-(m-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ja):



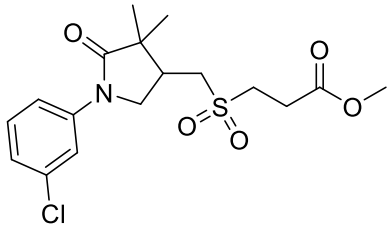
65.4 mg, 89%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.40 (m, 2H),7.23 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.10 (t, *J* = 8.0 Hz, 1H), 3.73-3.68 (m, 4H), 3.46-3,32 (m, 2H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.12 (t, *J* = 11.6 Hz, 1H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.81-2.74 (m, 1H), 2.34 (s, 3H), 1.28 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 170.9, 139.0, 138.7, 128.7, 125.6, 120.6, 117.1, 52.5, 50.3, 49.2, 44.5, 36.8, 26.8, 23.4, 21.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_5S([M+H]^+)$ 368.1526, found 368.1522.

methyl 3-(((1-(3-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ka):



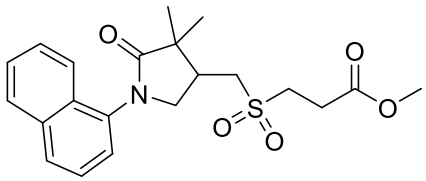
68.9 mg, 90%; yellow oil; eluent: petroleum ether/ethyl acetate = 1 : 1; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 (s, 1H), 7.25 (t, *J* = 8 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 9.2 Hz, 1H), 4.14 (t, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.76-3,68 (m, 4H), 3.47-3.35 (m, 2H), 3.25 (d, *J* = 13.2 Hz, 1H), 3.11 (t, *J* = 12.0 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.84-2.76 (m, 1H), 1.31 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 170.9, 160.0, 140.3, 129.5, 111.8, 110.7, 105.8, 55.4, 52.7, 52.6, 50.3, 49.4, 44.6, 36.8, 26.9, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_6S([M+H]^+)$ 384.1476, found 384.1473.

methyl 3-(((1-(3-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5la):



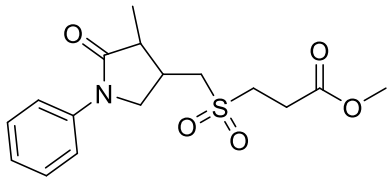
68.1 mg, 88%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.12 (t, *J* = 8.4 Hz, 1H), 3.76-3.68 (m, 4H), 3.48-3.36 (m, 2H), 3.27 (d, *J* = 13.2 Hz, 1H), 3.13 (t, *J* = 11.6 Hz, 1H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.84-2.77 (m, 1H), 1.30 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.0, 170.9, 140.1, 134.5, 129.9, 124.7, 119.8, 117.6, 52.6, 52.5, 50.0, 49.4, 44.6, 36.7, 26.9, 23.3, 18.9; HRMS *m/z* (ESI) calcd for $C_{17}H_{23}ClNO_5S([M+H]^+)$ 388.0980, found 388.0977.

methyl 3-(((4,4-dimethyl-1-(naphthalen-1-yl)-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ma):



52.4 mg, 65%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.54-7.45 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 1H), 4.08-4.04 (m, 1H), 3.79-3.72 (m, 4H), 3.41-3.32 (m, 2H), 3.27 (d, *J* = 13.2 Hz, 1H), 3.14 (t, *J* = 11.6 Hz, 1H), 3.06-2.99 (m, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.36 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.8, 170.9, 134.9, 134.5, 129.6, 128.7, 128.6, 126.9, 126.4, 125.6, 122.4, 53.5, 52.6, 52.6, 49.4, 43.6, 38.2, 26.9, 23.5, 19.1; HRMS *m/z* (ESI) calcd for $C_{21}H_{26}NO_5S$ ($[M+H]^+$) 404.1526, found 404.1523.

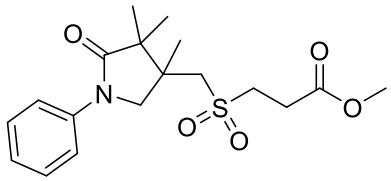
methyl 3-(((4-methyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5na):



38.6 mg, 57%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 4.17 (t, *J* = 9.6 Hz, 1H), 3.78-3.73 (m, 4H), 3.43-3.37 (m, 3H), 3.17 (t, *J* = 12.4

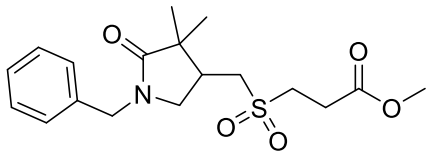
Hz, 1H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.75-2.65 (m, 1H), 2.46-2.38 (m, 1H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7, 170.9, 138.9, 128.9, 124.8, 120.0, 119.9, 56.0, 52.6, 51.8, 49.4, 43.7, 34.5, 26.9, 14.4; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_5S$ ($[M+H]^+$) 340.1213, found 340.1210.

methyl 3-(((3,4,4-trimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5oa):



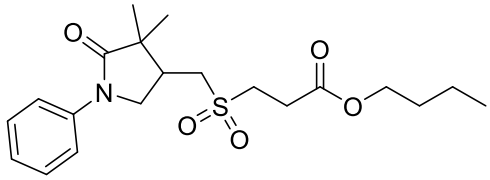
65.4 mg, 89%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 10.4 Hz, 1H), 3.83 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 3H), 3.41-3.37 (m, 2H), 3.28 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 14.0 Hz, 1H), 2.92 (t, *J* = 6.8 Hz, 2H), 1.47 (s, 3H),1.15 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 171.0, 139.3, 128.9, 124.7, 119.9, 57.7, 55.9, 52.6, 51.5, 49.5, 41.0, 26.9, 20.8, 20.6, 18.4; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_5S$ ($[M+H]^+$) 368.1526, found 368.1523.

methyl 3-(((1-benzyl-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5pa):



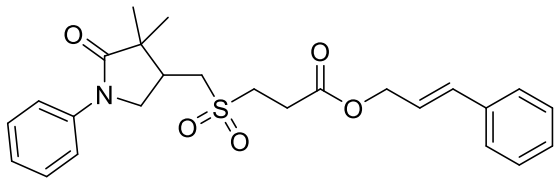
66.1 mg, 90%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.27 (m, 3H), 7.20 (d, *J* = 6.4 Hz, 2H), 4.59 (d, *J* = 14.8 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H), 3.73 (s, 3H), 3.57-3.52 (m, 1H), 3.39-3.27 (m, 2H), 3.17-3.06 (m, 2H), 2.98-2.8 (m, 3H), 2.69-2.61 (m, 1H), 1.25 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.5, 170.9, 136.2, 128.8, 128.1, 127.7, 52.7, 52.6, 49.4, 48.7, 46.7, 43.2, 37.3, 26.8, 23.3, 18.8; HRMS *m/z* (ESI) calcd for $C_{18}H_{26}NO_5S$ ($[M+H]^+$) 368.1526, found 368.1521.

butyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ac):



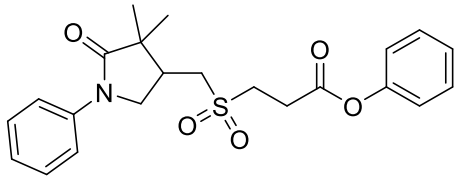
70.3 mg, 89%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.16 (t, *J* = 6.8 Hz, 3H), 3.74 (t, *J* = 9.6 Hz, 1H), 3.50-3.35 (m, 2H), 3.25 (d, *J* = 13.2 Hz, 1H), 3.11 (t, *J* = 12.0 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.85-2.78 (m, 1H), 1.67-1.60 (m, 2H), 1.44-1.34 (m, 2H), 1.31 (s, 3H), 1.08 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 170.5, 139.0, 128.9, 124.8, 119.9, 65.6, 52.7, 50.2, 49.5, 44.5, 36.9, 30.5, 27.2, 23.5, 19.1, 19.0, 13.7; HRMS *m/z* (ESI) calcd for $C_{20}H_{30}NO_5S$ ($[M+H]^+$) 396.1839, found 396.1836.

cinnamyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5am):



80.1 mg, 88%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 7.6 Hz, 2H), 7.40-7.26 (m, 7H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.30-6.23 (m, 1H), 4.81-4.79 (m, 2H), 4.16-4.11 (m, 1H), 3.71 (t, *J* = 9.6 Hz, 1H), 3.45-3.40 (m, 2H), 3.26-3.22 (m, 1H), 3.10 (t, *J* = 11.6 Hz, 1H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.84-2.76 (m, 1H), 1.29 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 170.3, 139.0, 135.9, 135.2, 128.9, 128.7, 128.4, 126.7, 124.8, 122.2, 119.9, 66.3, 52.7, 50.2, 49.4, 44.5, 36.9, 27.2, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{25}H_{30}NO_5S$ ($[M+H]^+$) 456.1839, found 456.1837.

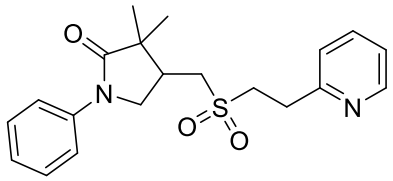
phenyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ae):



68.1 mg, 82%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.4 Hz, 2H), 7.42-7.34 (m, 4H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.17-7.09 (m, 3H), 4.19-4.11 (m, 1H), 3.74 (t, *J* = 10.0 Hz, 1H), 3.51 (t,, *J* = 7.6 Hz,

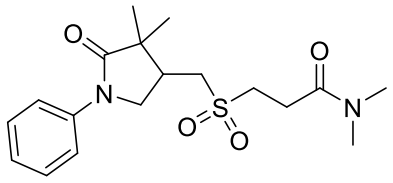
2H), 3.28 (d, *J* = 13.6 Hz, 1H), 3.22-3.12 (m, 3H), 2.88-2.80 (m, 1H), 1.30 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 169.2, 150.3, 139.0, 129.6, 128.9, 126.4, 124.8, 121.2, 119.9, 52.9, 50.2, 49.5, 44.5, 36.9, 27.3, 23.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{22}H_{26}NO_5S$ ($[M+H]^+$) 416.1526, found 416.1522.

3,3-dimethyl-1-phenyl-4-(((2-(pyridin-2-yl)ethyl)sulfonyl)methyl)pyrrolidin-2-one (5ag):



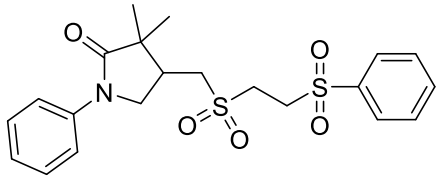
67.0 mg, 90%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (d, *J* = 4.0 Hz, 1H), 7.68-7.61 (m, 3H), 7.35 (t, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 1H), 7.20 (t, *J* = 6.8 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.13 (t, *J* = 10.4 Hz, 1H), 3.72-3.62 (m, 3H), 3.36 (t, *J* = 7.6 Hz, 2H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.94 (t, *J* = 11.6 Hz, 1H), 2.80-2.73 (m, 1H), 1.23 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 156.9, 149.6, 139.0, 137.0, 128.9, 124.7, 123.7, 122.3, 119.9, 53.0, 52.4, 50.2, 44.5, 36.7, 30.4, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{20}H_{25}N_2O_3S$ ($[M+H]^+$) 373.1581, found 373.1582.

3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)-N,N-dimethyl Propenamide (5ah):



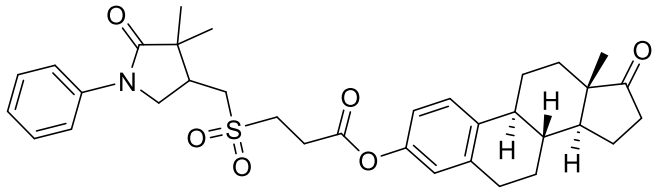
64.4 mg, 88%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.14 (t, *J* = 8.8 Hz, 1H), 3.75 (t, *J* = 10.0 Hz, 1H), 3.54-3.42 (m, 2H), 3.33 (d, *J* = 13.6 Hz, 1H), 3.15 (t, *J* = 11.2 Hz, 1H), 3.06 (s, 3H), 2.98 (s, 3H), 2.93-2,89 (m, 2H), 2.76-2.78 (m, 1H), 1.31 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.9, 168.8, 139.1, 128.9, 124.7, 119.9, 53.1, 50.2, 50.0, 44.6, 37.1, 36.9, 35.8, 26.2, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{27}N_2O_4S$ ($[M+H]^+$) 367.1686, found 367.1683.

3,3-dimethyl-1-phenyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methyl)pyrrolidin-2-one (5ai):



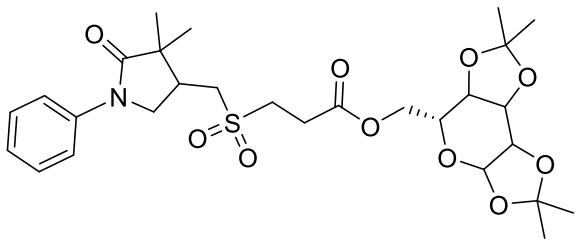
79.3 mg, 91%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.62 (q, *J* = 7.6 Hz, 4H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.09 (t, *J* = 9.2 Hz, 1H), 3.71 (t, *J* = 9.6 Hz, 1H), 3.62-3.51 (m, 4H), 3.32 (d, *J* = 13.2 Hz, 1H), 3.19 (t, *J* = 11.6 Hz, 1H), 2.83-2.75 (m, 1H), 1.28 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 138.9, 138.0, 134.8, 129.9, 128.9, 128.1, 124.9, 119.9, 52.9, 50.1, 48.7, 47.1, 44.5, 36.8, 23.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{21}H_{26}NO_5S_2$ ($[M+H]^+$) 436.1247, found 436.1245.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ak):



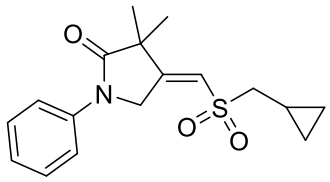
89.8 mg, 76%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 8 Hz, 2H), 4.17 (t, *J* = 9.6 Hz, 1H), 3.75 (t, *J* = 10.0 Hz, 1H), 3.53-3.39 (m, 2H), 3.31-3.27 (m, 1H), 3.20-3.11 (m, 3H), 2.96-2.80 (m, 4H), 2.55-2.48 (m, 1H), 2.43-2.38 (m, 1H), 2.31-1.95 (m, 4H), 1.65-1.45 (m, 5H), 1.31 (s, 3H), 1.07 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 220.7, 176.7, 169.5, 148.2, 139.0, 138.3, 138.0, 128.9, 126.6, 124.8, 121.2, 119.9, 118.4, 52.9, 50.4, 50.2, 49.5, 47.9, 44.5, 44.2, 38.0, 36.9, 35.9, 31.5, 29.4, 27.3, 26.3, 25.8, 23.5, 21.6, 19.0, 13.8; HRMS *m/z* (ESI) calcd for $C_{34}H_{42}NO_6S$ ($[M+H]^+$) 592.2728, found 592.2724.

((5R)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5al):



98.8 mg, 85%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 8.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 5.53 (q, *J* = 2.8 Hz, 1H), 4.64-4.62 (m, 1H), 4.36-4.28 (m, 3H), 4.24-4.22 (m, 1H), 4.17-4.10 (m, 1H), 4.06-4.02 (m, 1H), 3.74 (t, *J* = 10.0 Hz, 1H), 3.48-3.33 (m, 2H), 3.27-3.23 (m, 1H), 3.11 (t, *J* = 12.8 Hz, 1H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.85-2.78 (m, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 1.33 (t, *J* = 4.8 Hz, 9H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 170.3, 139.0, 128.9, 124.8, 119.9, 109.8, 108.9, 96.3, 71.0, 70.7, 70.4, 65.9, 64.6, 52.6, 50.2, 49.5, 44.5, 36.8, 27.3, 26.1, 26.0, 24.9, 24.5, 23.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{28}H_{40}NO_{10}S$ ($[M+H]^+$) 582.2368, found 582.2365.

(Z)-4-(((cyclopropylmethyl)sulfonyl)methylene)-3,3-dimethyl-1-phenylpyrrolidin -2-one (8aa, Z/E > 99:1):



21.1 mg, 33%; yellow oil; eluent: petroleum ether/ethyl acetate = 2 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.27 (t, *J* = 2.8 Hz, 1H), 5.03 (d, *J* = 2.4 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 1.44 (s, 6H), 1.19-1.13 (m, 1H), 0.76-0.71 (m, 2H), 0.40-0.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 159.9, 138.2, 129.1, 125.3, 120.6, 119.9, 60.9, 49.8, 47.6, 25.6, 4.8, 4.6; HRMS *m/z* (ESI) calcd for $C_{17}H_{22}NO_3S$ ($[M+H]^+$) 320.1315, found 320.1317.

(D) References

[1] M. Li, Y. Li, W.-Y. Jia, G.-Q. Sun, F. Gao, G.-X. Zhao, Y.-F. Qiu, X.-C. Wang, Y.-M. Liang, Z.-J. Quan, *Org. Lett.*, **2022**, *24*, 2738.

[2] Q. Shen, X. Zheng, L. Li, T. Zhong, C. Yin, C. Yu, *Org. Lett.*, **2022**, *24*, 2556.

[3] R. I. Rodriguez, M. Sicignano, M. J. Garcia, R. G. Enriquez, S. Cabrera, J. Aleman, *Green Chem.*, **2022**, *24*, 6613.

(E) Spectra

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) propanoate (3aa, Z/E = 92 : 8):

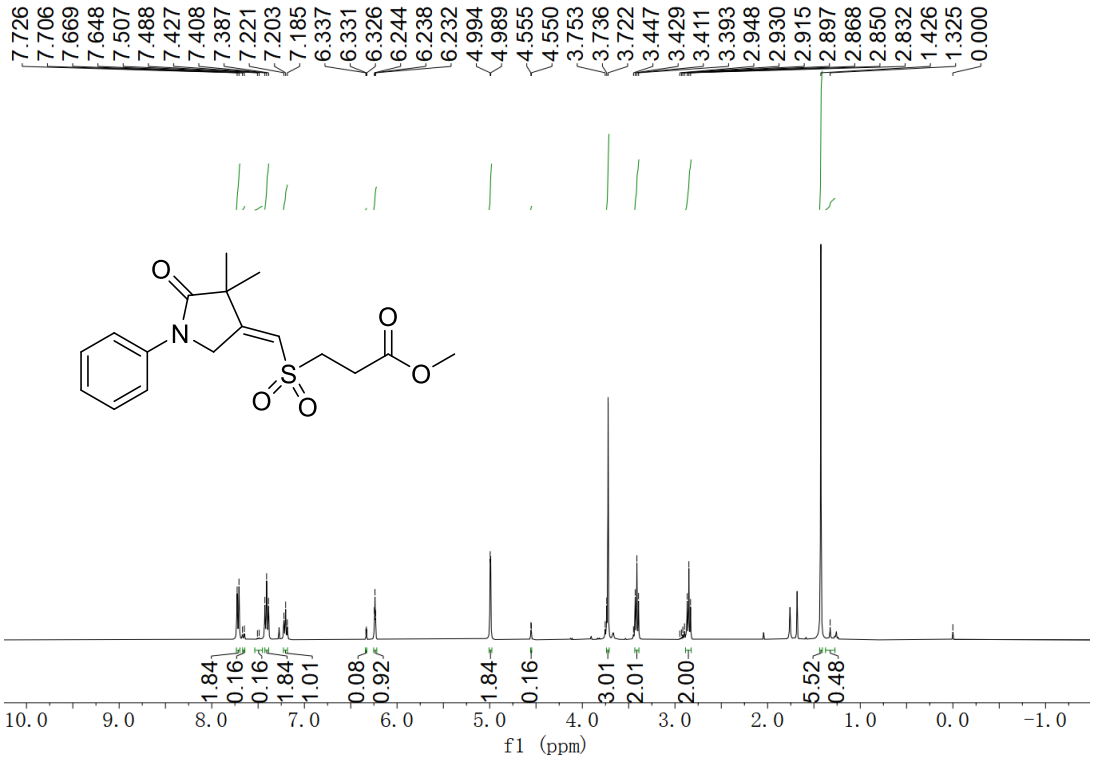


Figure S8 ^{1}H NMR (400 MHz, $CDCl_3$)

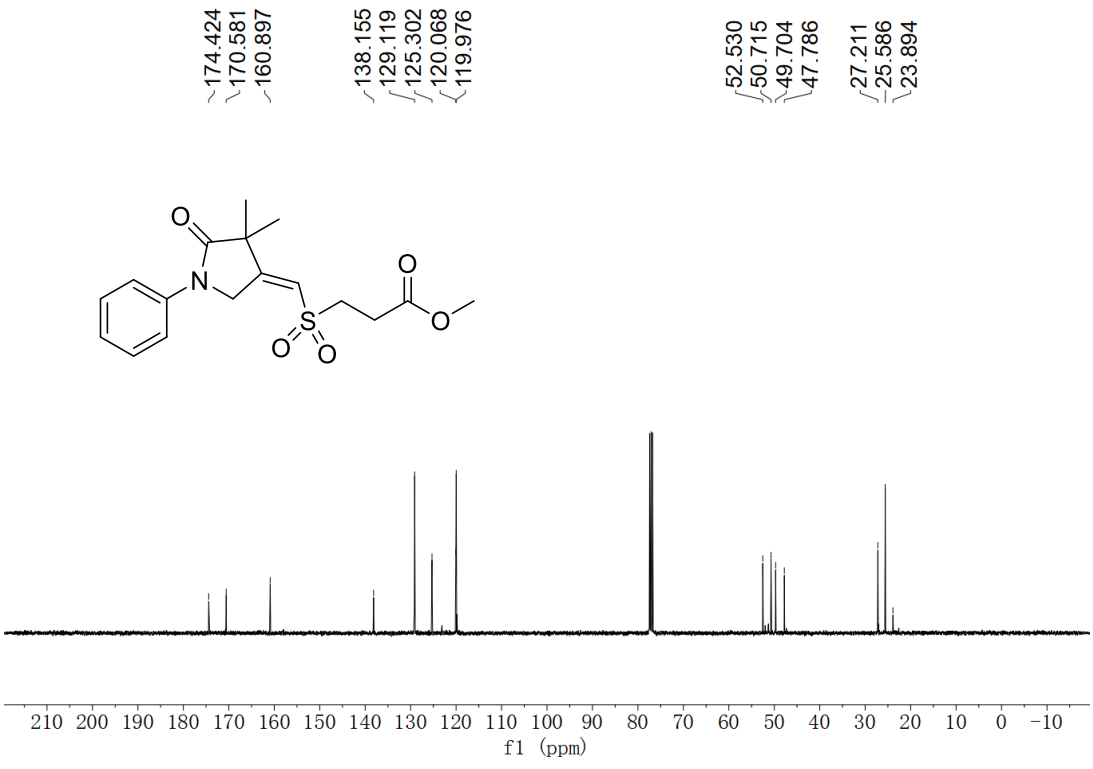


Figure S9 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(p-tolyl)pyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ba, Z/E = 95 : 5):

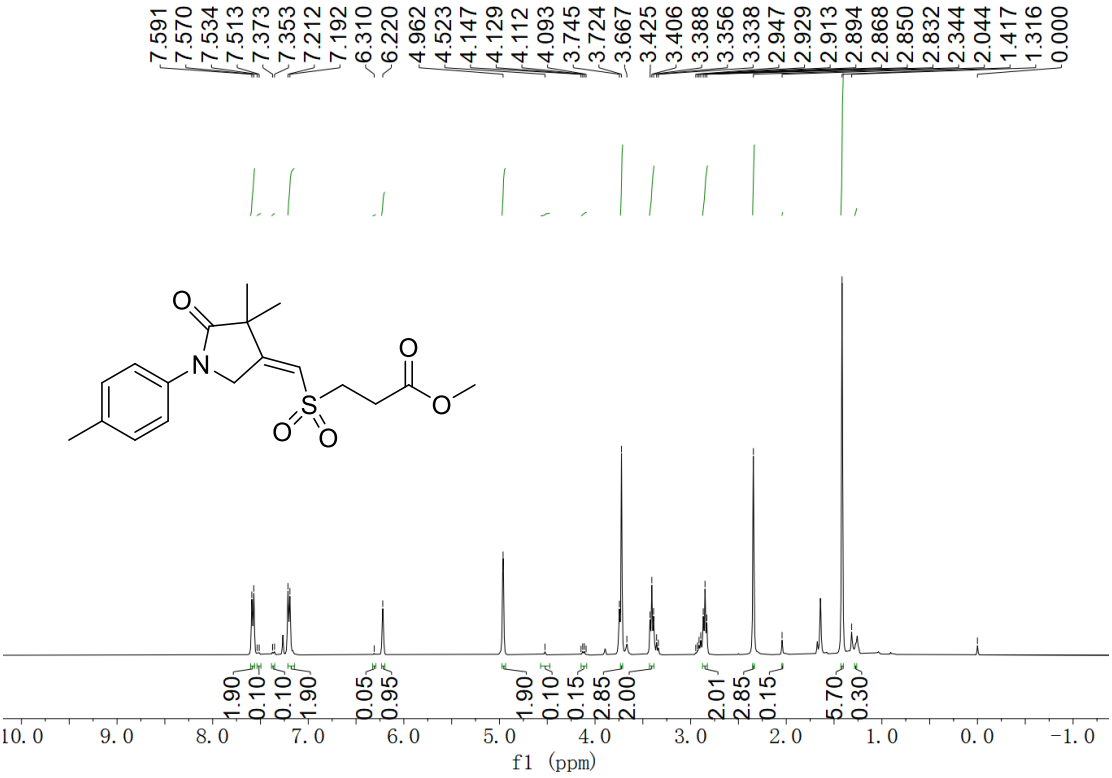


Figure S10 ^{1}H NMR (400 MHz, $CDCl_3$)

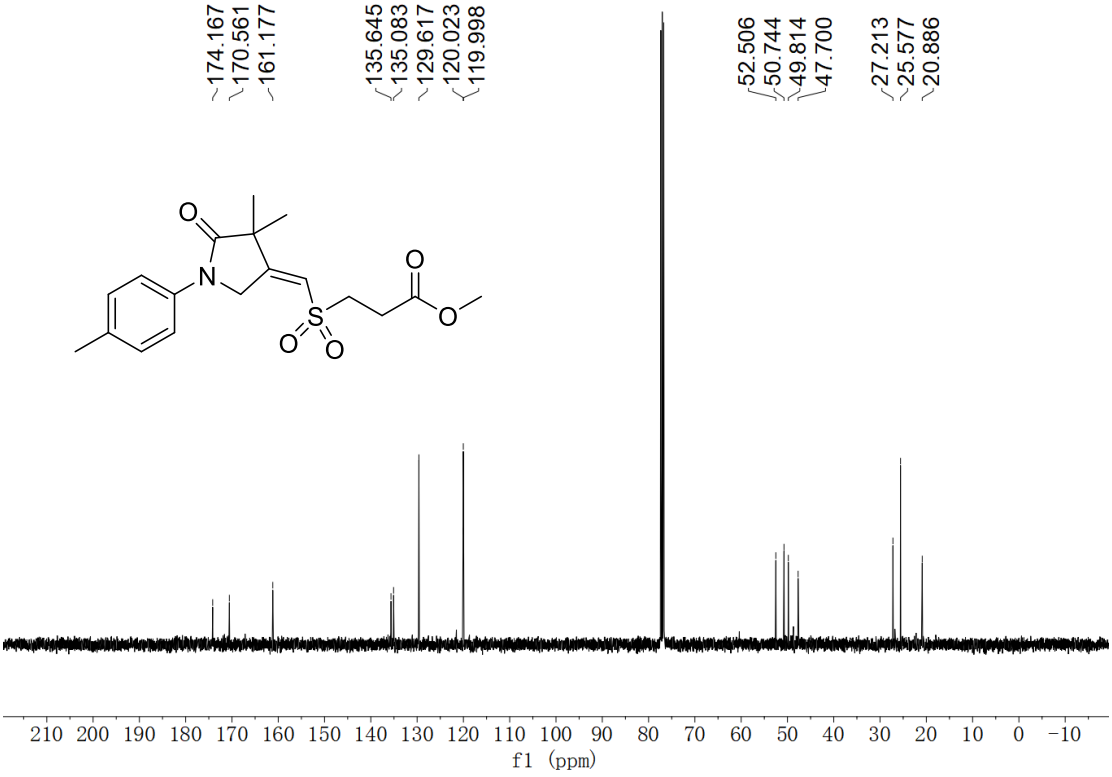


Figure S11 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ca, Z/E = 90 :10):

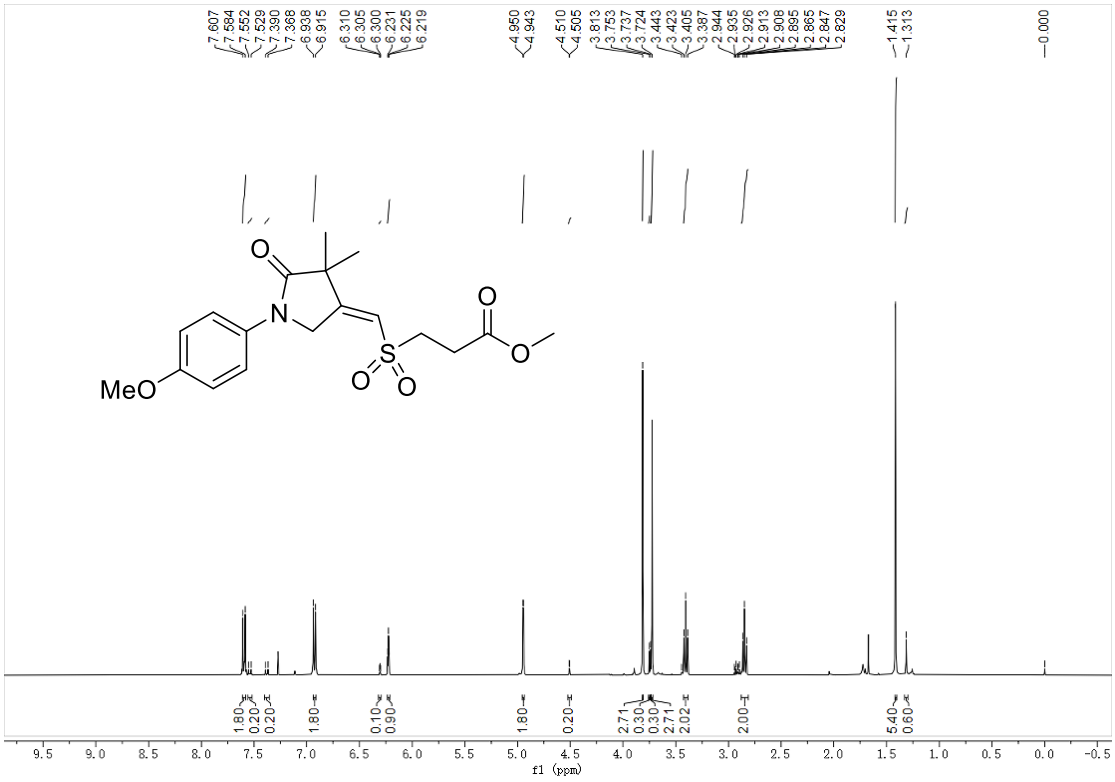


Figure S12 ^{1}H NMR (400 MHz, $CDCl_3$)

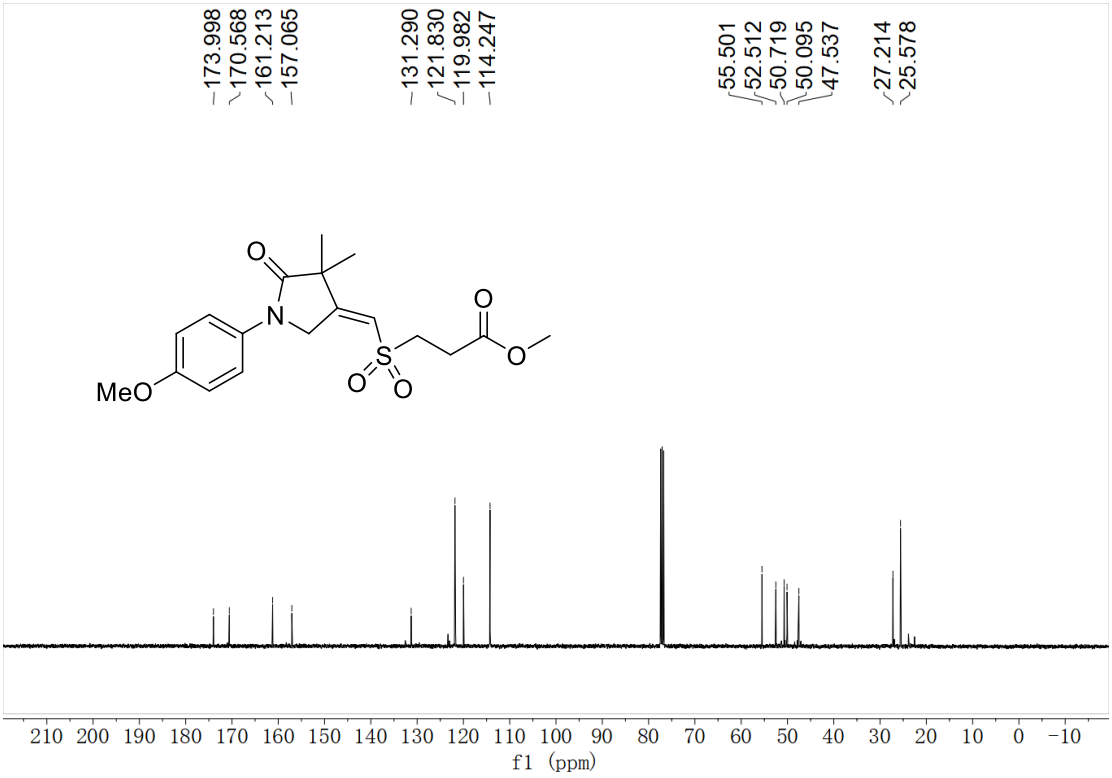


Figure S13 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-ethylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3da, Z/E > 99 : 1):

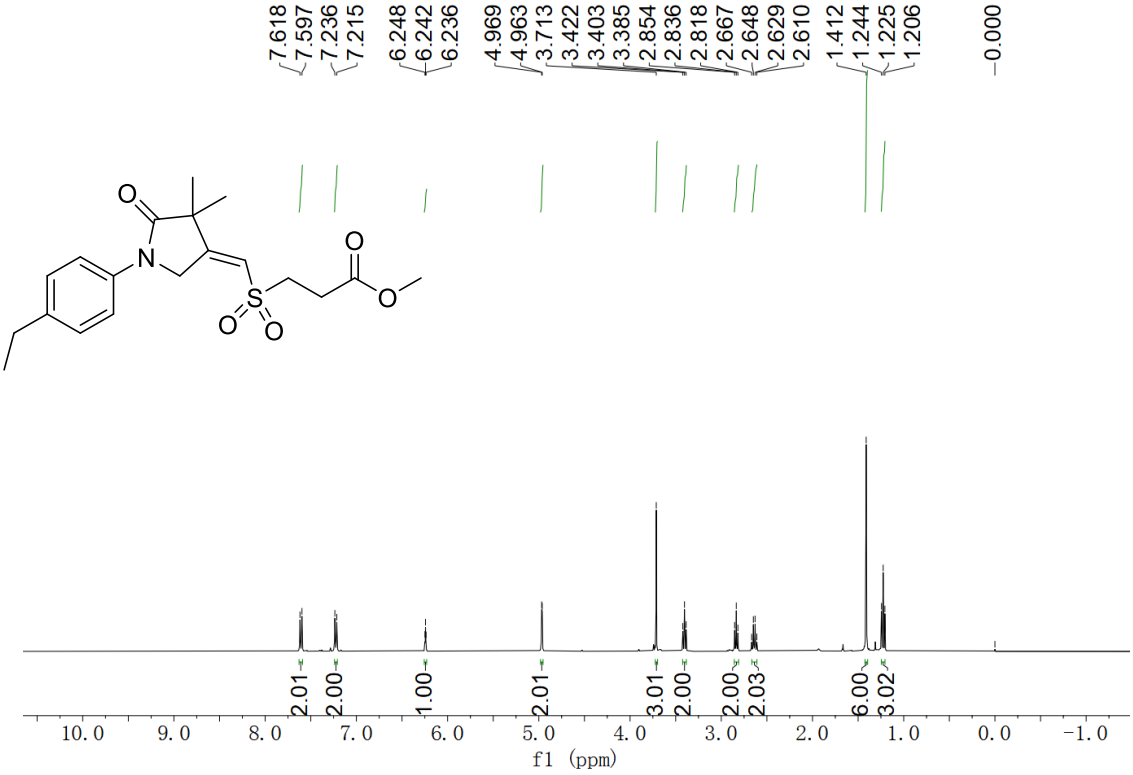


Figure S14 ^{1}H NMR (400 MHz, $CDCl_3$)

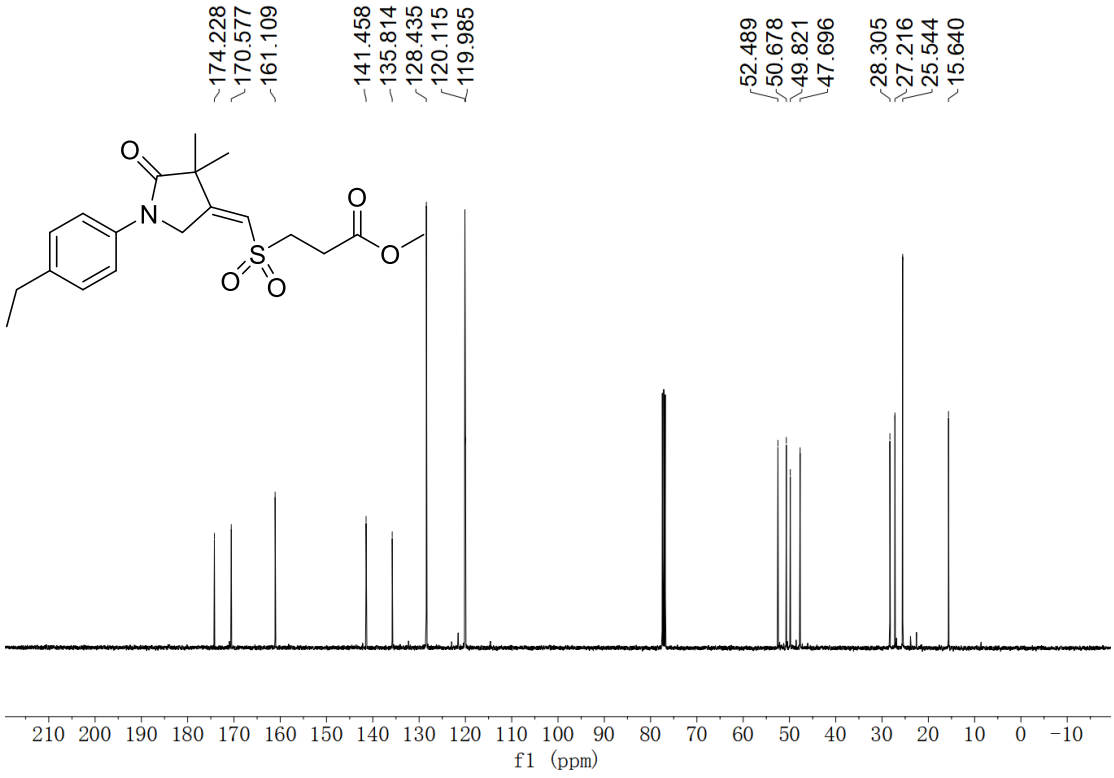


Figure S15 ^{13}C NMR (100 MHz, $CDCl_3$)

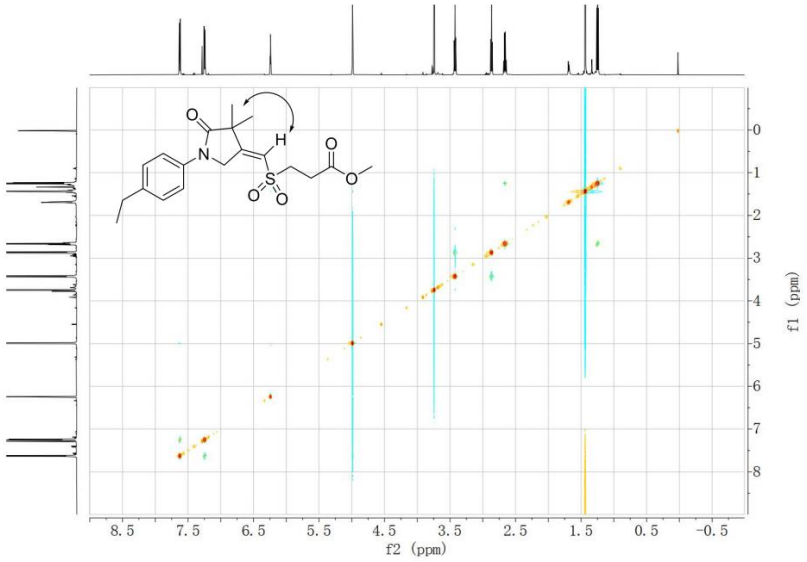


Figure S16 Noesy of compound 3da

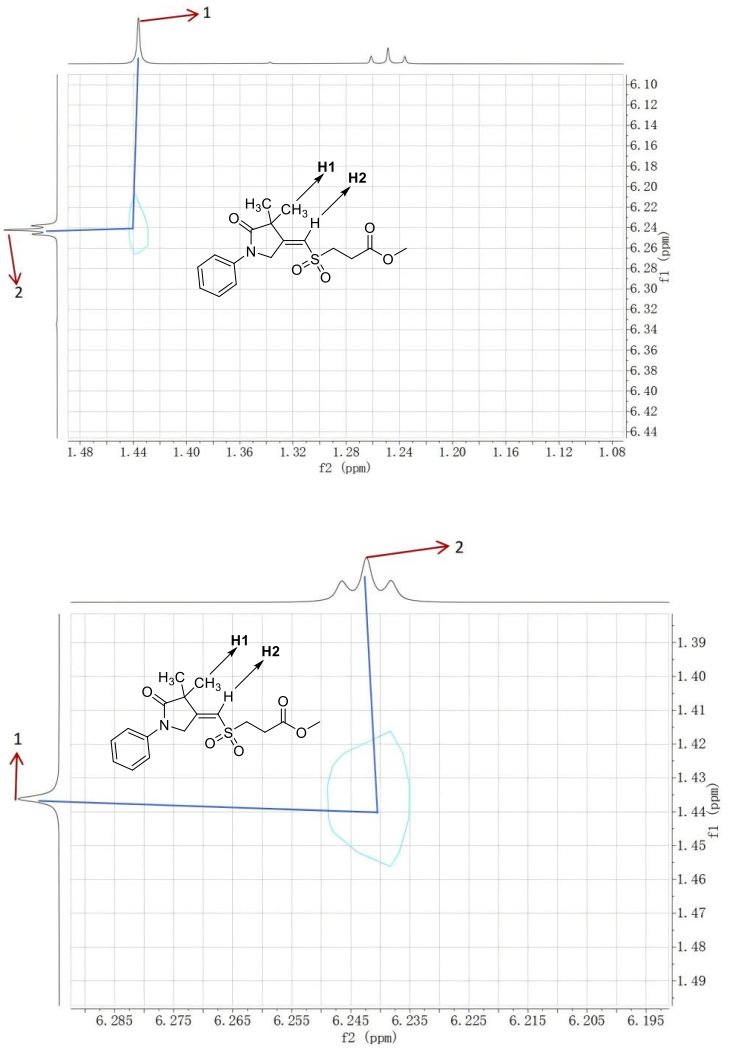


Figure S17 Noesy of compound 3da

methyl (Z)-3-(((4,4-dimethyl-1-(4-(methylthio)phenyl)-5-oxopyrrolidin-3-ylidene) methyl)sulfonyl)propanoate (3ea, Z/E = 99 : 1):

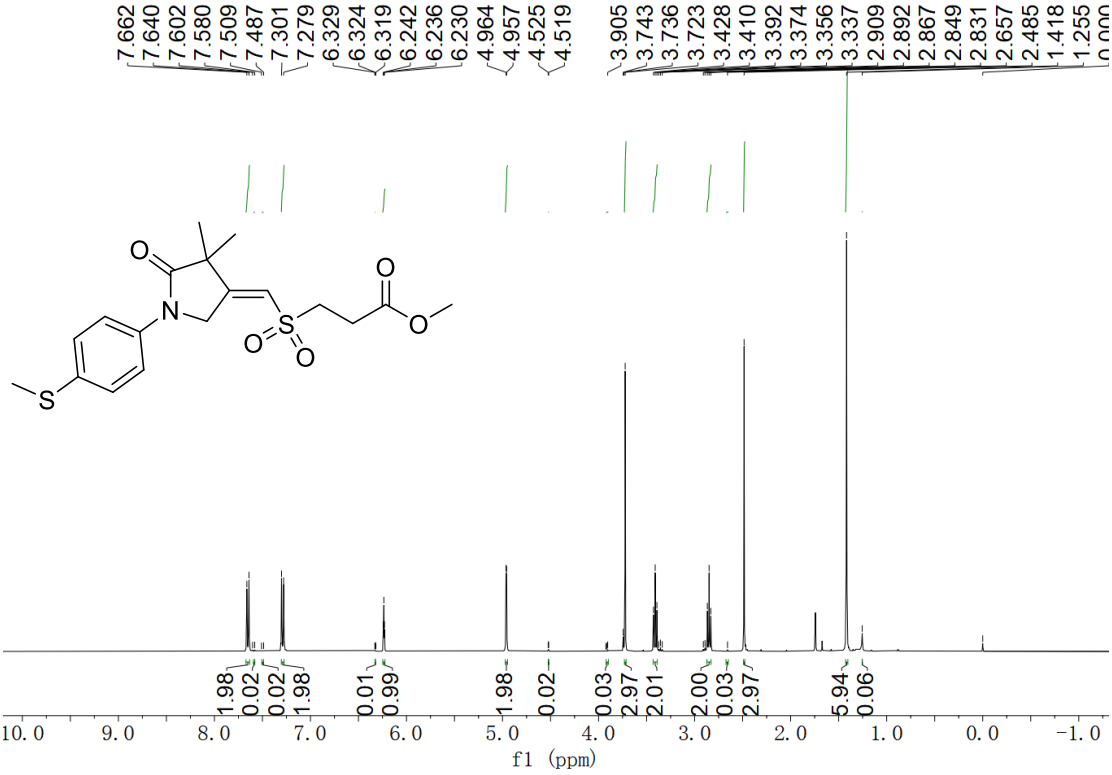


Figure S18 ^{1}H NMR (400 MHz, $CDCl_3$)

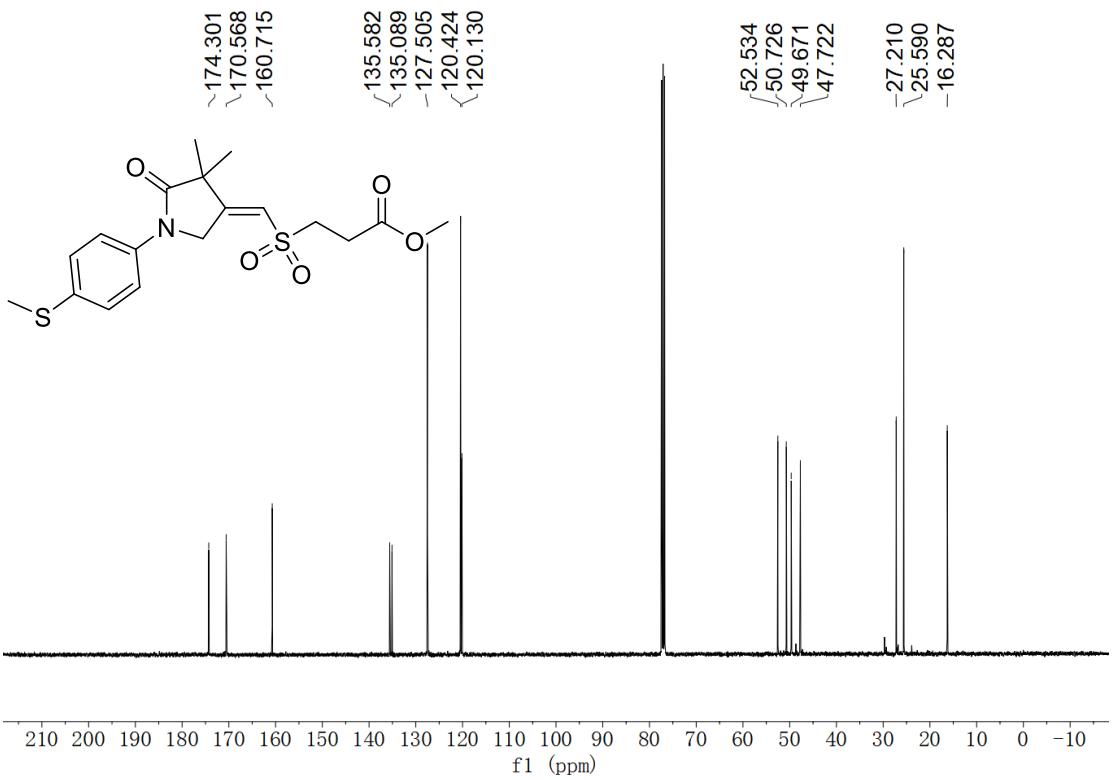


Figure S19 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-benzylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3fa, Z/E = 95 : 5):

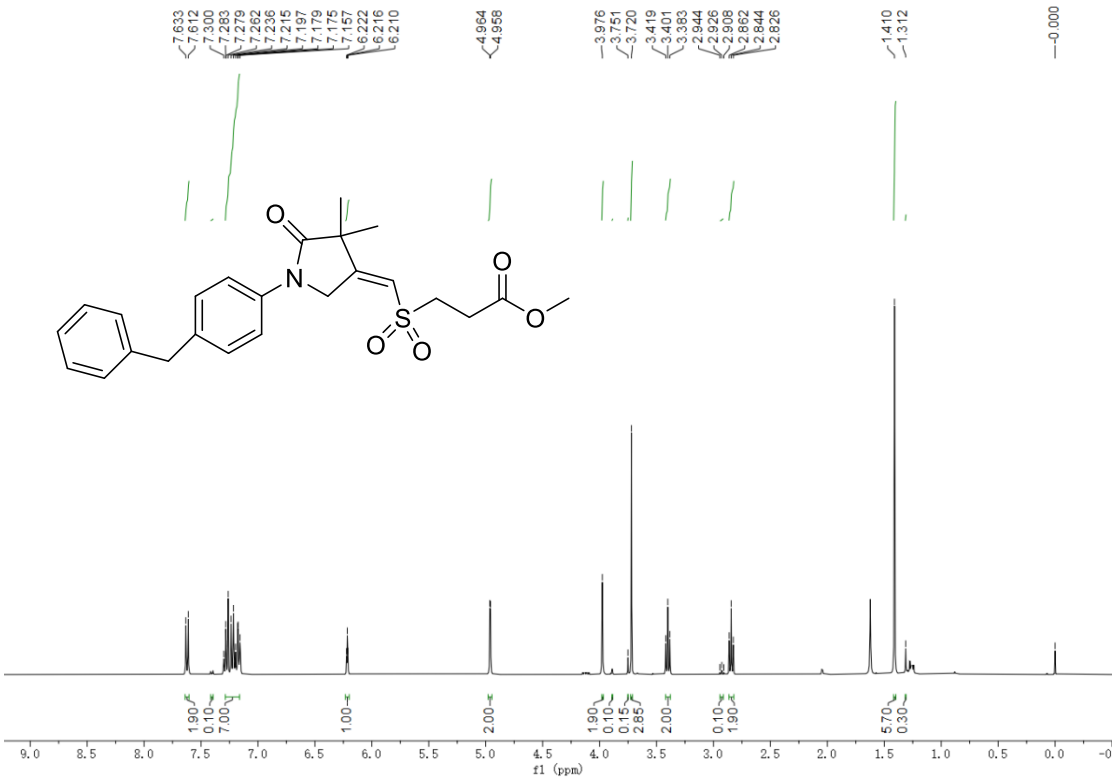


Figure S20 ^{1}H NMR (400 MHz, $CDCl_3$)

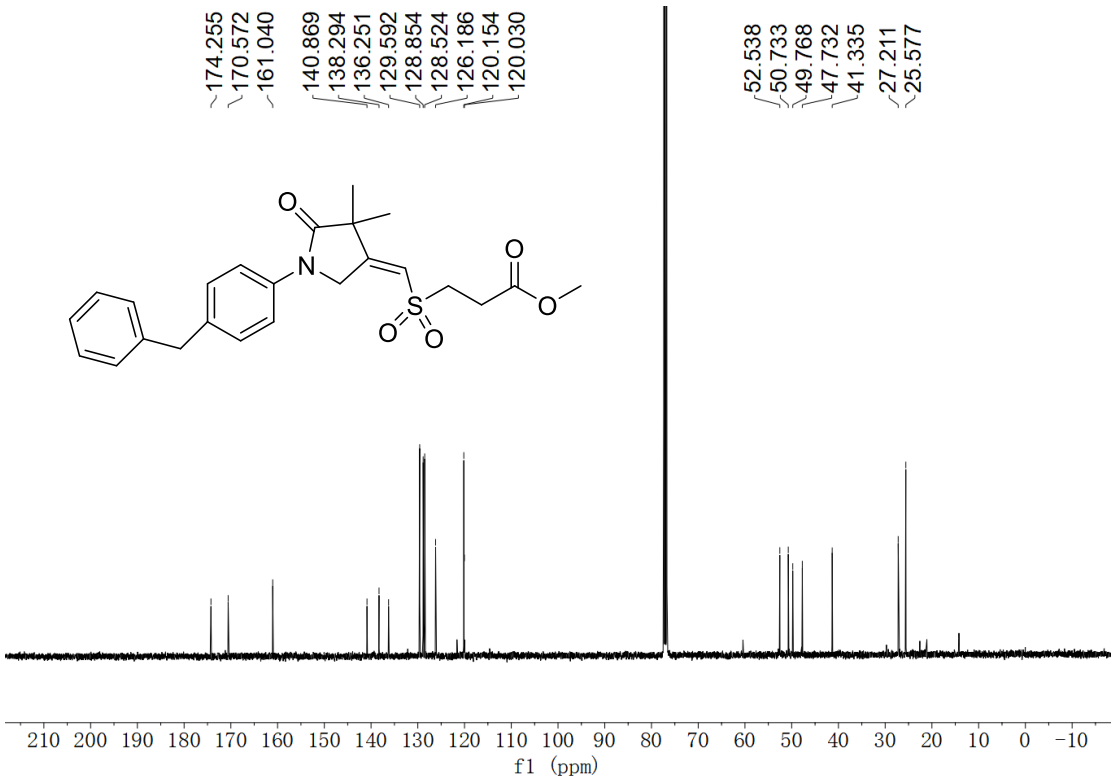


Figure S21 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ga, Z/E = 95 : 5):

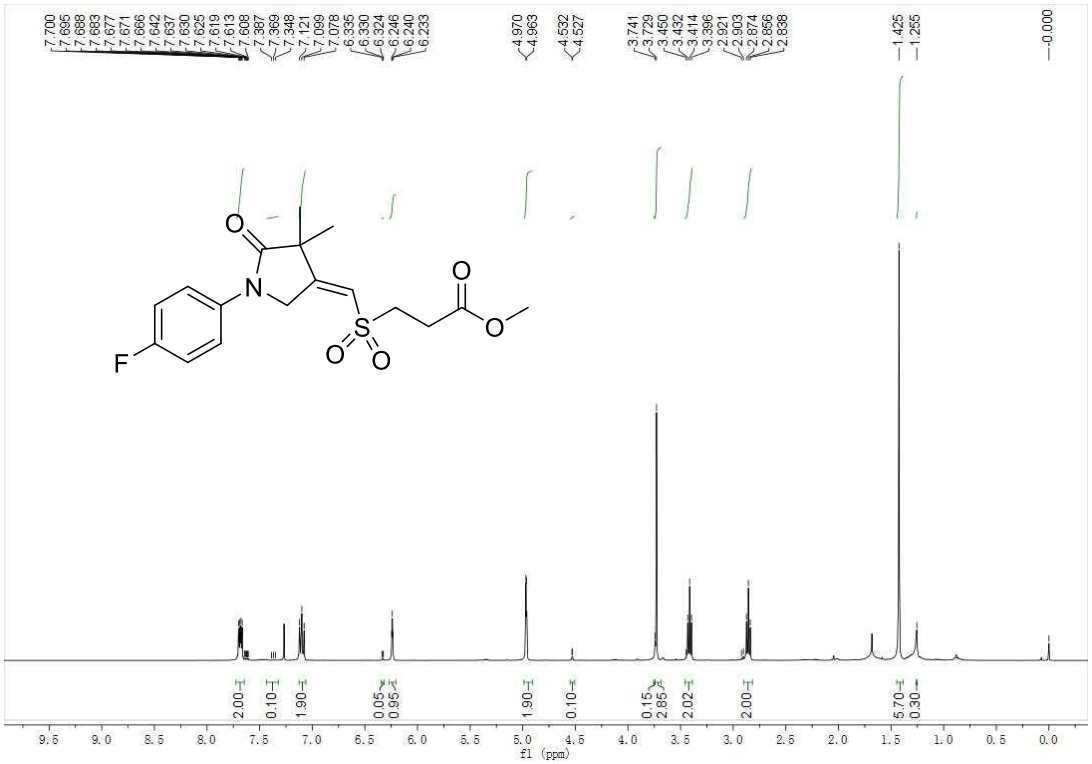


Figure S22 ^{1}H NMR (400 MHz, $CDCl_3$)

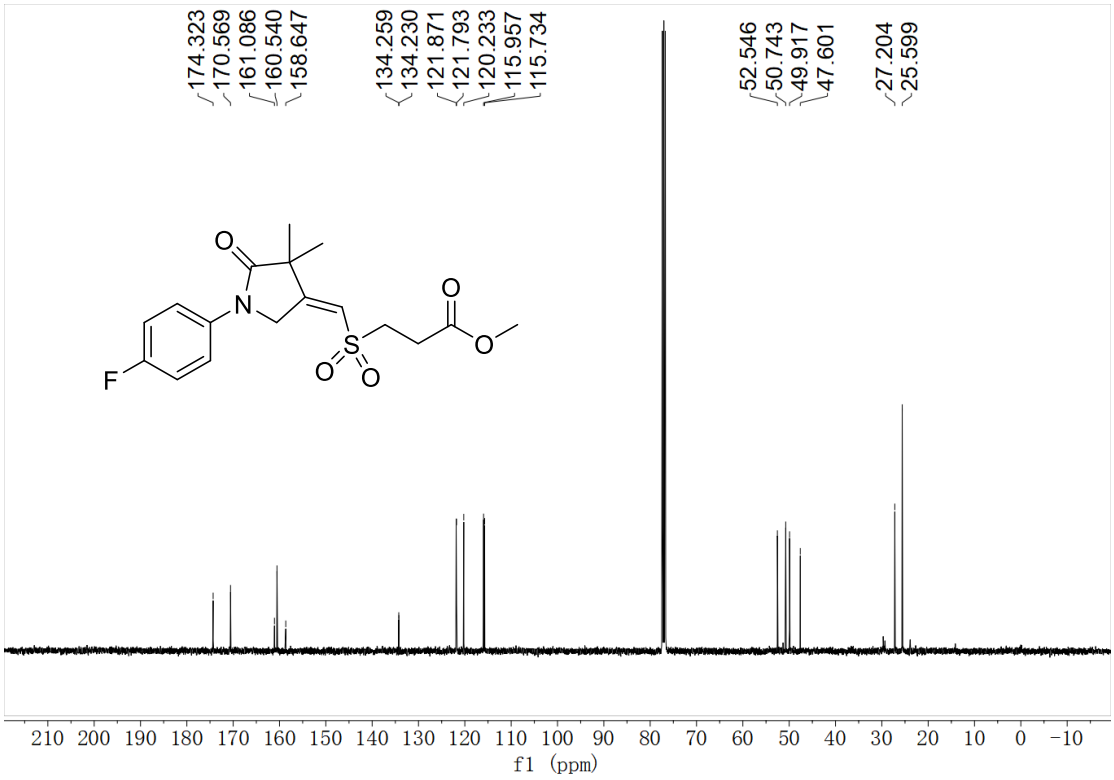


Figure S23 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ha, Z/E = 90 : 10):

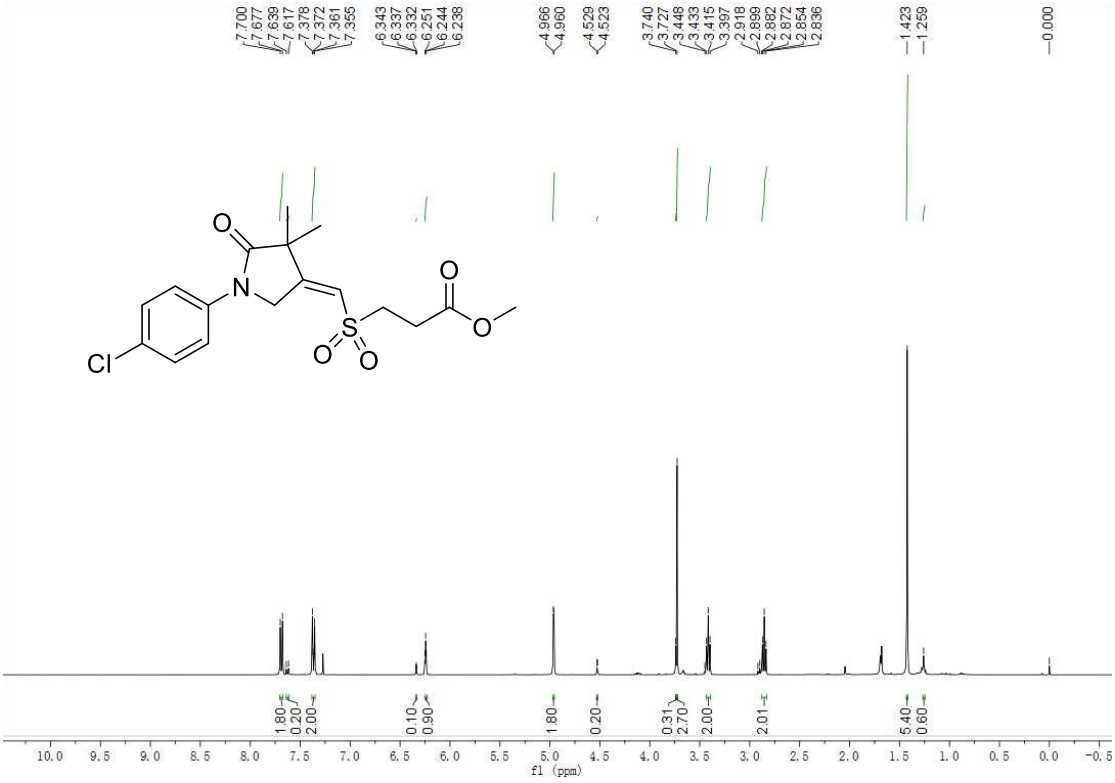


Figure S24 ^{1}H NMR (400 MHz, $CDCl_3$)

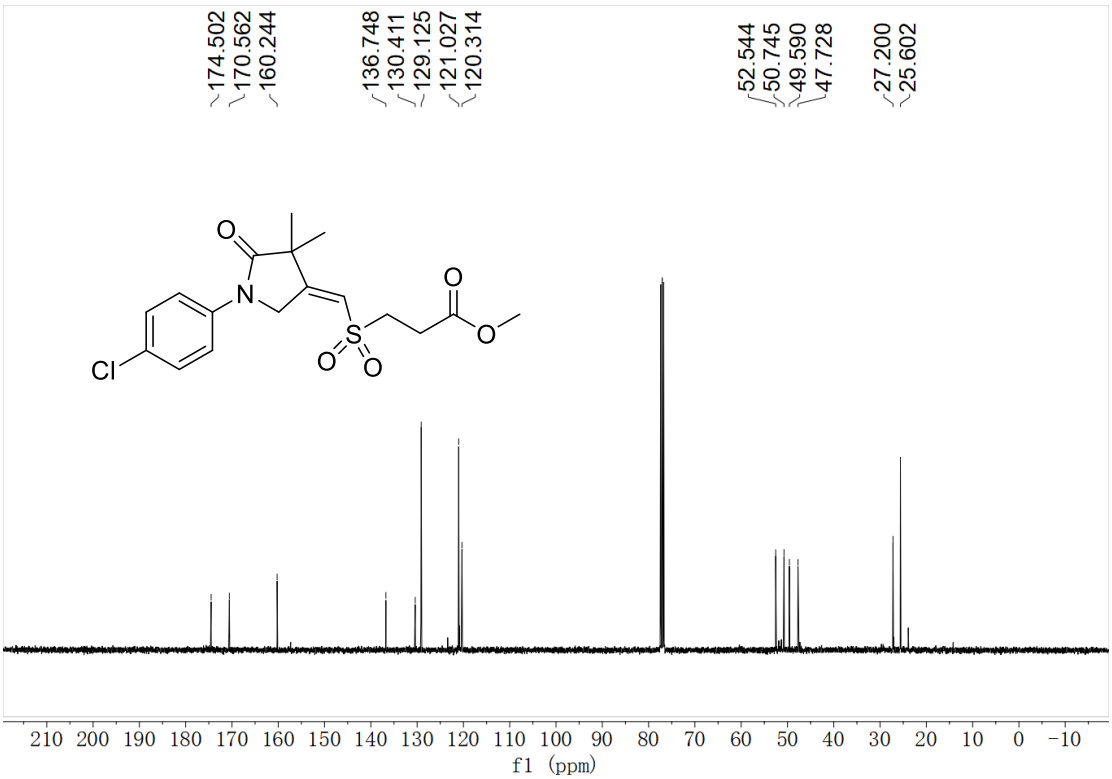


Figure S25 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-bromophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ia, Z/E = 98 : 2):

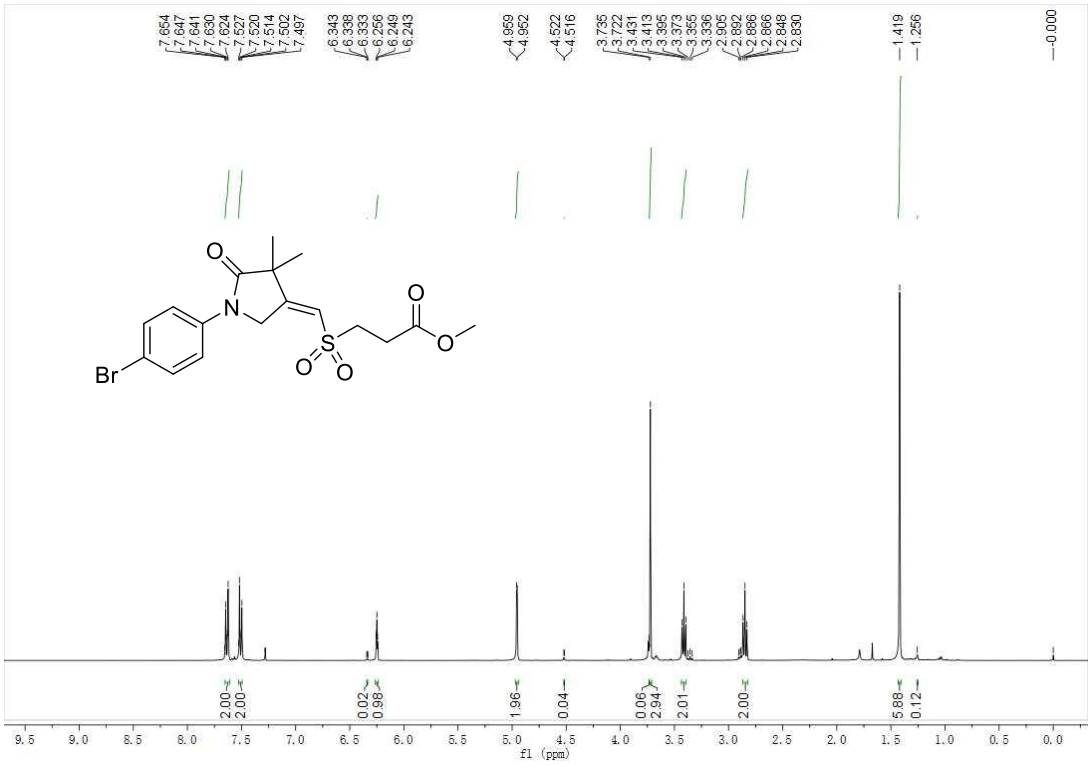


Figure S26 ^{1}H NMR (400 MHz, $CDCl_3$)

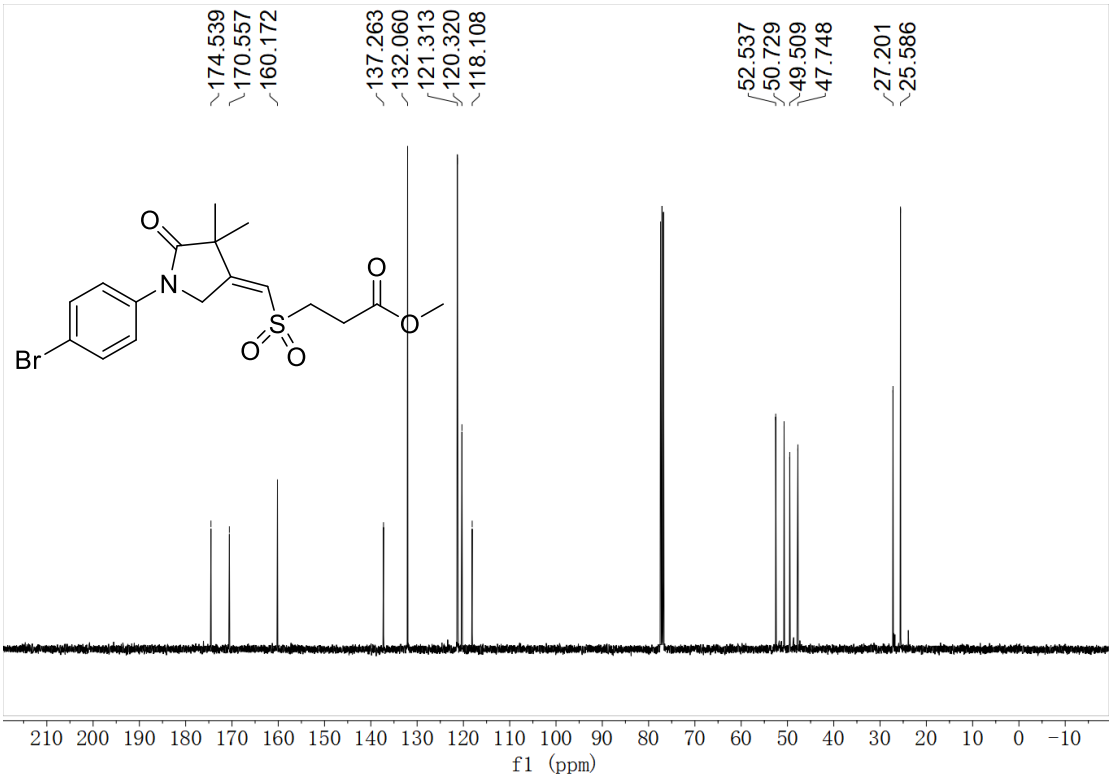


Figure S27 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(m-tolyl)pyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ja, Z/E = 95 : 5):

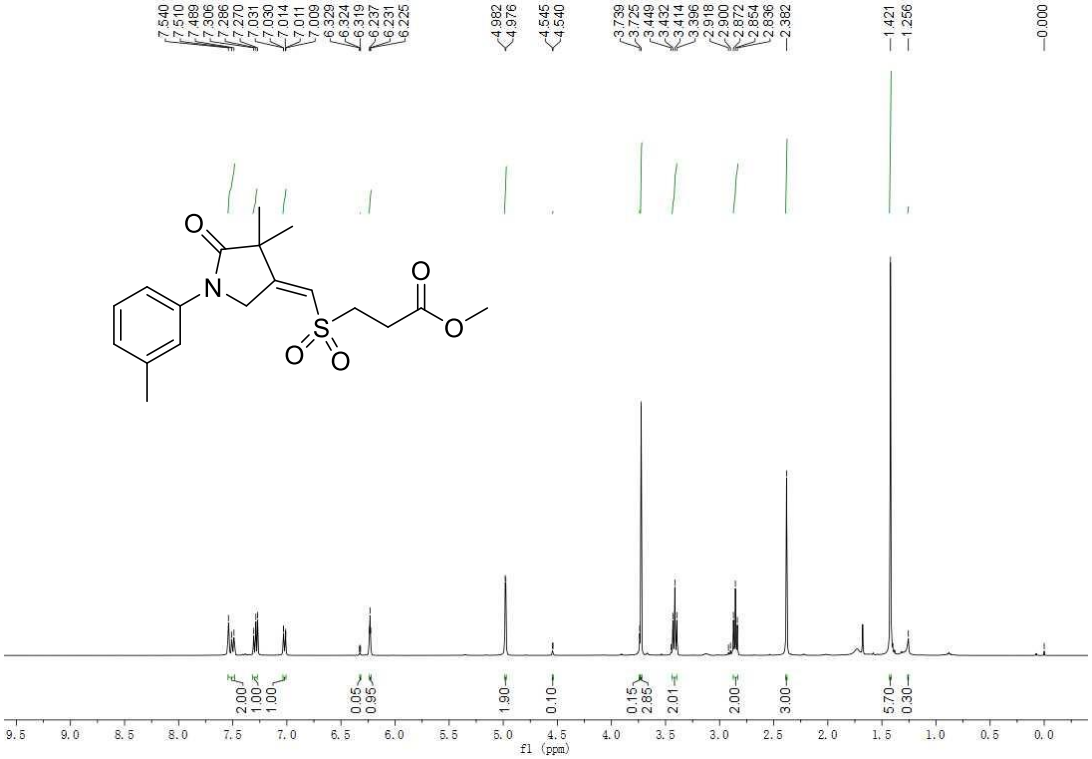


Figure S28 ^{1}H NMR (400 MHz, $CDCl_3$)

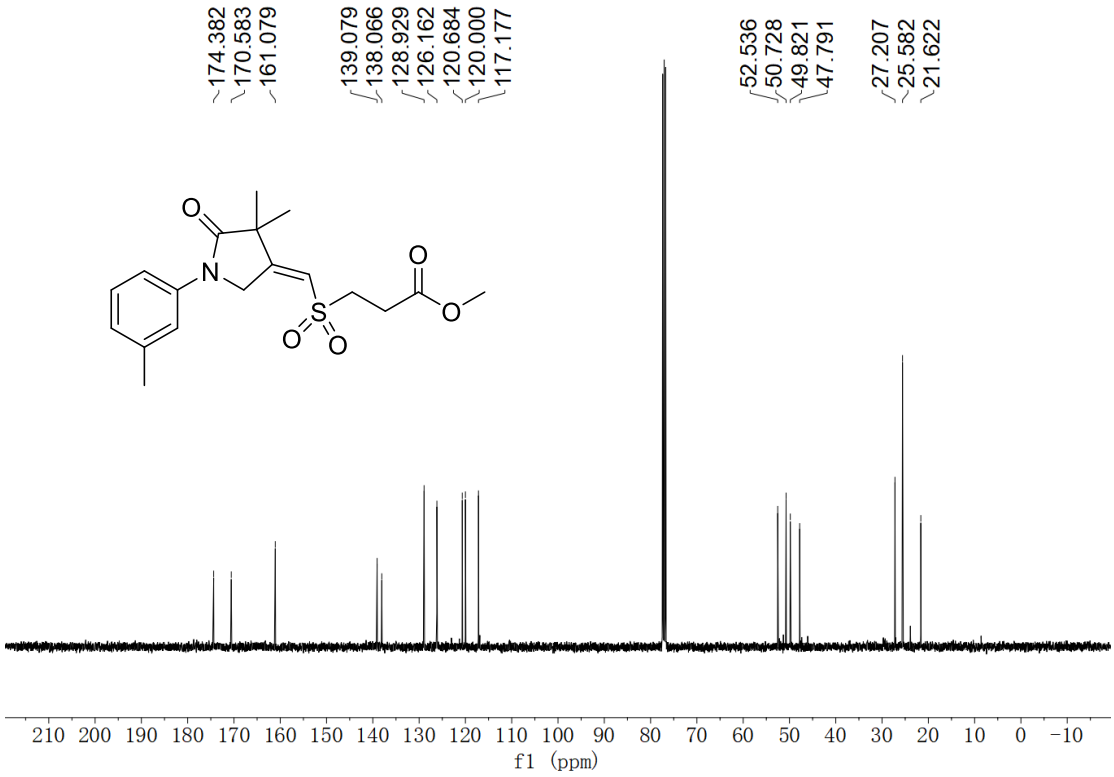


Figure S29 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(3-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ka, Z/E = 95 : 5):

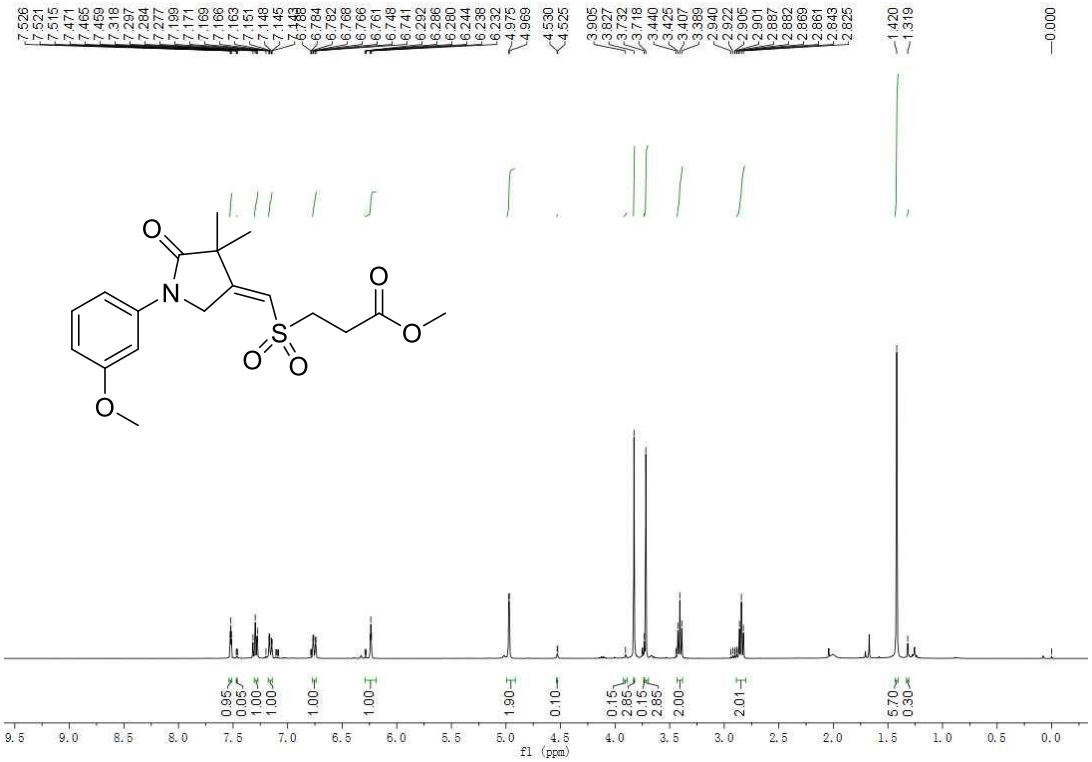


Figure S30 ^{1}H NMR (400 MHz, $CDCl_3$)

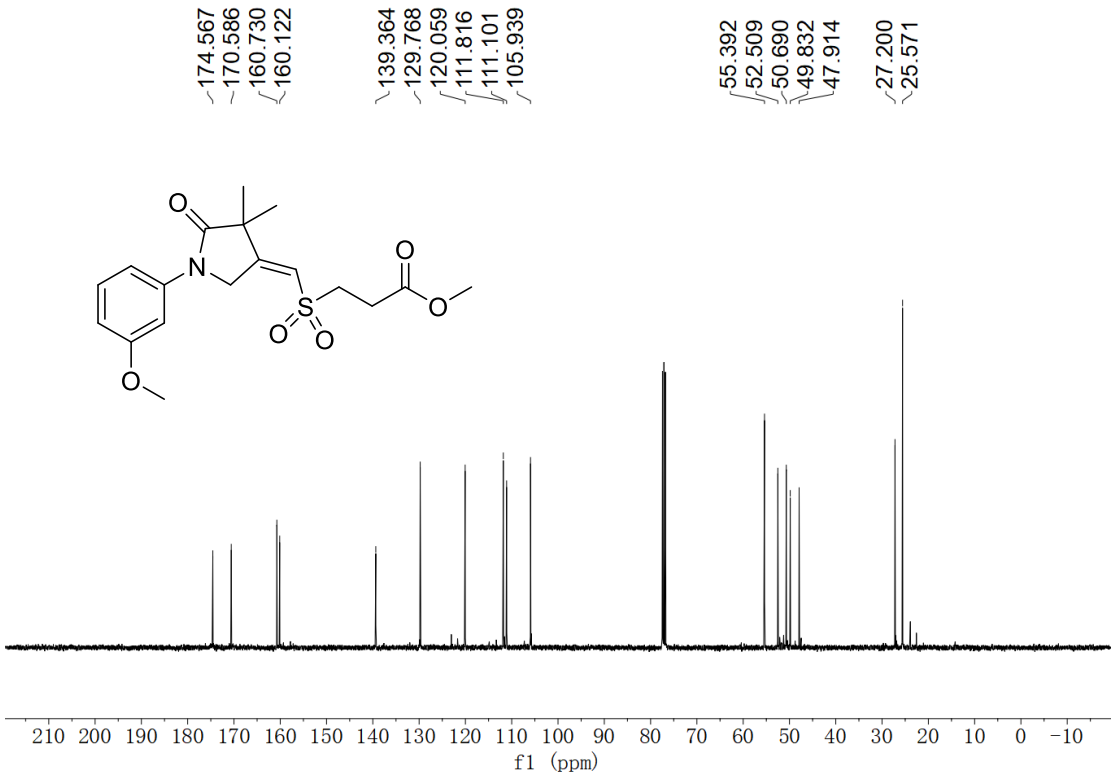


Figure S31 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4,4-dimethyl-1-(3-(methylthio)phenyl)-5-oxopyrrolidin-3-ylidene) methyl)sulfonyl)propanoate (3la, Z/E = 95 : 5)：

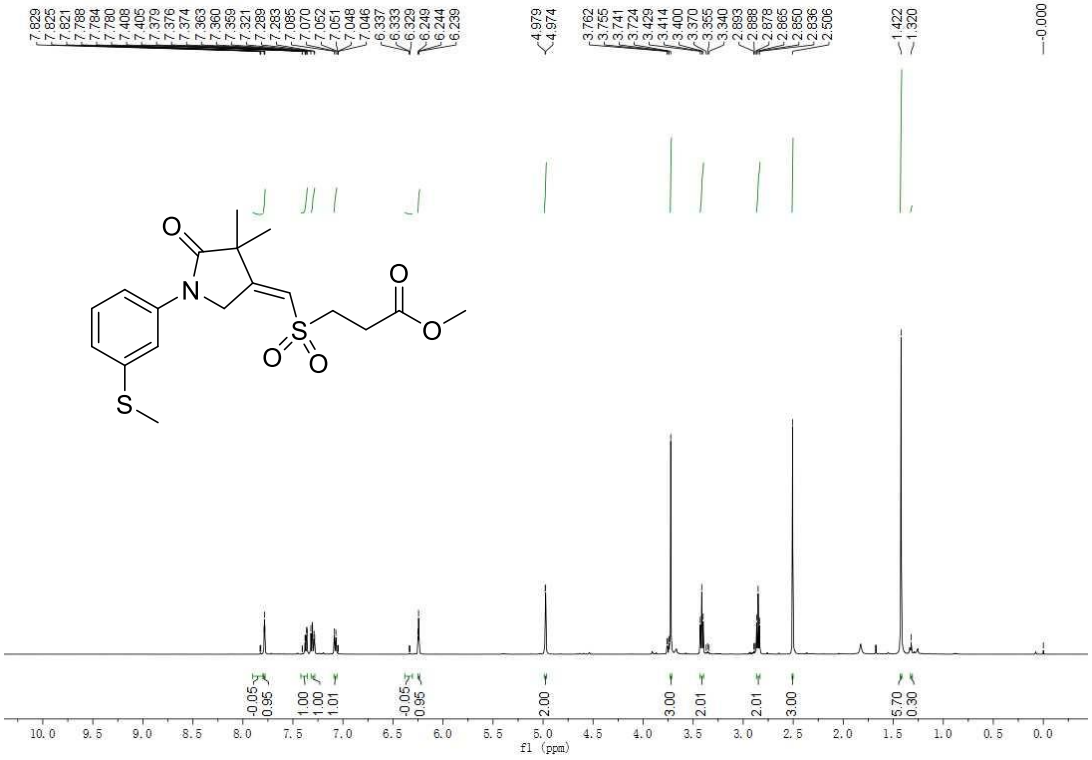


Figure S32 ^{1}H NMR (400 MHz, $CDCl_3$)

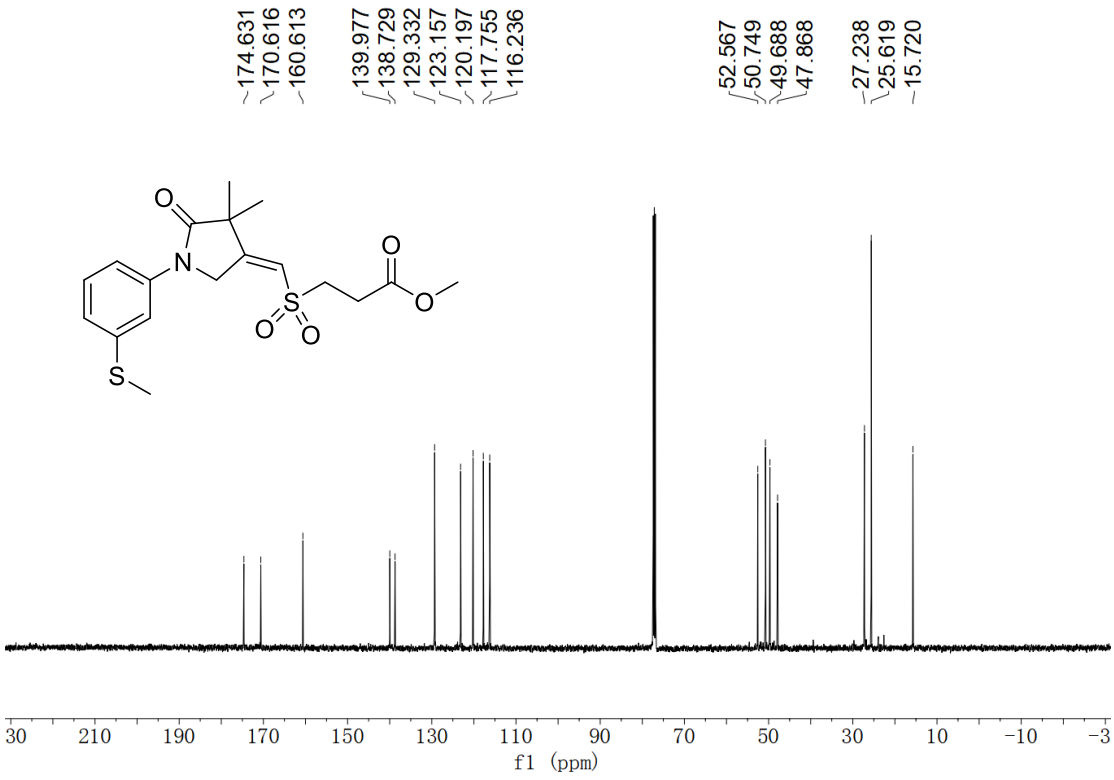


Figure S33 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(3-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ma, Z/E = 96 : 4):

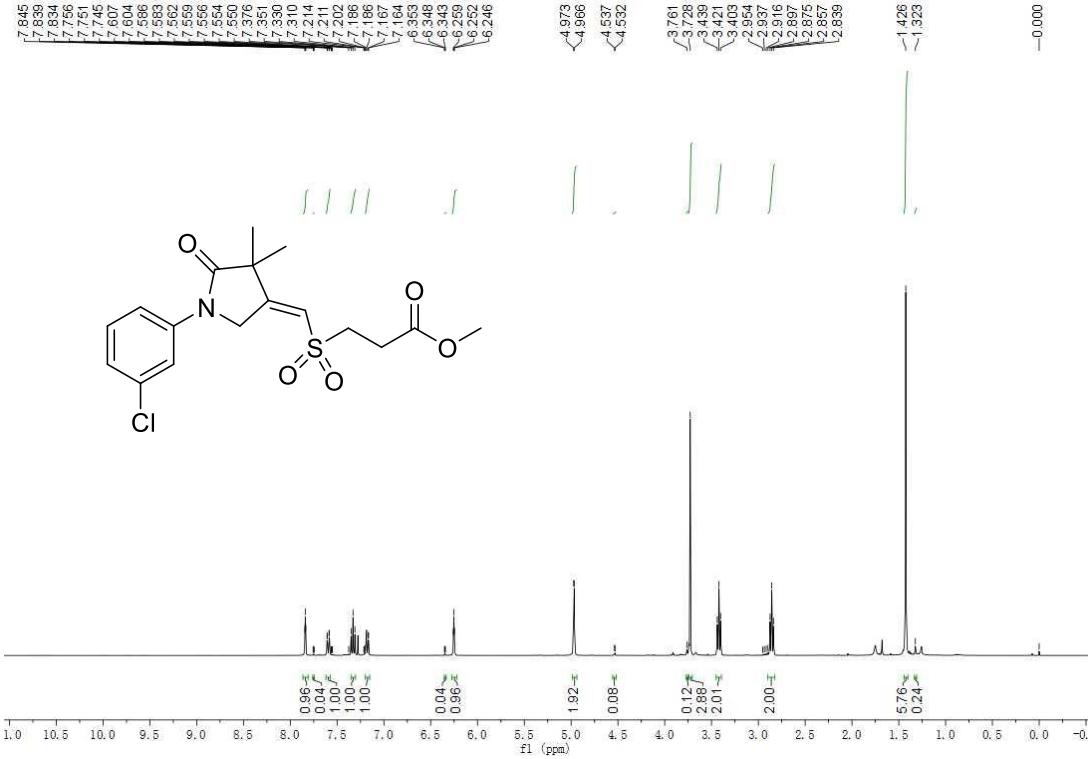


Figure S34 ^{1}H NMR (400 MHz, $CDCl_3$)

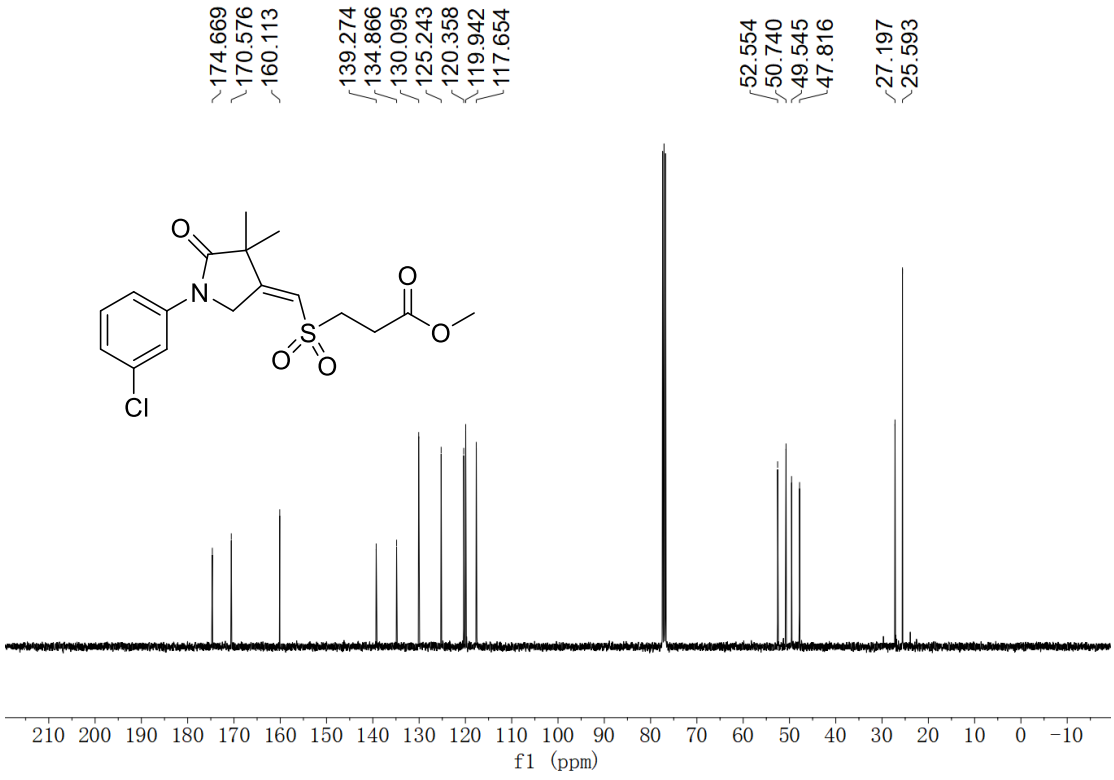


Figure S35 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4,4-dimethyl-5-oxo-1-(o-tolyl)pyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3na, Z/E = 90 : 10):

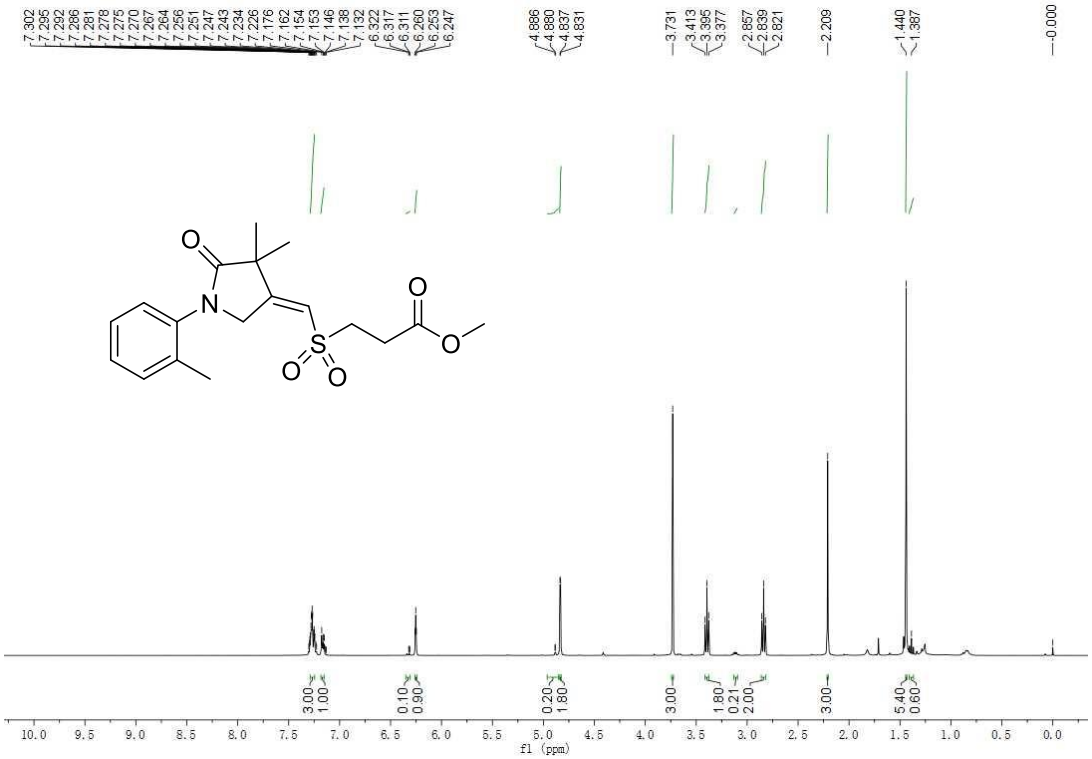


Figure S36 ^{1}H NMR (400 MHz, $CDCl_3$)

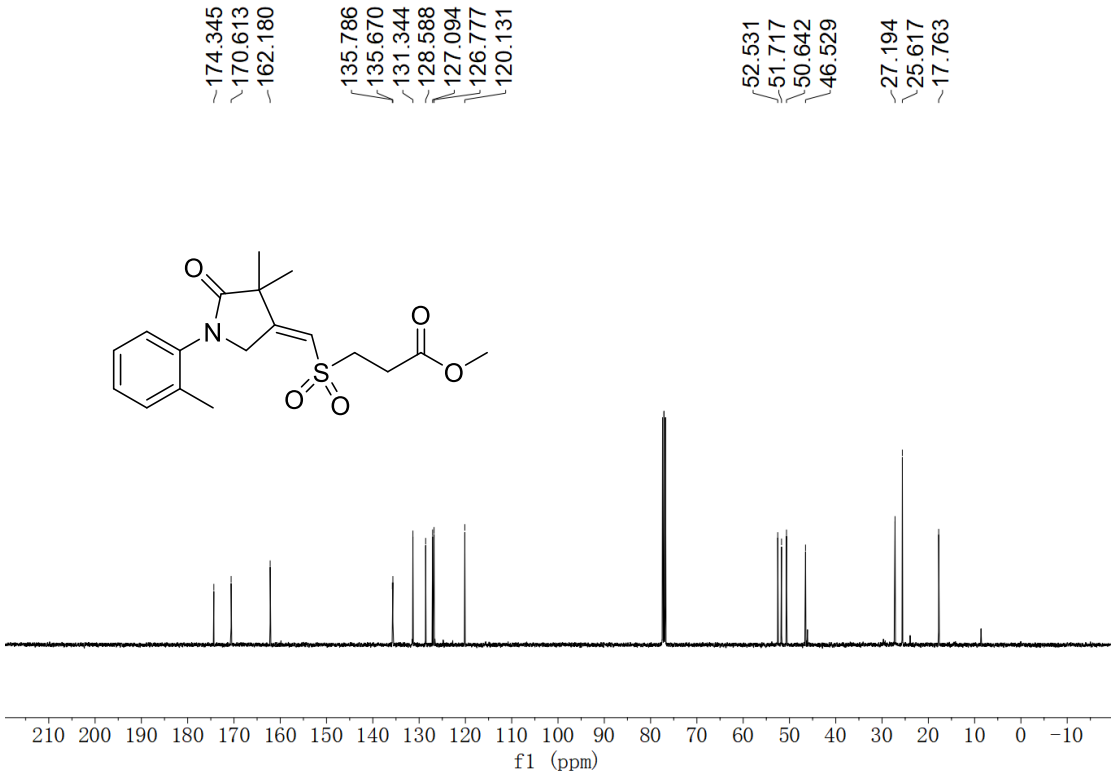


Figure S37 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(2-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3oa, Z/E = 95 : 5):

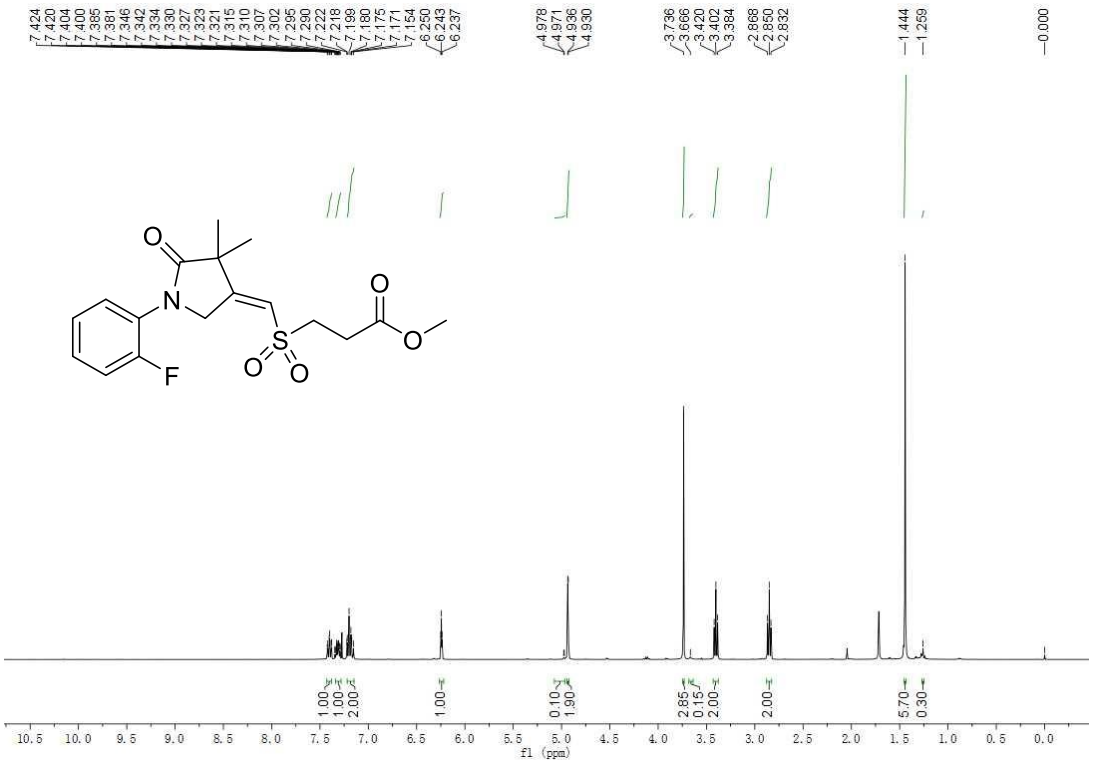


Figure S38 ^{1}H NMR (400 MHz, $CDCl_3$)

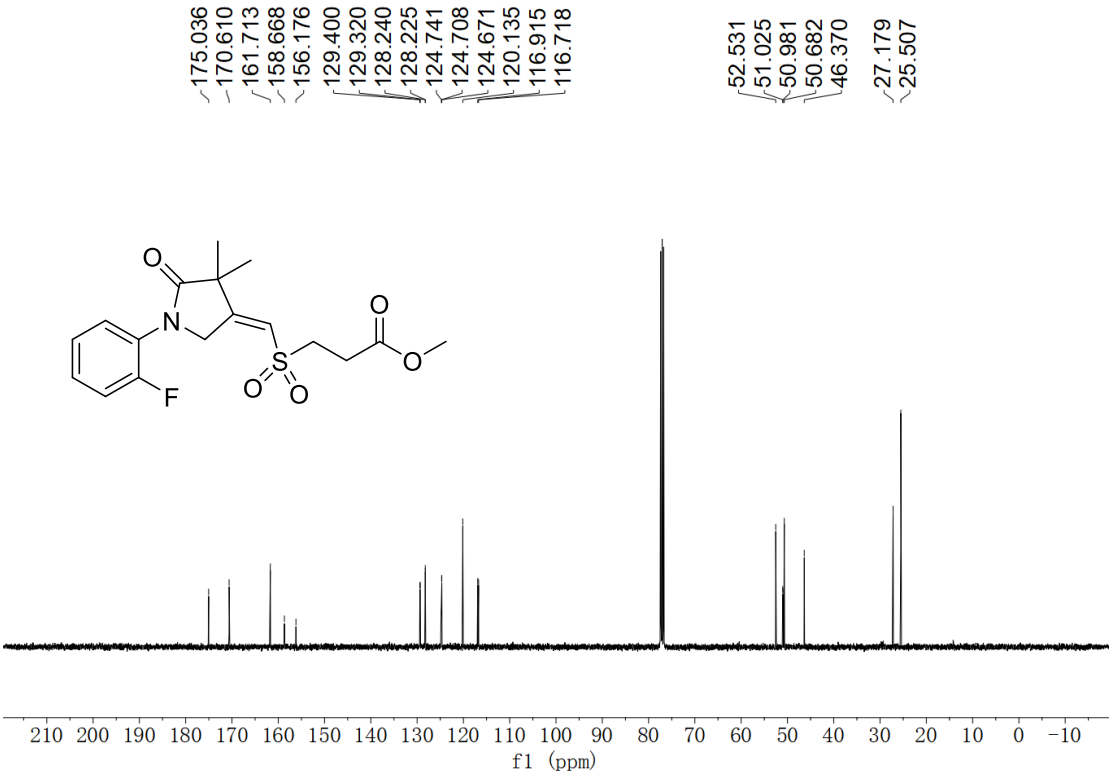


Figure S39 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(3,4-dimethylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3pa, Z/E = 97 : 3):

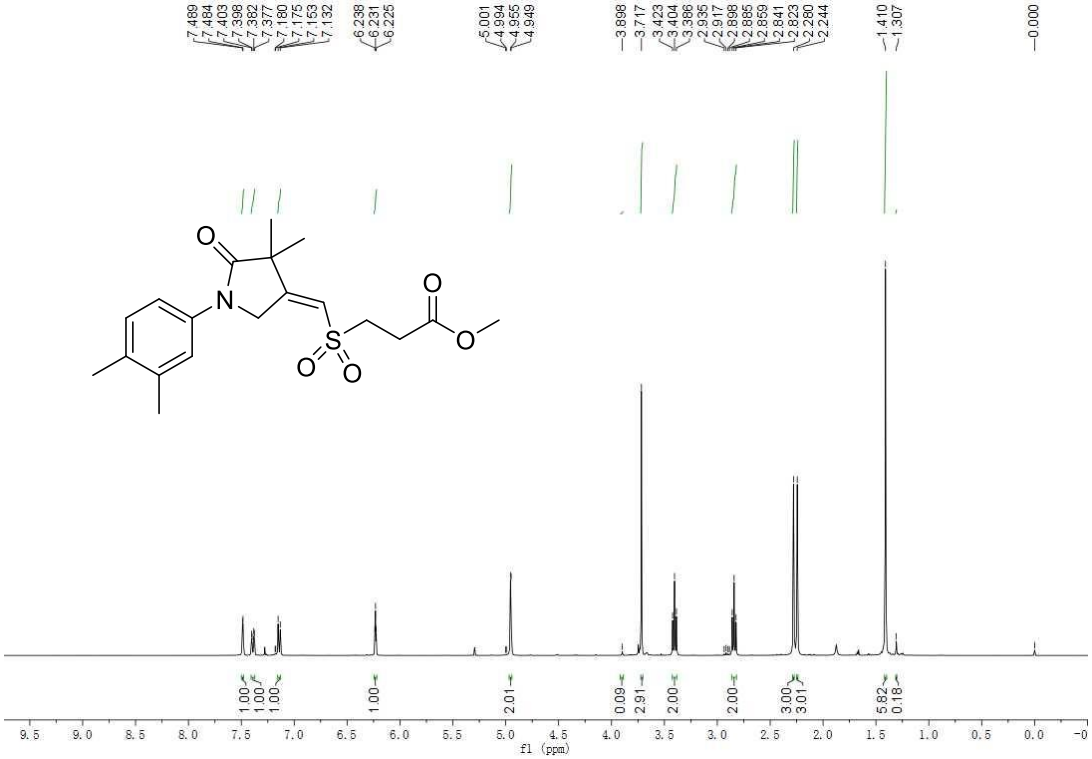


Figure S40 ^{1}H NMR (400 MHz, $CDCl_3$)

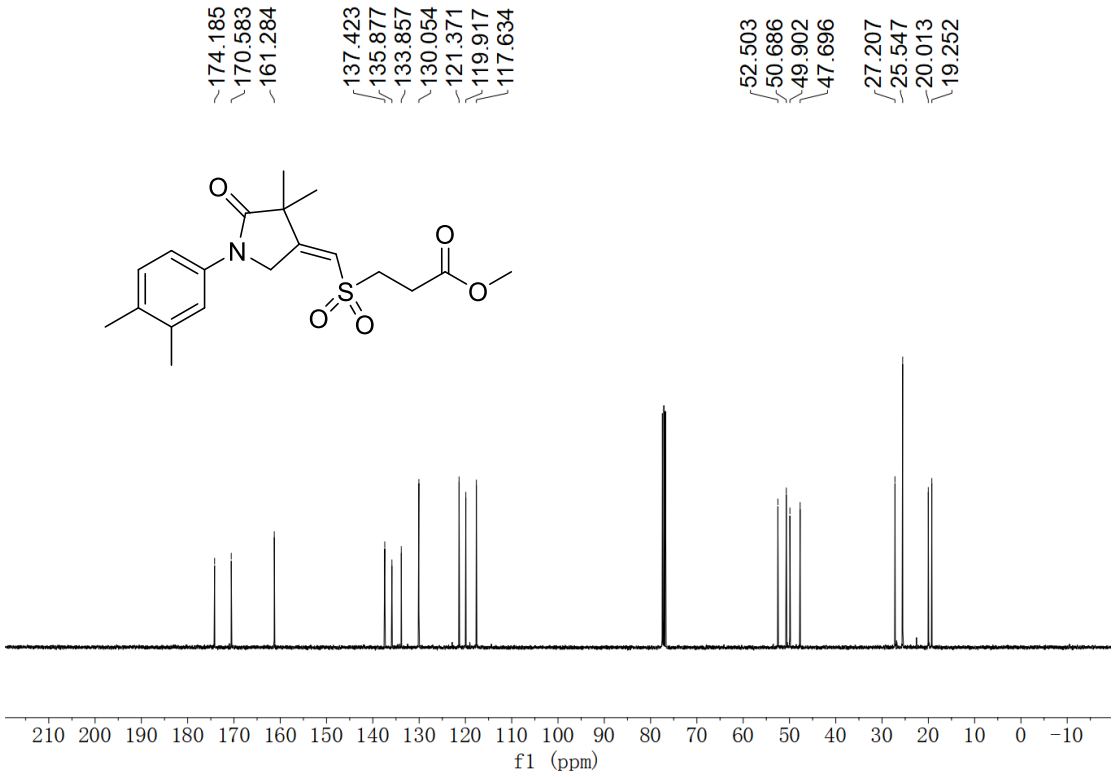


Figure S41 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((1-(4-chloro-3-methylphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3qa, Z/E = 90 : 10):

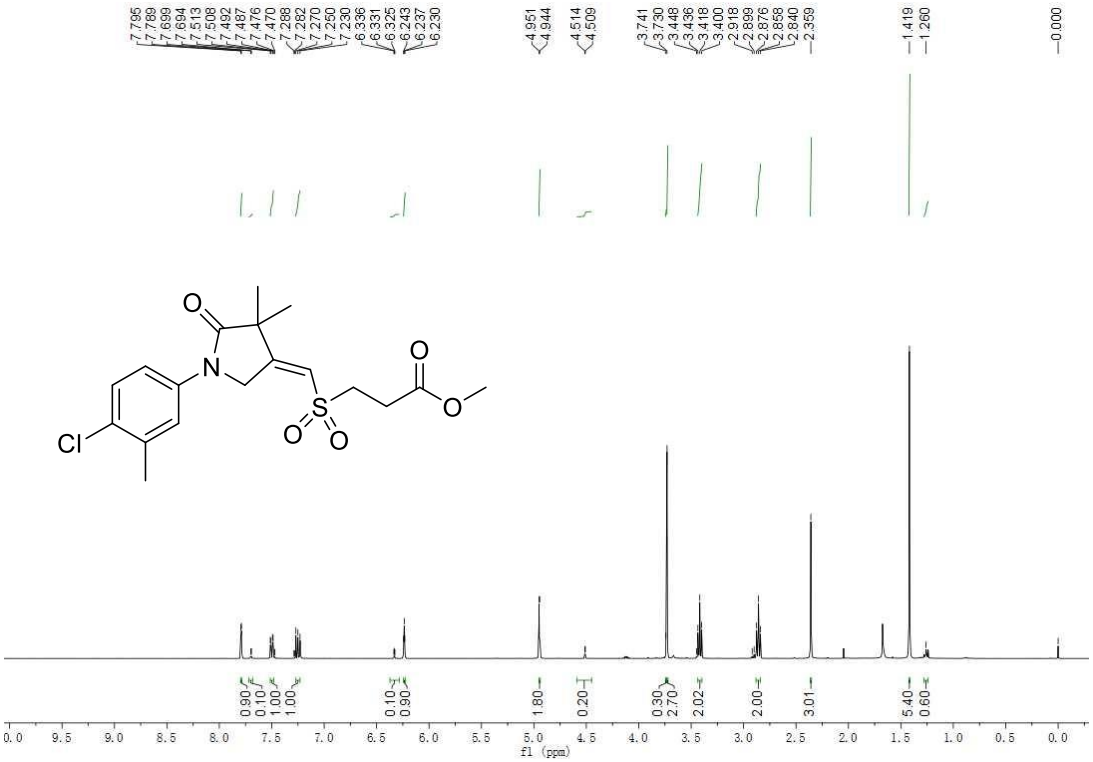


Figure S42 ^{1}H NMR (400 MHz, $CDCl_3$)

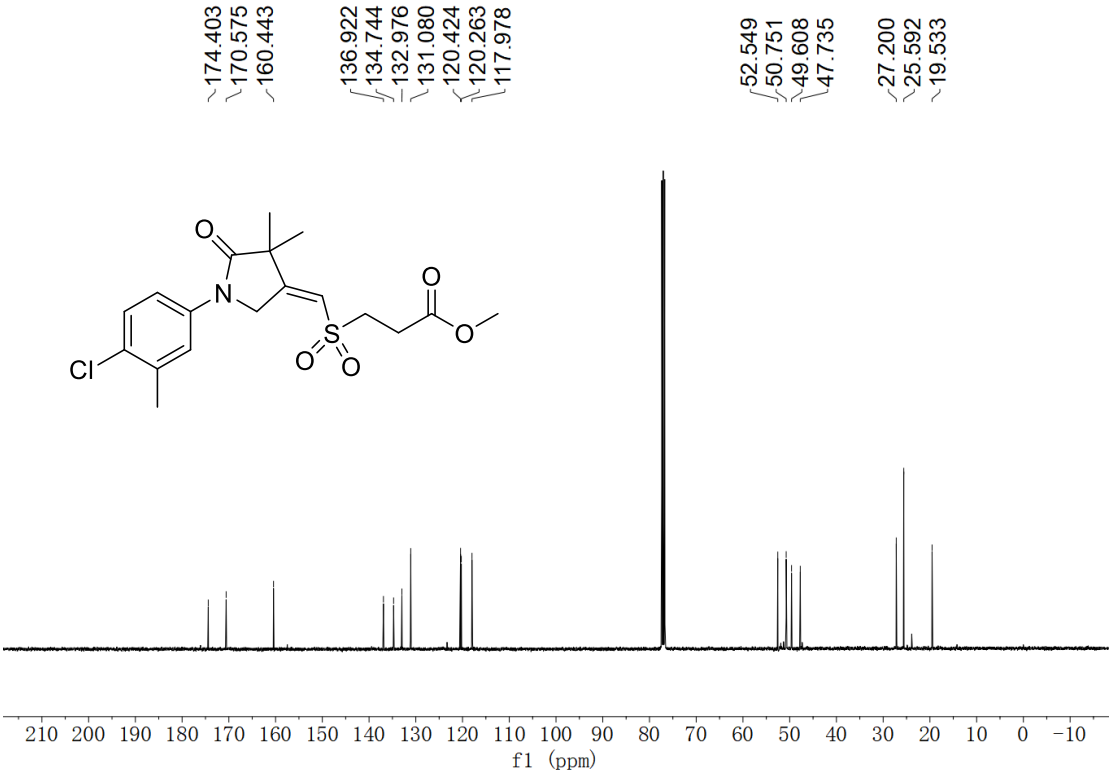


Figure S43 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4,4-dimethyl-1-(naphthalen-1-yl)-5-oxopyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ra, Z/E > 99 : 1):

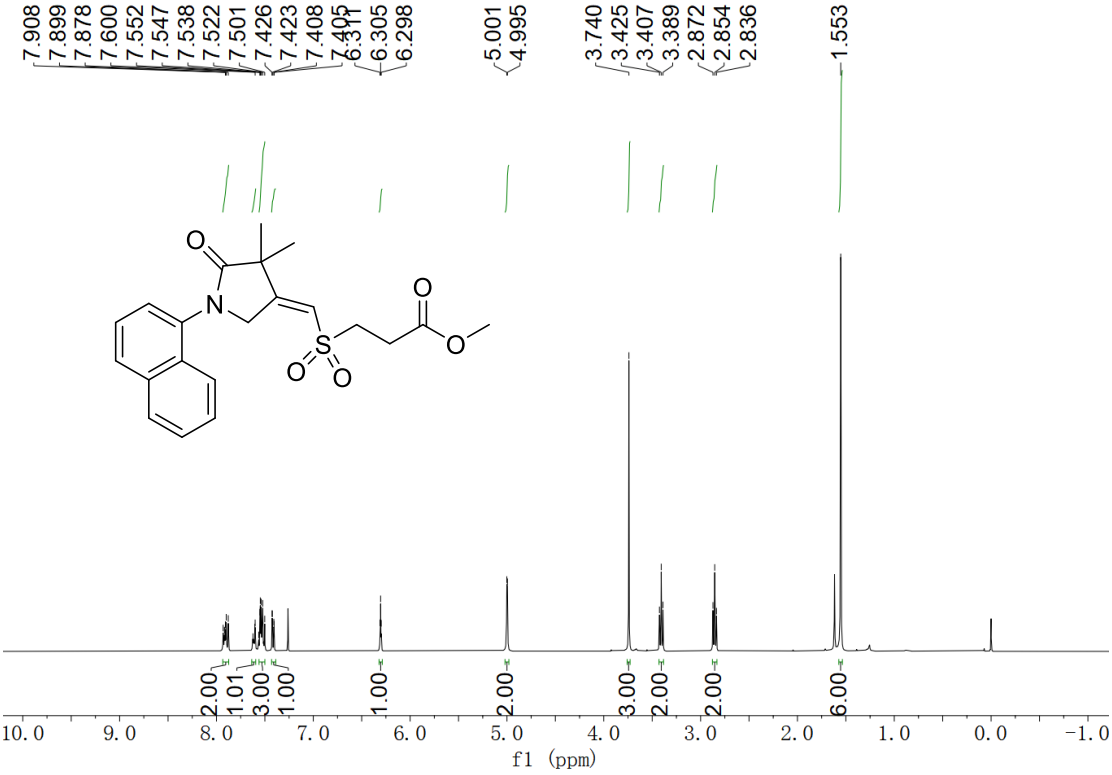


Figure S44 ^{1}H NMR (400 MHz, $CDCl_3$)

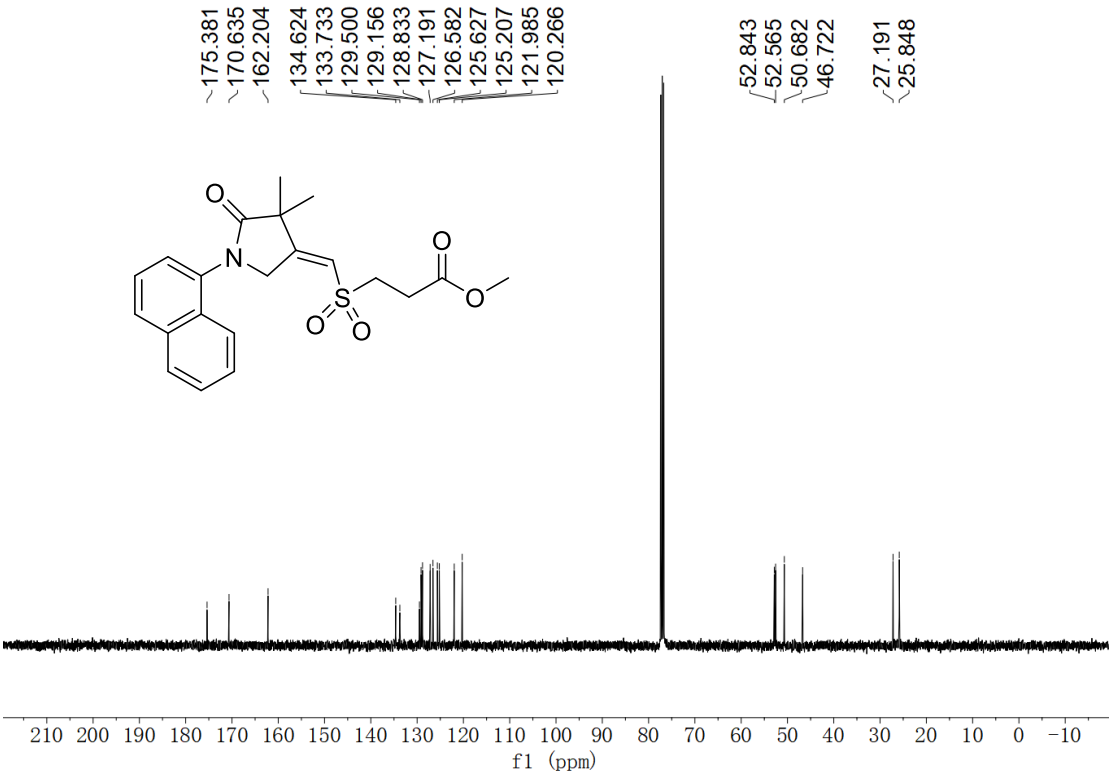


Figure S45 ^{13}C NMR (100 MHz, $CDCl_3$)

(Z)-1-benzyl-3,3-dimethyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methylene)pyrrolidin-2-one (3si, Z/E = 99 : 1):

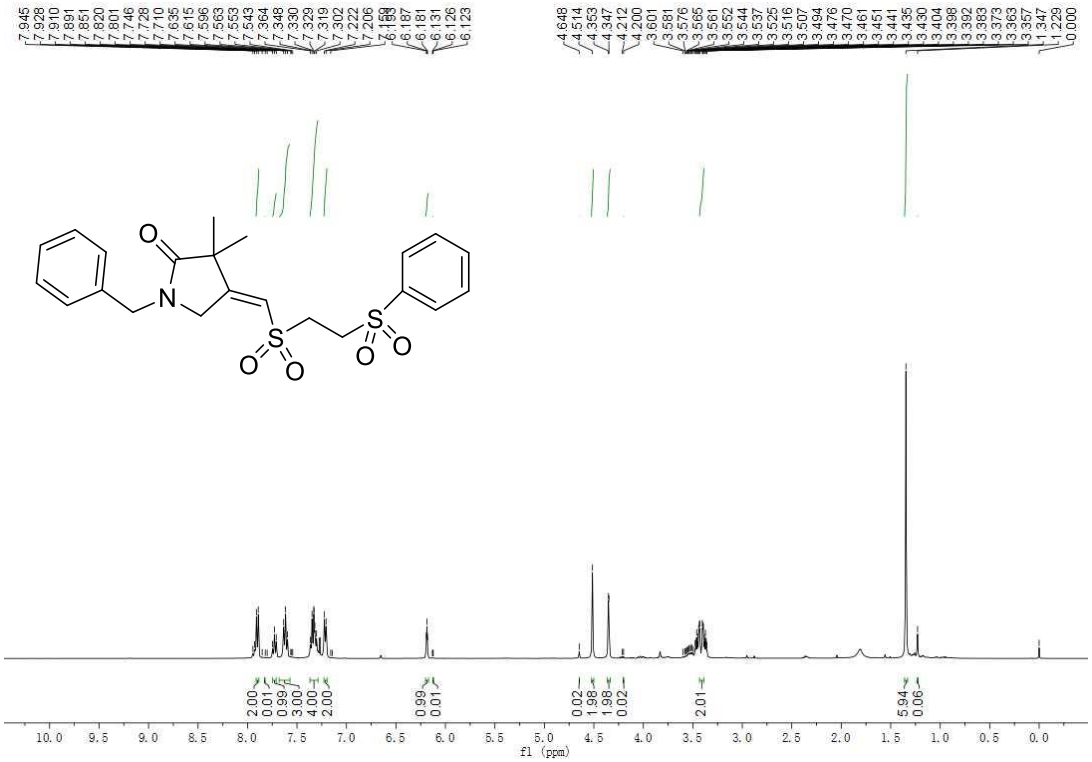


Figure S46 ^{1}H NMR (400 MHz, $CDCl_3$)

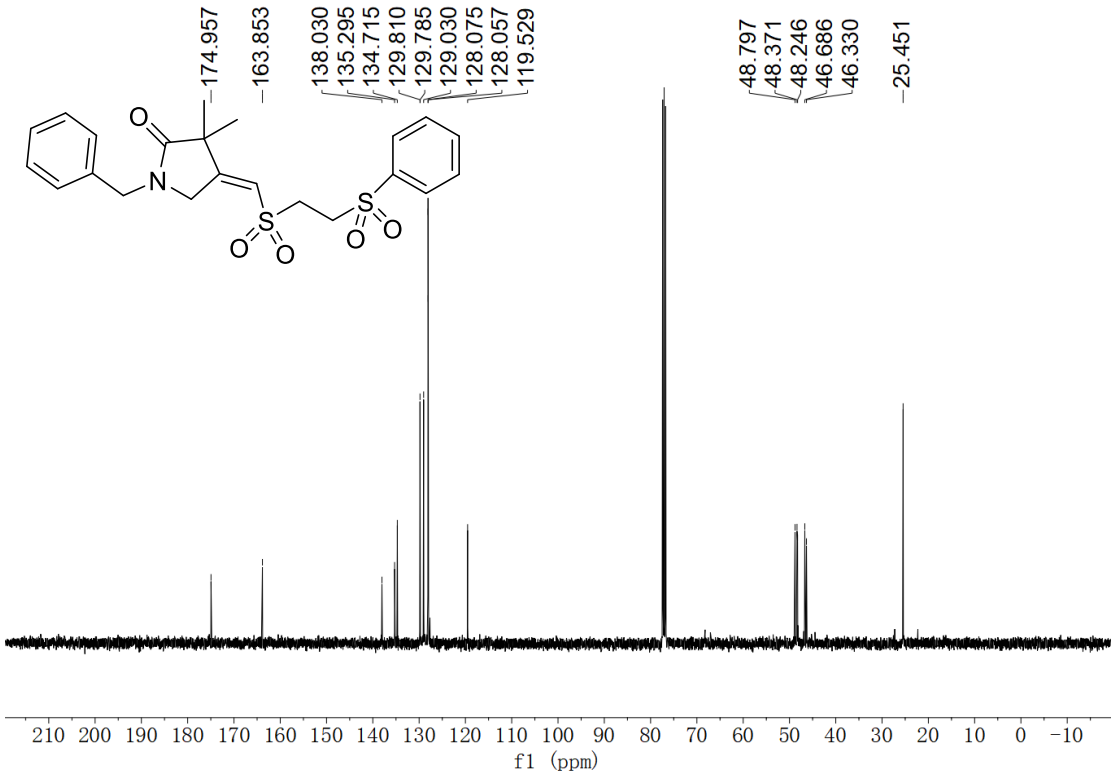


Figure S47 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl (Z)-3-(((4-methyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ta, Z/E > 99 : 1):

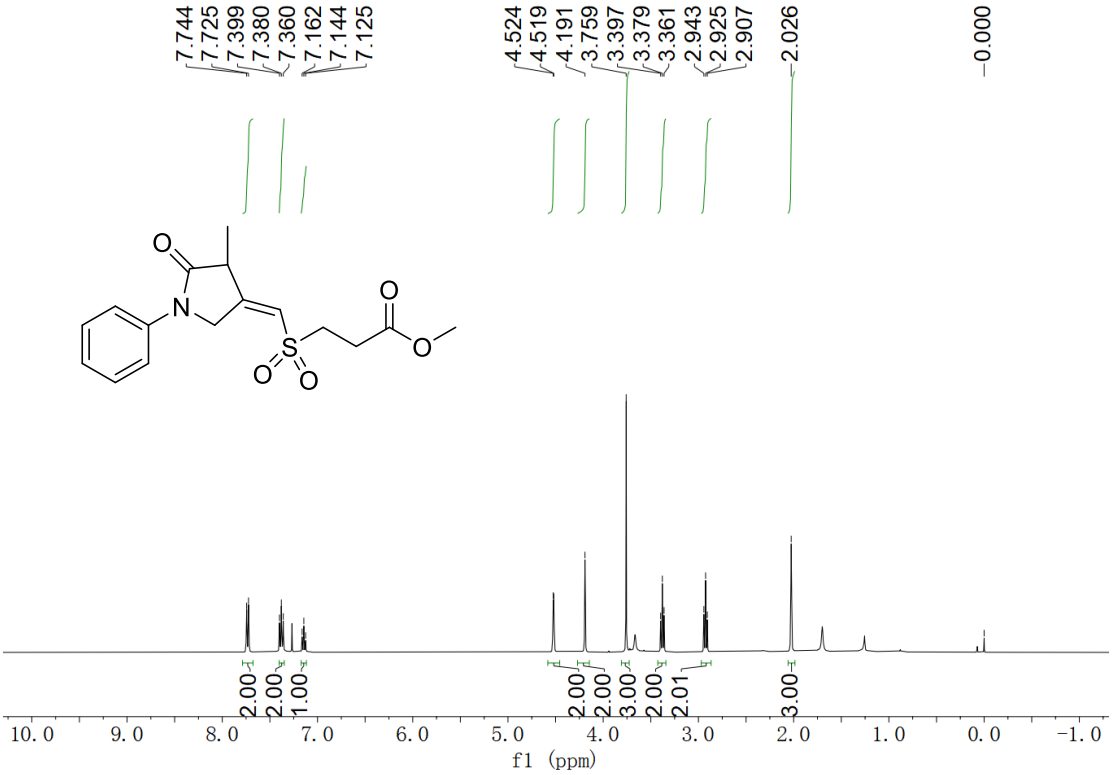


Figure S48 ^{1}H NMR (400 MHz, $CDCl_3$)

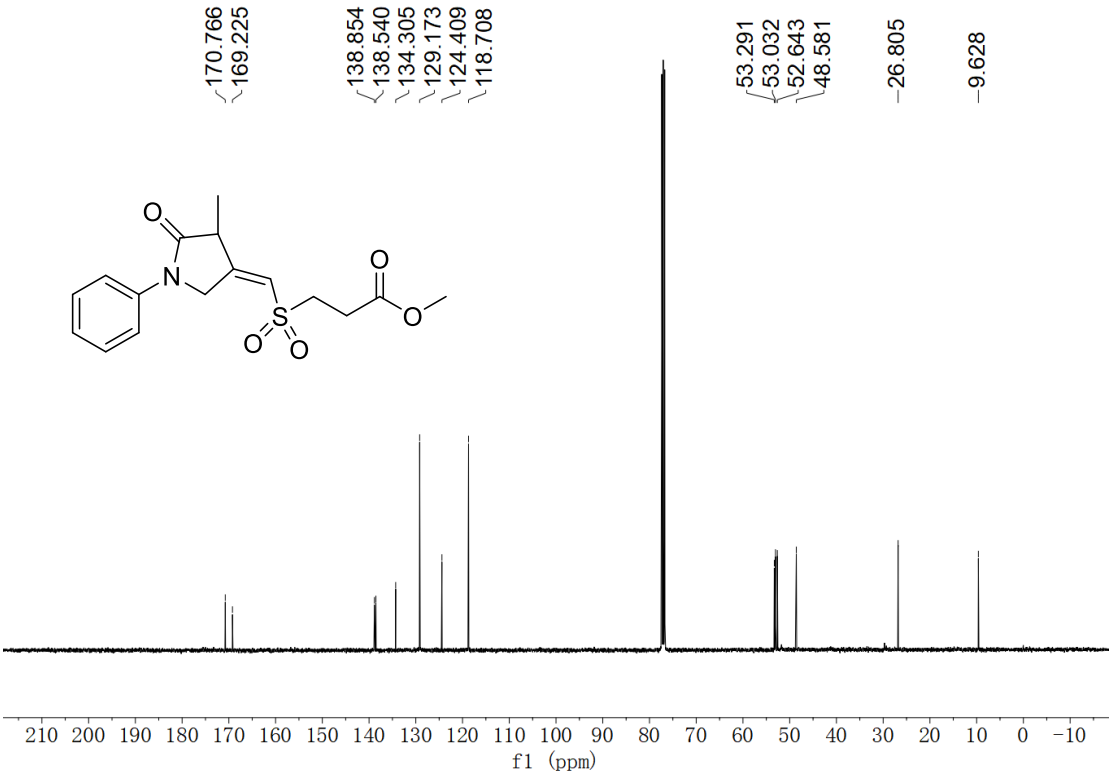


Figure S49 ^{13}C NMR (100 MHz, $CDCl_3$)

ethyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ab, Z/E = 90 : 10):

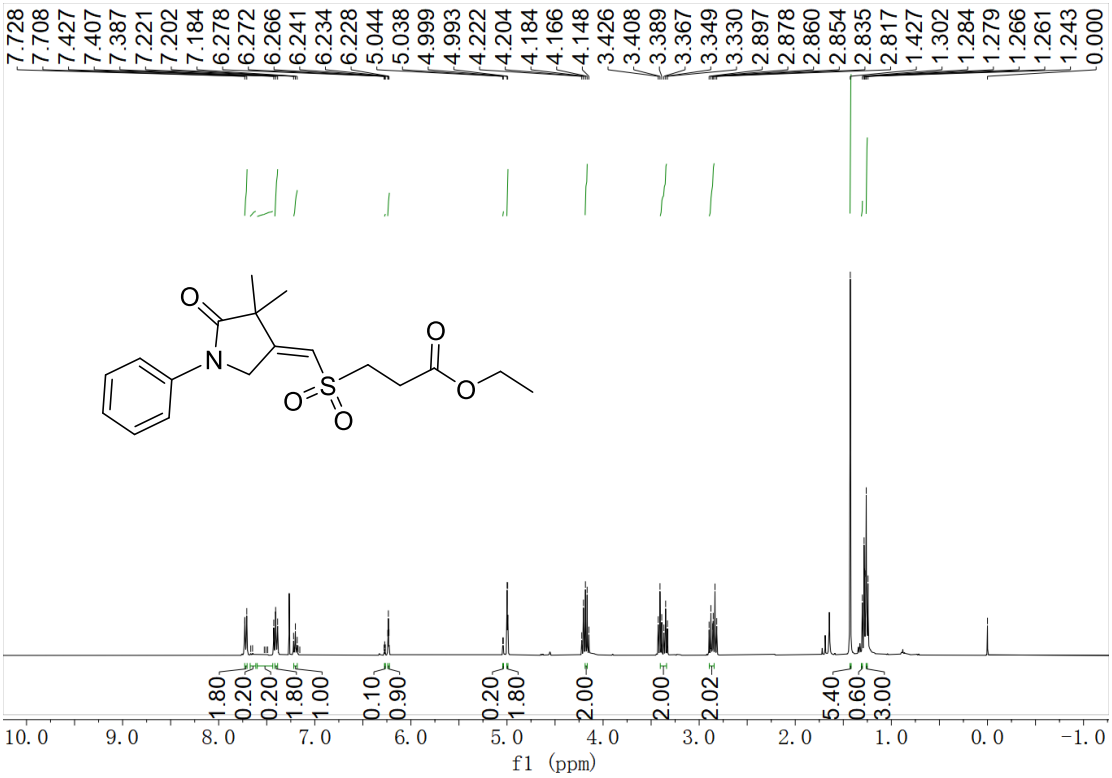


Figure S50 ^{1}H NMR (400 MHz, $CDCl_3$)

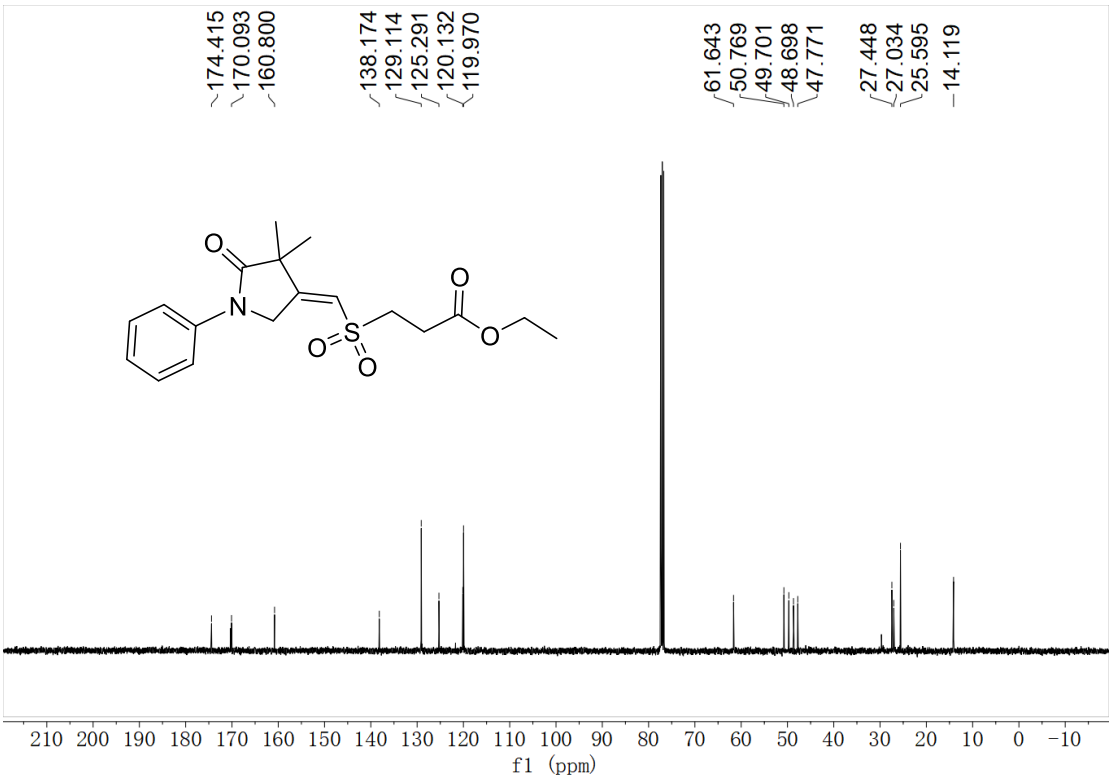


Figure S51 ^{13}C NMR (100 MHz, $CDCl_3$)

butyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3ac, Z/E = 95 : 5):

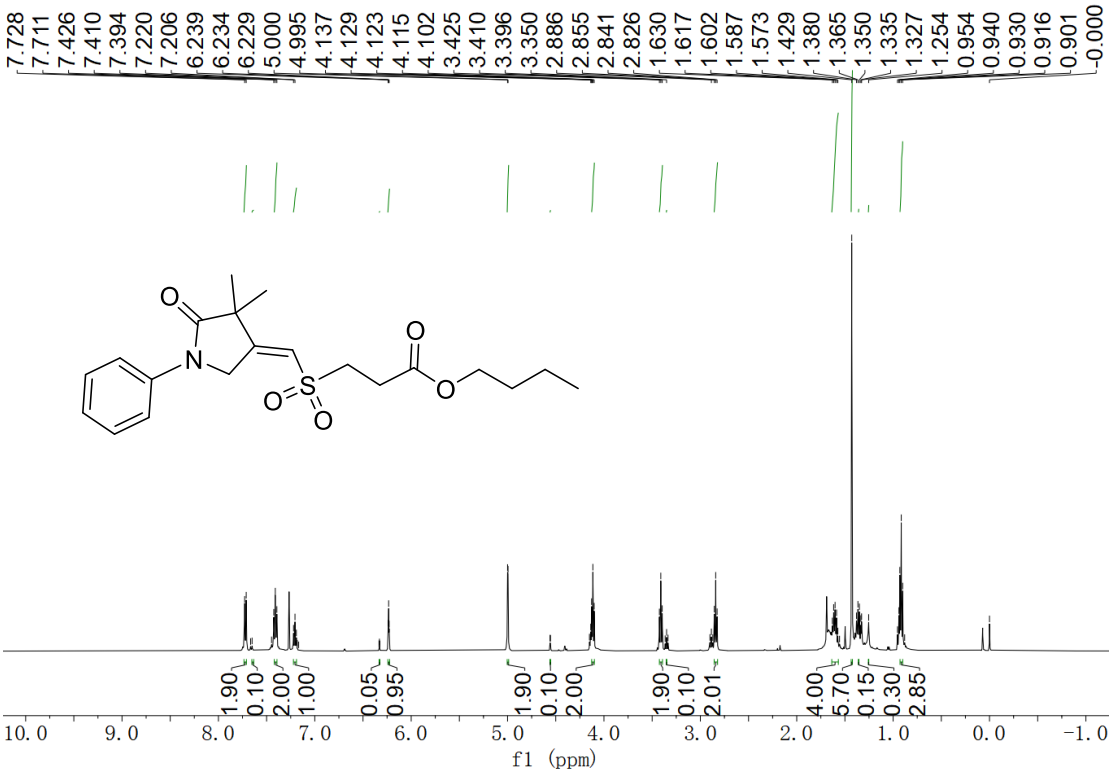


Figure S52 ^{1}H NMR (400 MHz, $CDCl_3$)

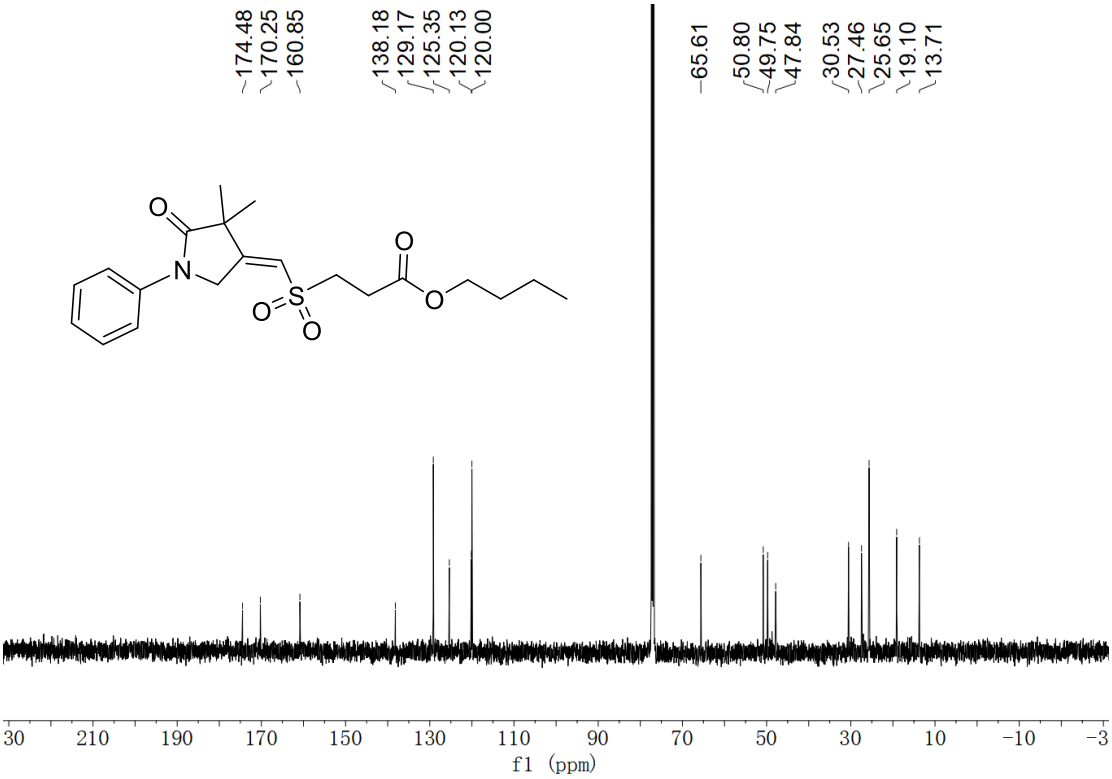


Figure S53 ^{13}C NMR (100 MHz, $CDCl_3$)

2-methoxyethyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl) propanoate(3ad, Z/E = 95 : 5):

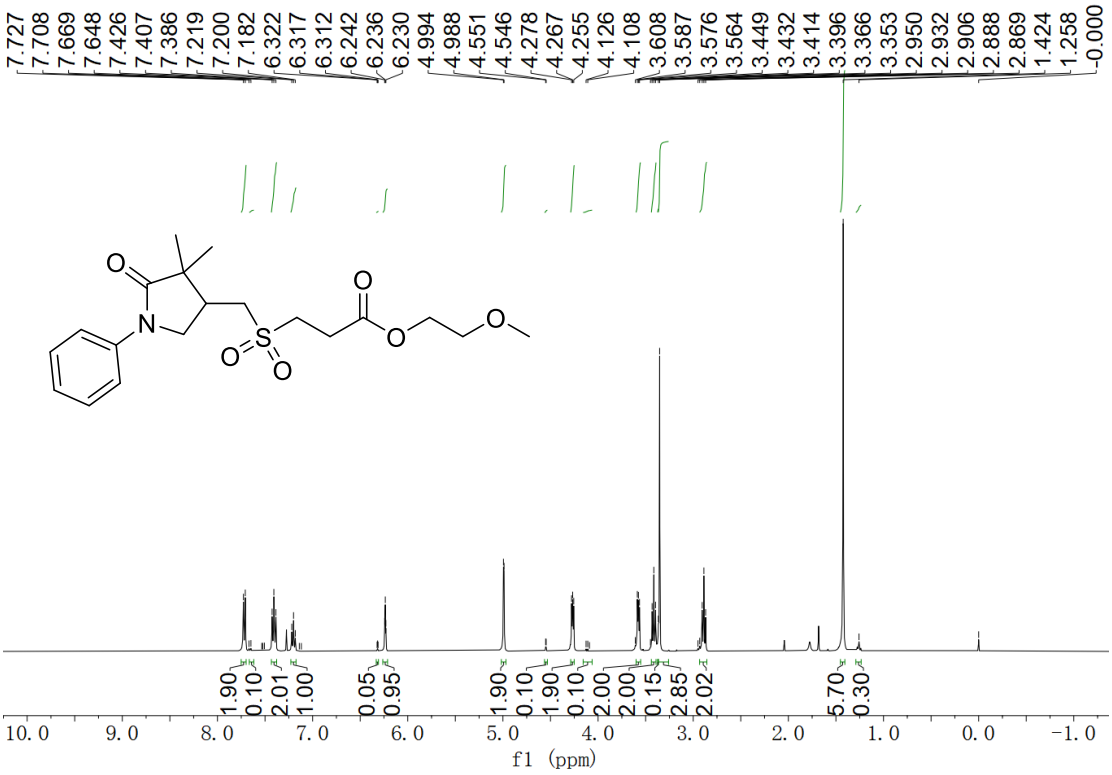


Figure S54 ^{1}H NMR (400 MHz, $CDCl_3$)

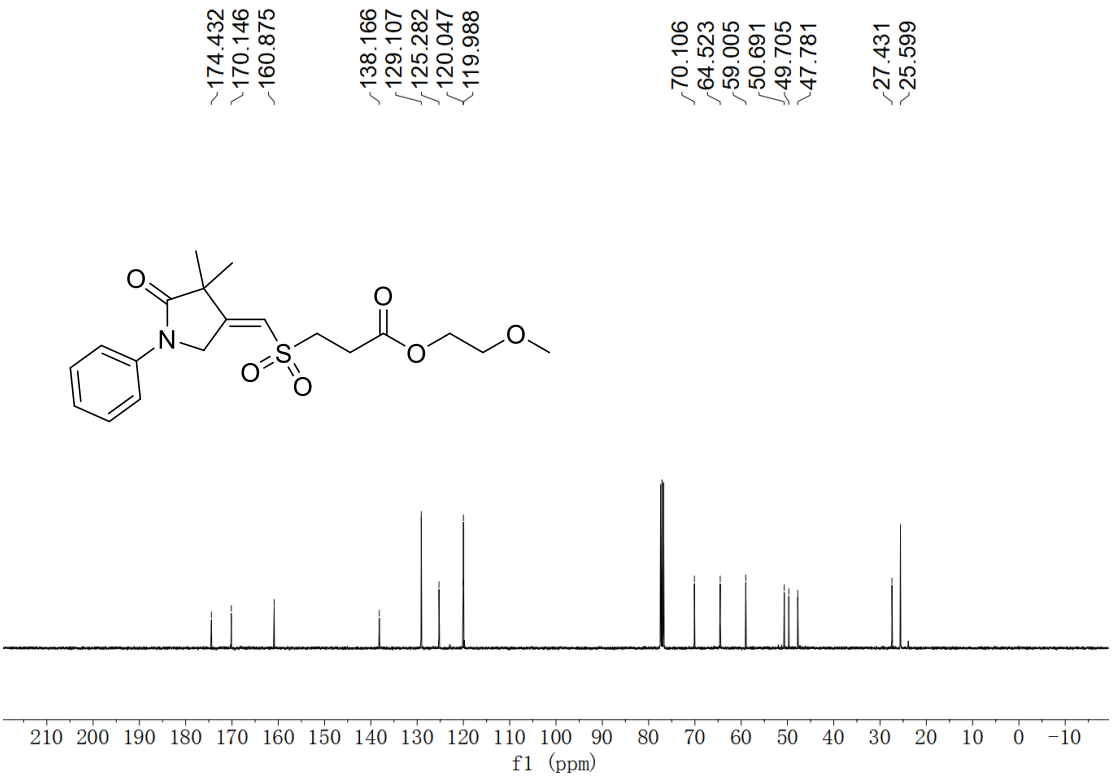


Figure S55 ^{13}C NMR (100 MHz, $CDCl_3$)

phenyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) propanoate (3ae, Z/E = 90 : 10):

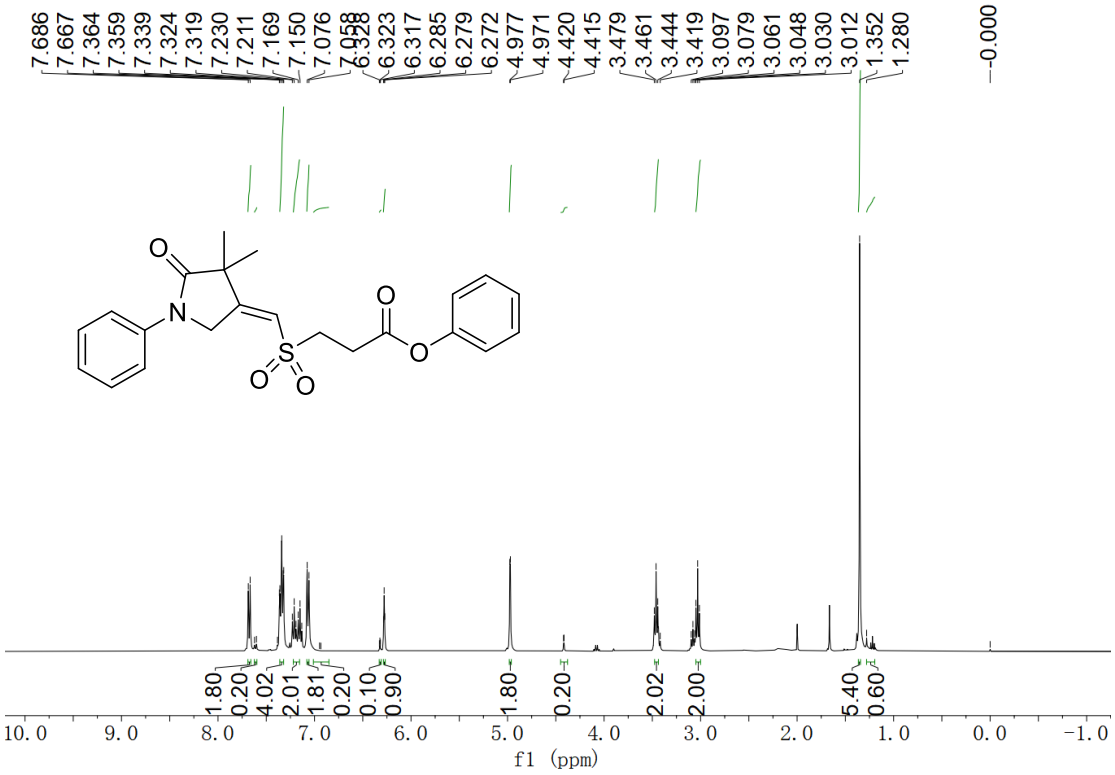


Figure S56 ^{1}H NMR (400 MHz, $CDCl_3$)

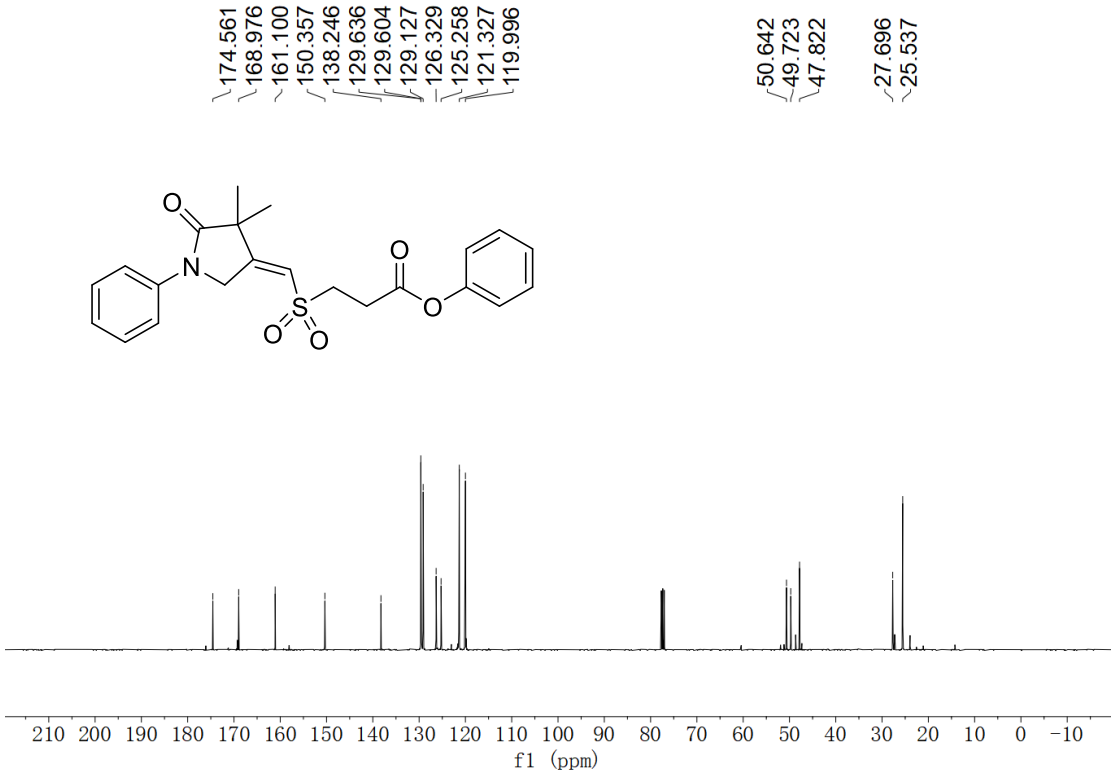


Figure S57 ^{13}C NMR (100 MHz, $CDCl_3$)

phenyl (Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) -2-methylpropanoate (3af, Z/E = 95 : 5):

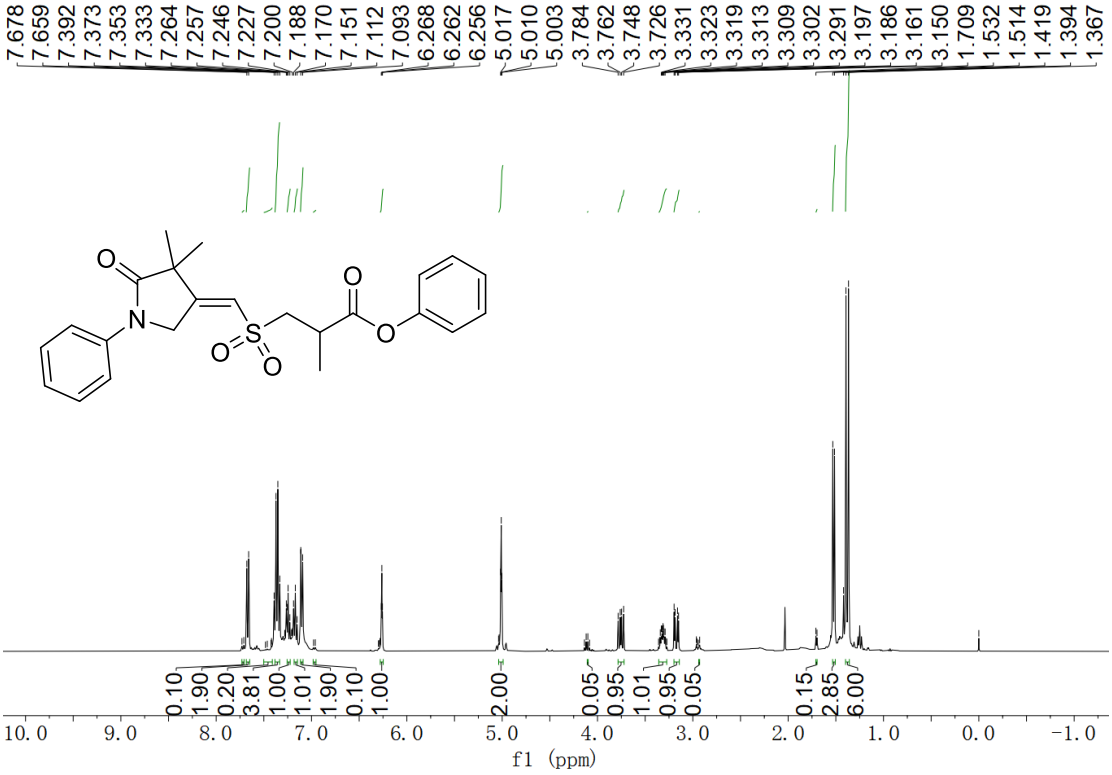


Figure S58 ^{1}H NMR (400 MHz, $CDCl_3$)

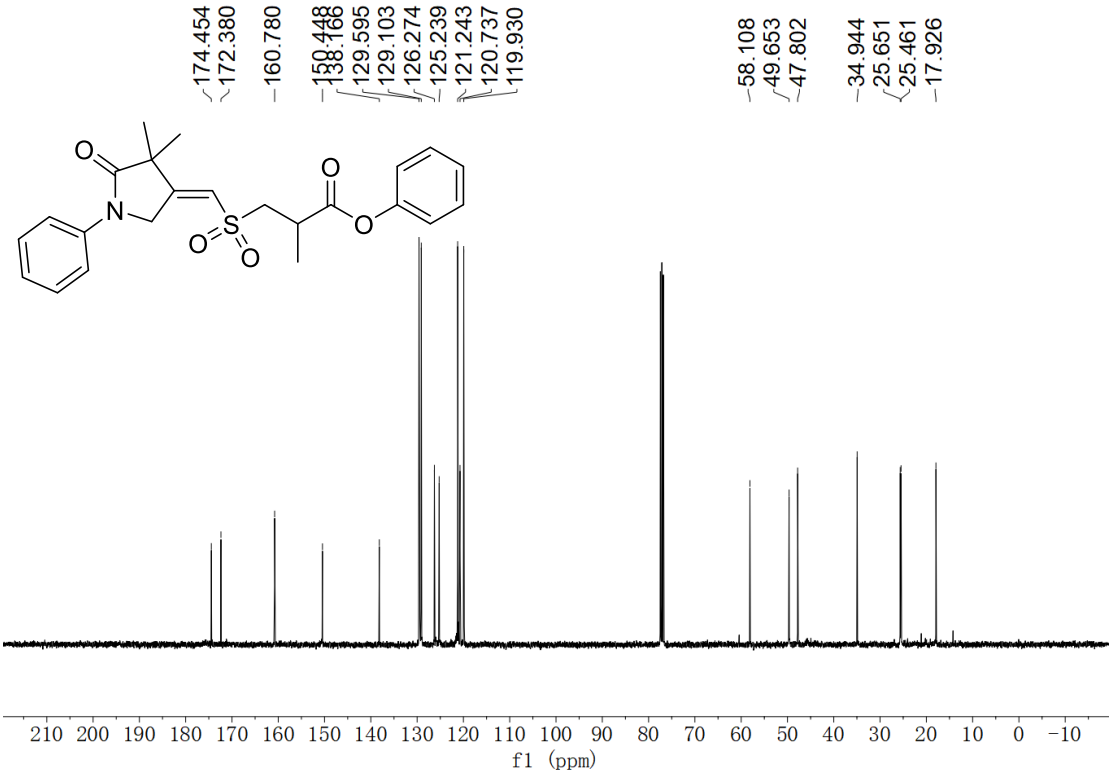


Figure S59 ^{13}C NMR (100 MHz, $CDCl_3$)

(Z)-3,3-dimethyl-1-phenyl-4-(((2-(pyridin-2-yl)ethyl)sulfonyl)methylene)pyrrolidin-2-one (3ag, Z/E = 95 : 5):

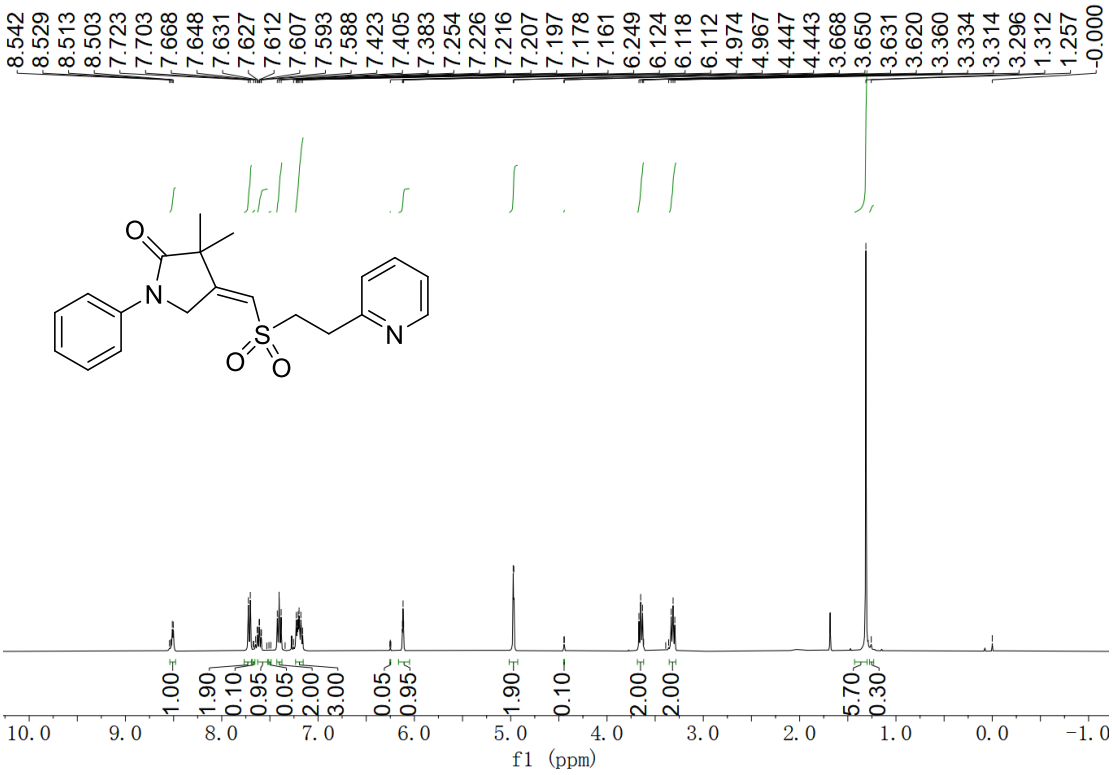


Figure S60 ^{1}H NMR (400 MHz, $CDCl_3$)

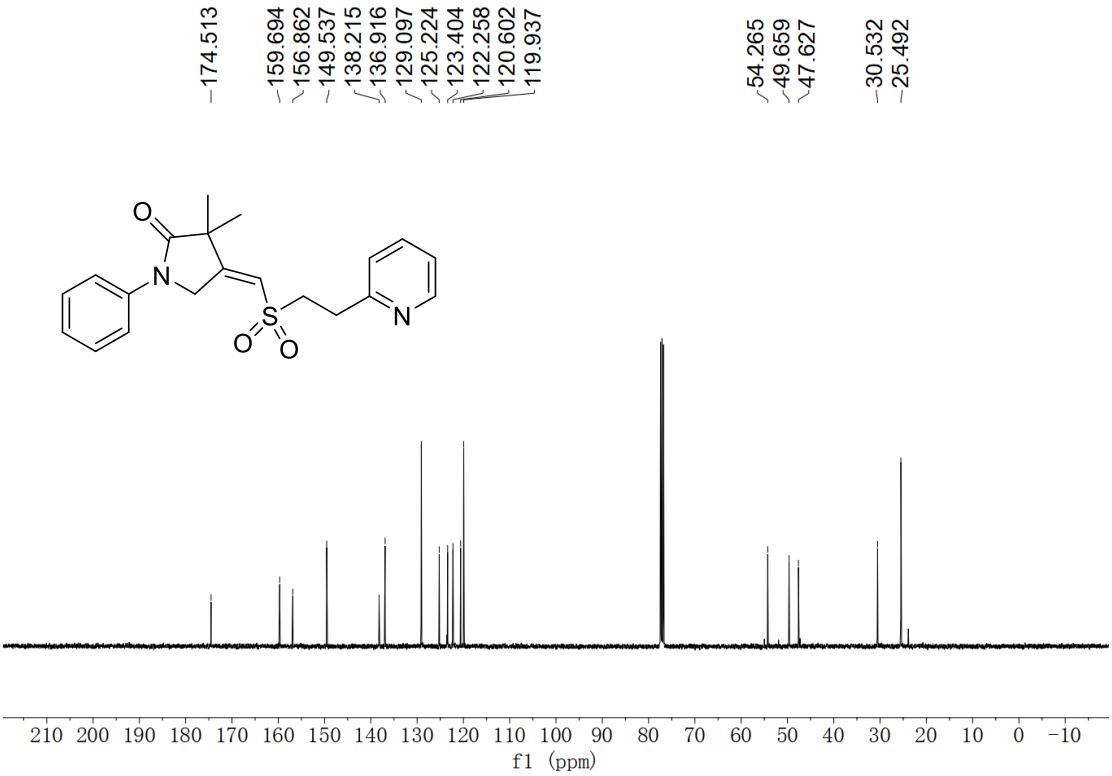


Figure S61 ^{13}C NMR (100 MHz, $CDCl_3$)

(Z)-3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)-N,N-dimethylpropanamide (3ah, Z/E > 99:1):

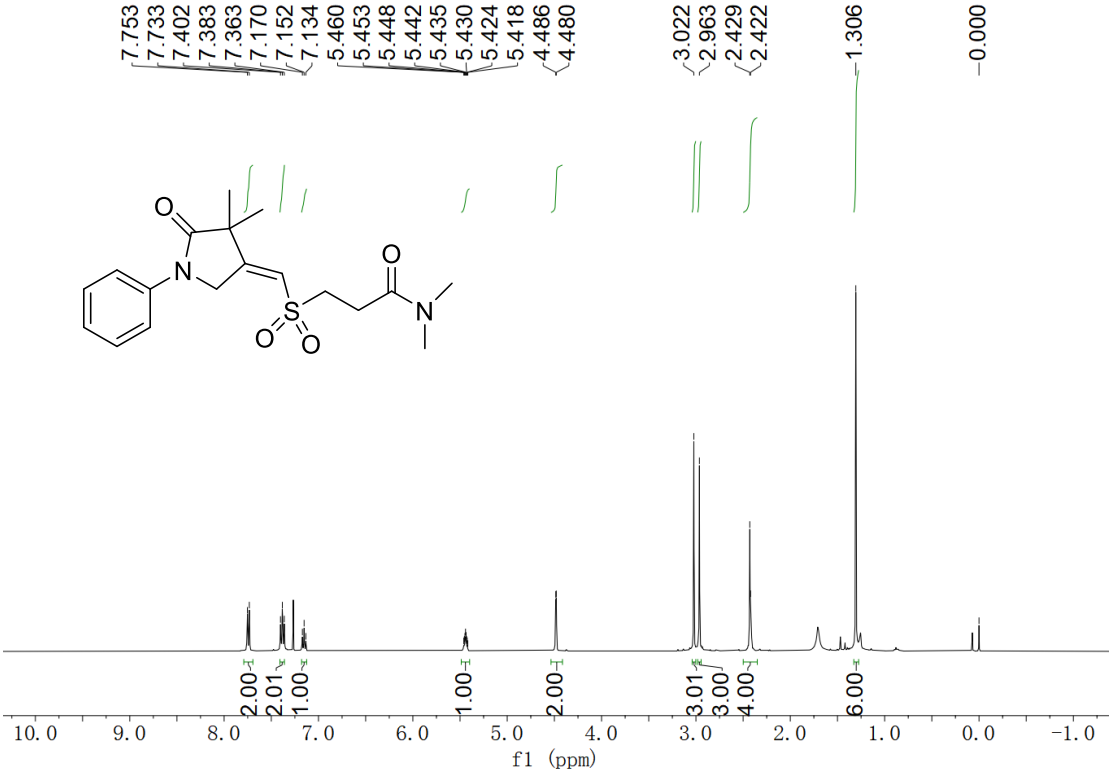


Figure S62 ^{1}H NMR (400 MHz, $CDCl_3$)

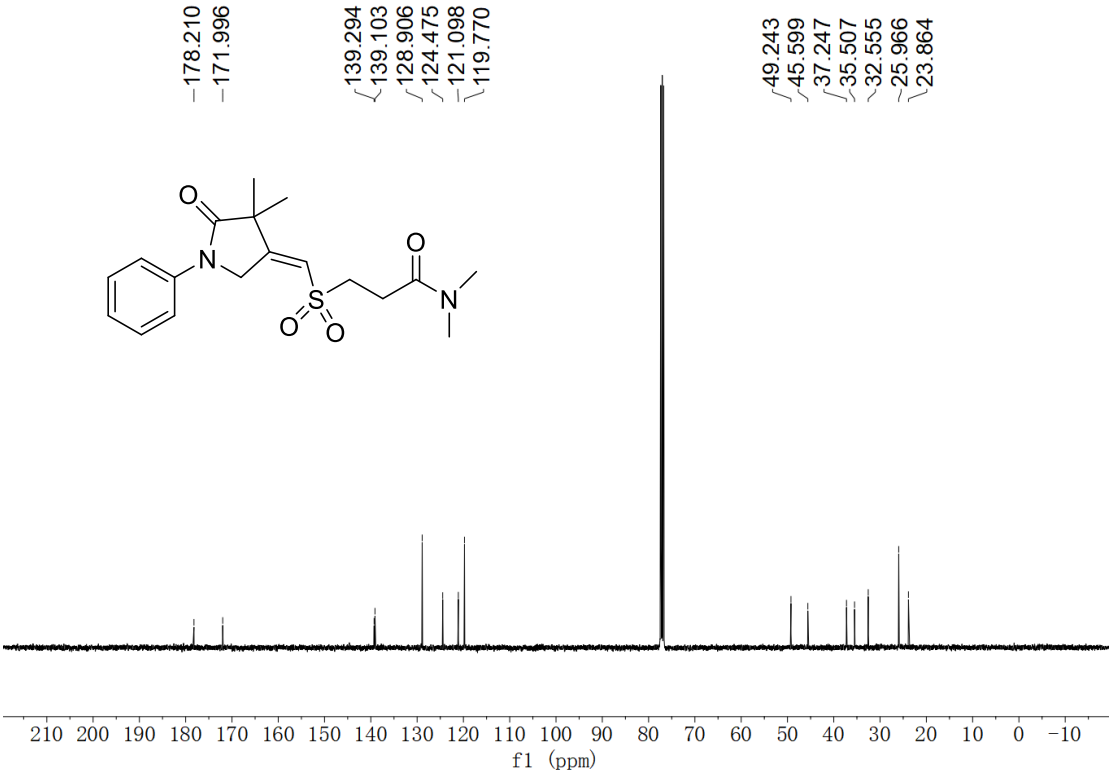


Figure S63 ^{13}C NMR (100 MHz, $CDCl_3$)

(Z)-3,3-dimethyl-1-phenyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methylene)pyrrolidin-2-one (3ai, Z/E = 92 : 8):

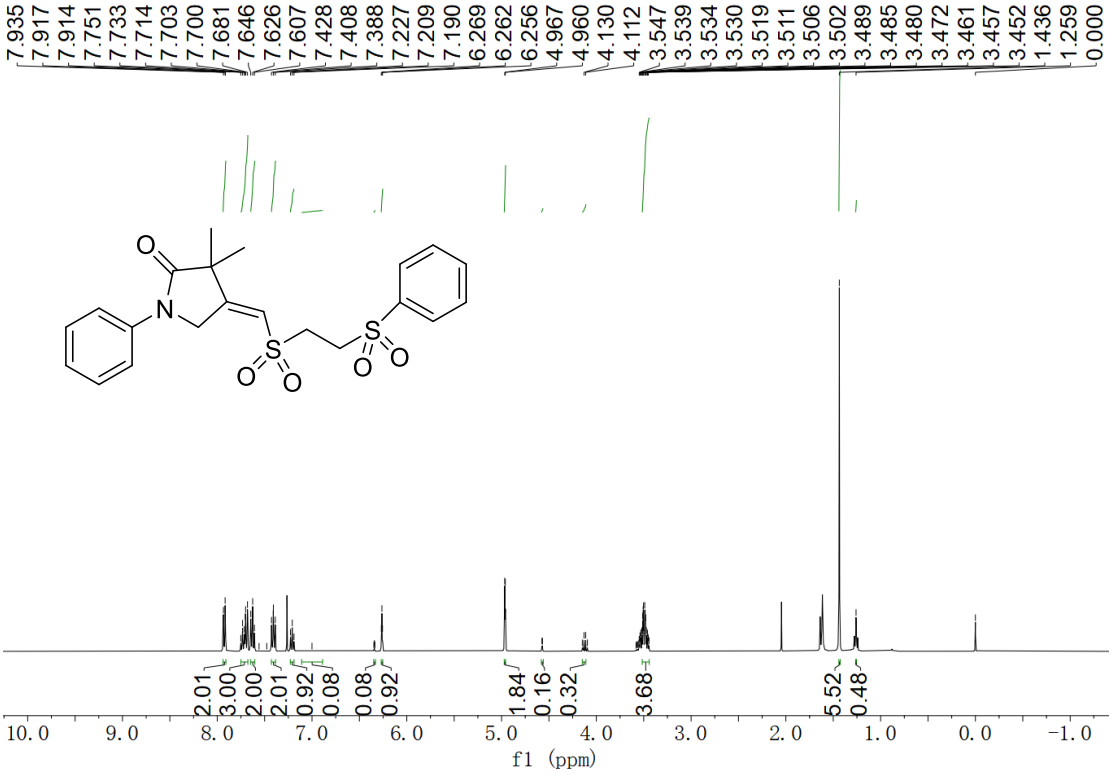


Figure S64 ^{1}H NMR (400 MHz, $CDCl_3$)

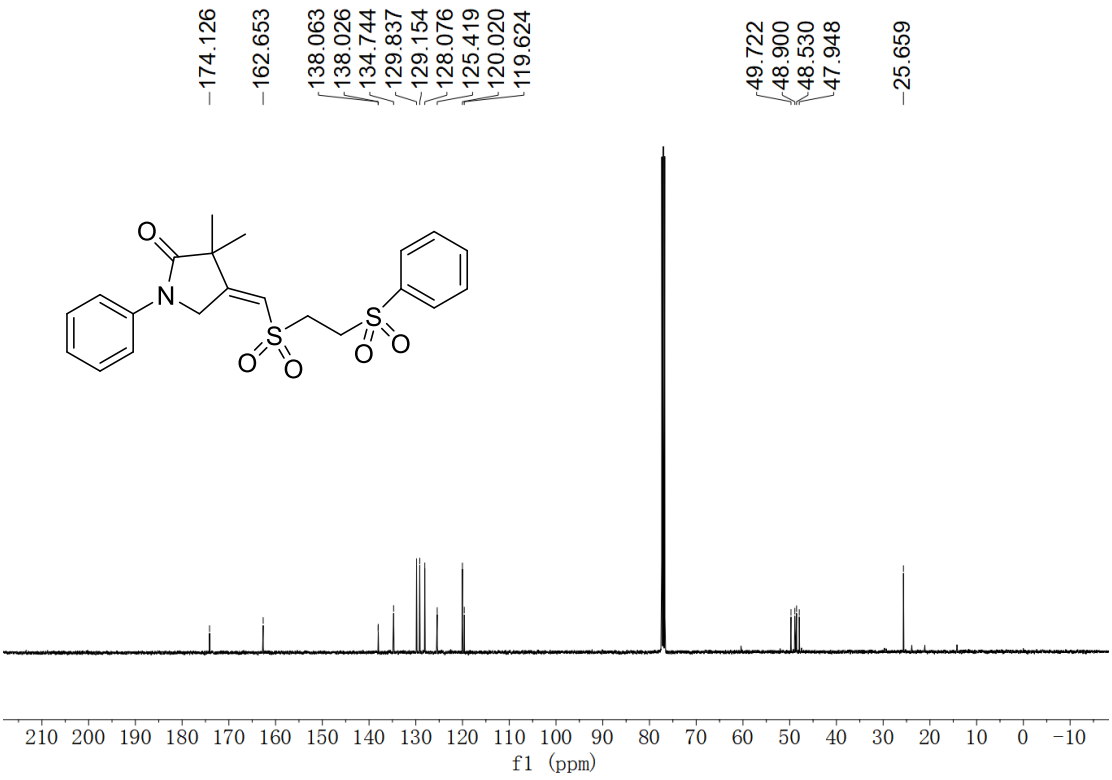


Figure S65 ^{13}C NMR (100 MHz, $CDCl_3$)

(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(((Z)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3aj, Z/E > 99 : 1):

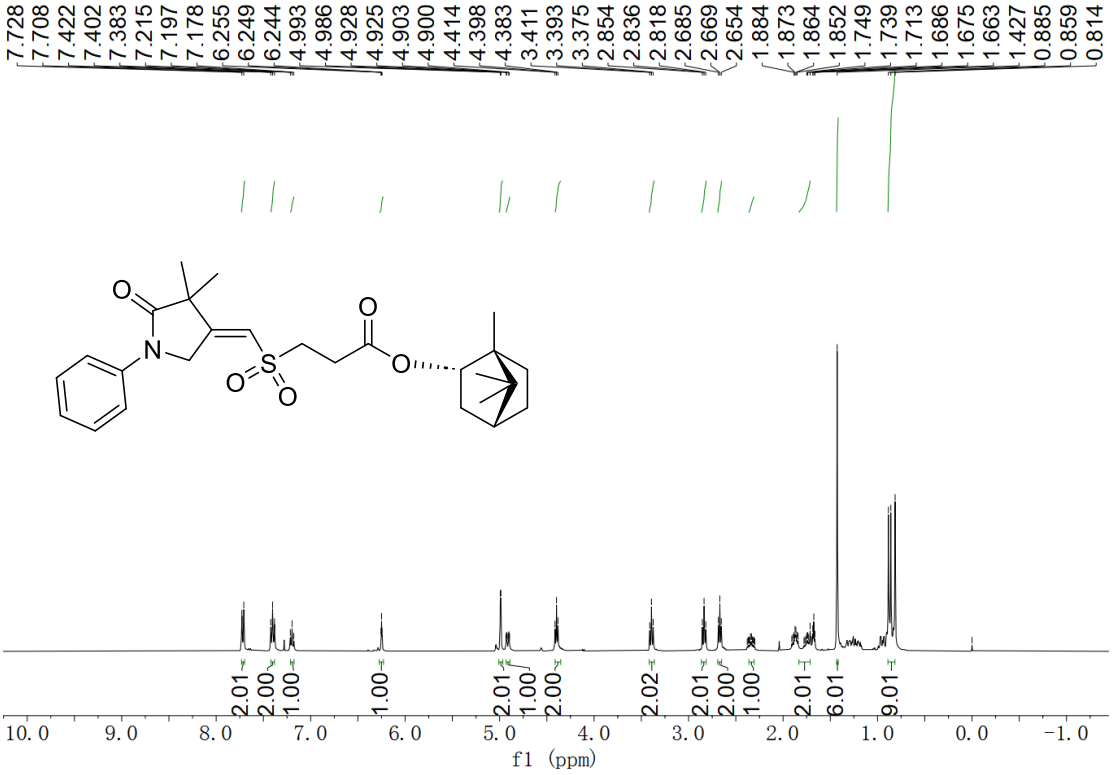


Figure S66 ^{1}H NMR (400 MHz, $CDCl_3$)

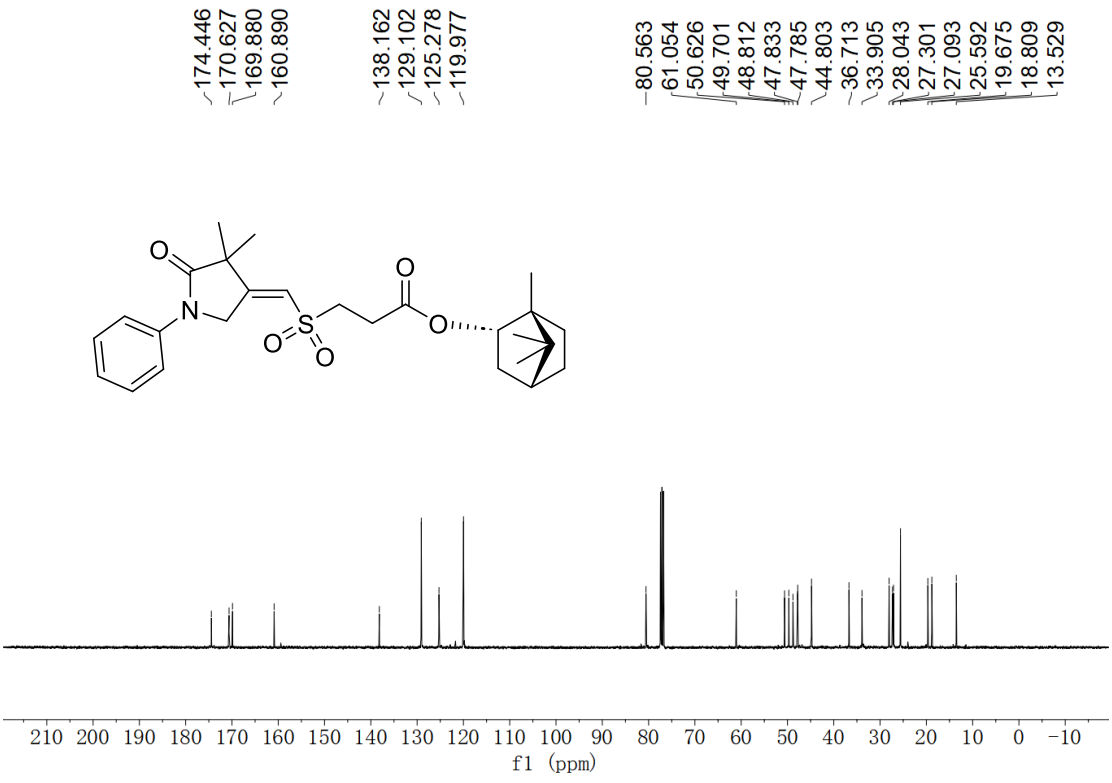


Figure S67 ^{13}C NMR (100 MHz, $CDCl_3$)

((5R)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl) methyl 3-(((E)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl) propanoate (3ak, Z/E = 97 : 3):

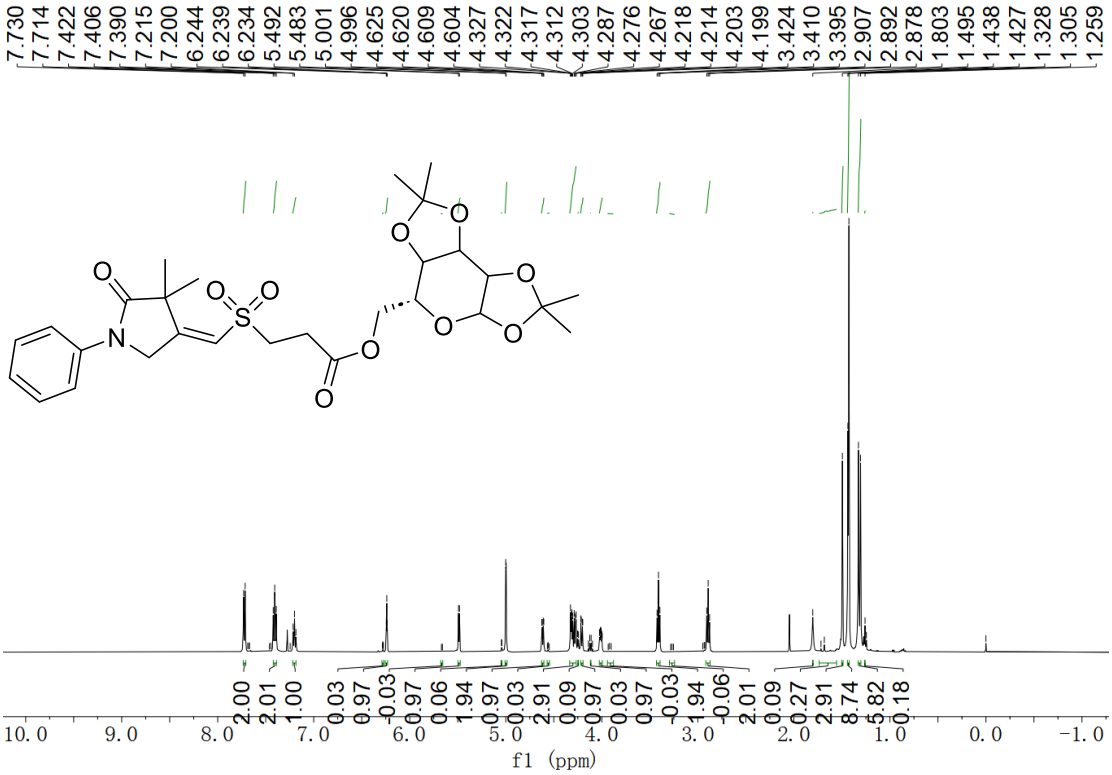


Figure S68 ^{1}H NMR (400 MHz, $CDCl_3$)

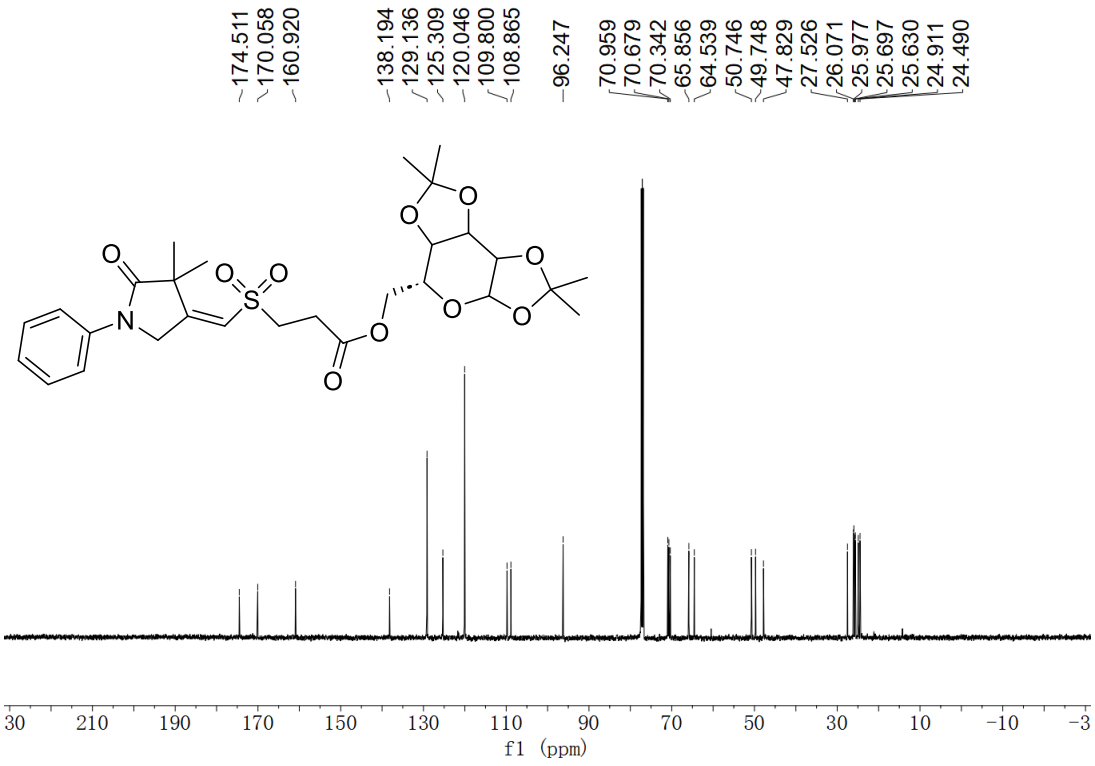


Figure S69 ^{13}C NMR (100 MHz, $CDCl_3$)

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3-(((Z)-(4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-ylidene)methyl)sulfonyl)propanoate (3al, Z/E = 90 : 10):

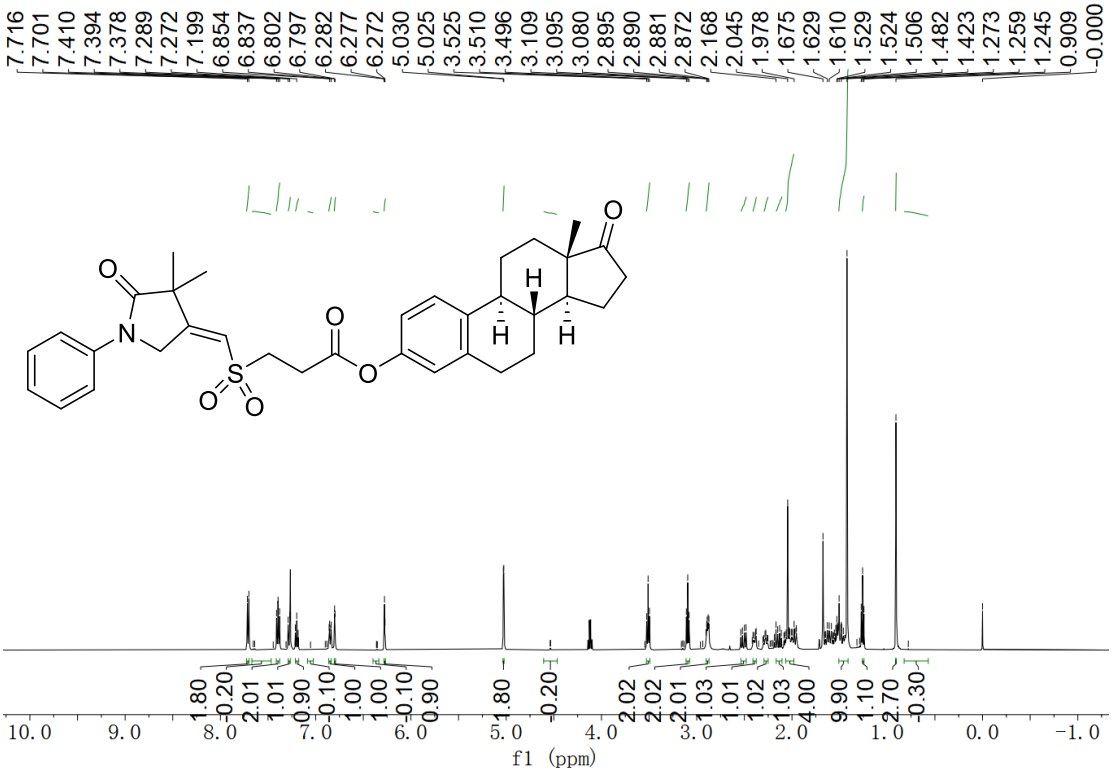


Figure S70 ^{1}H NMR (400 MHz, $CDCl_3$)

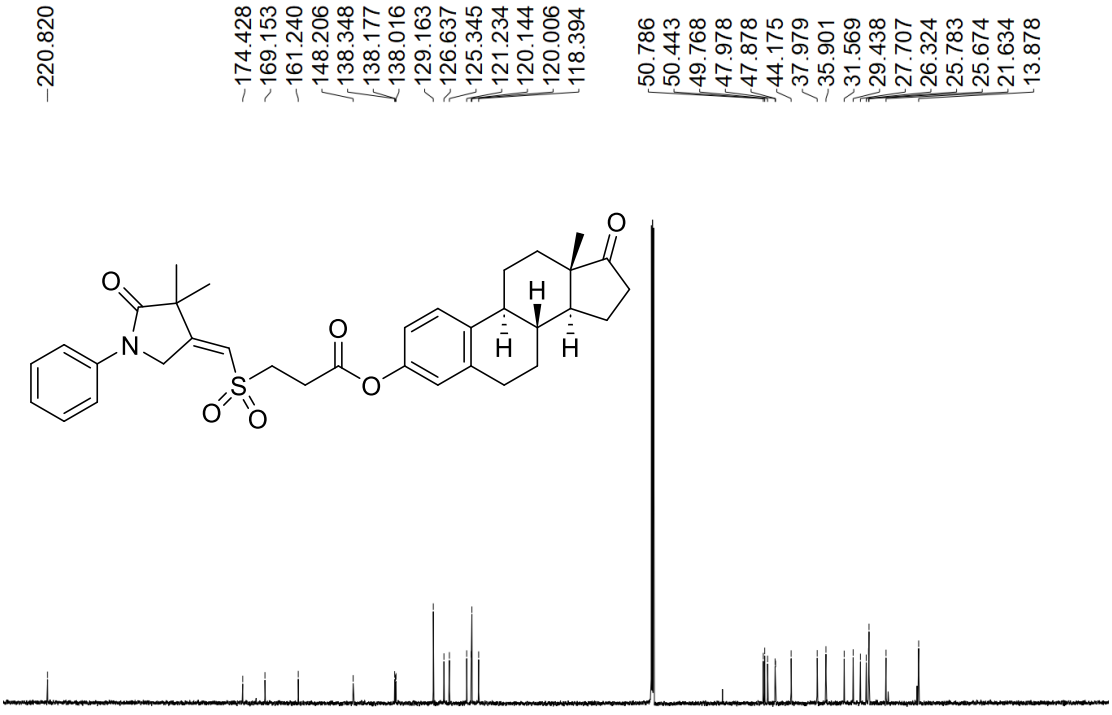


Figure S71 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5aa):

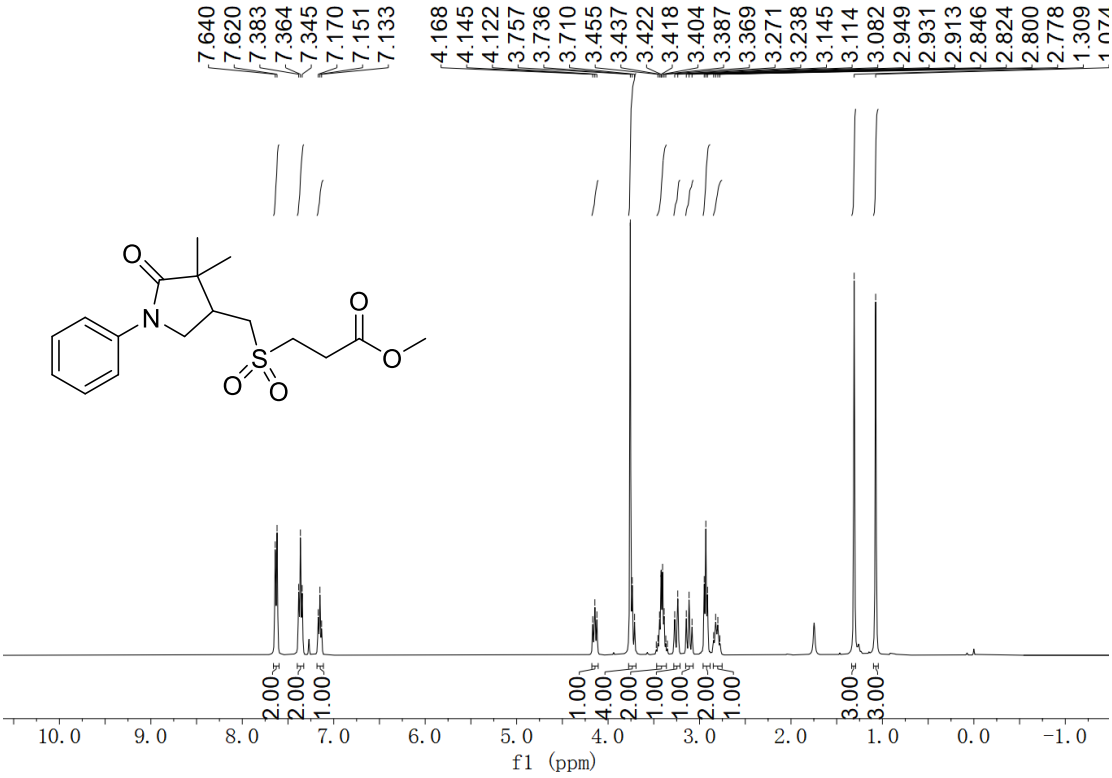


Figure S72 ^{1}H NMR (400 MHz, $CDCl_3$)

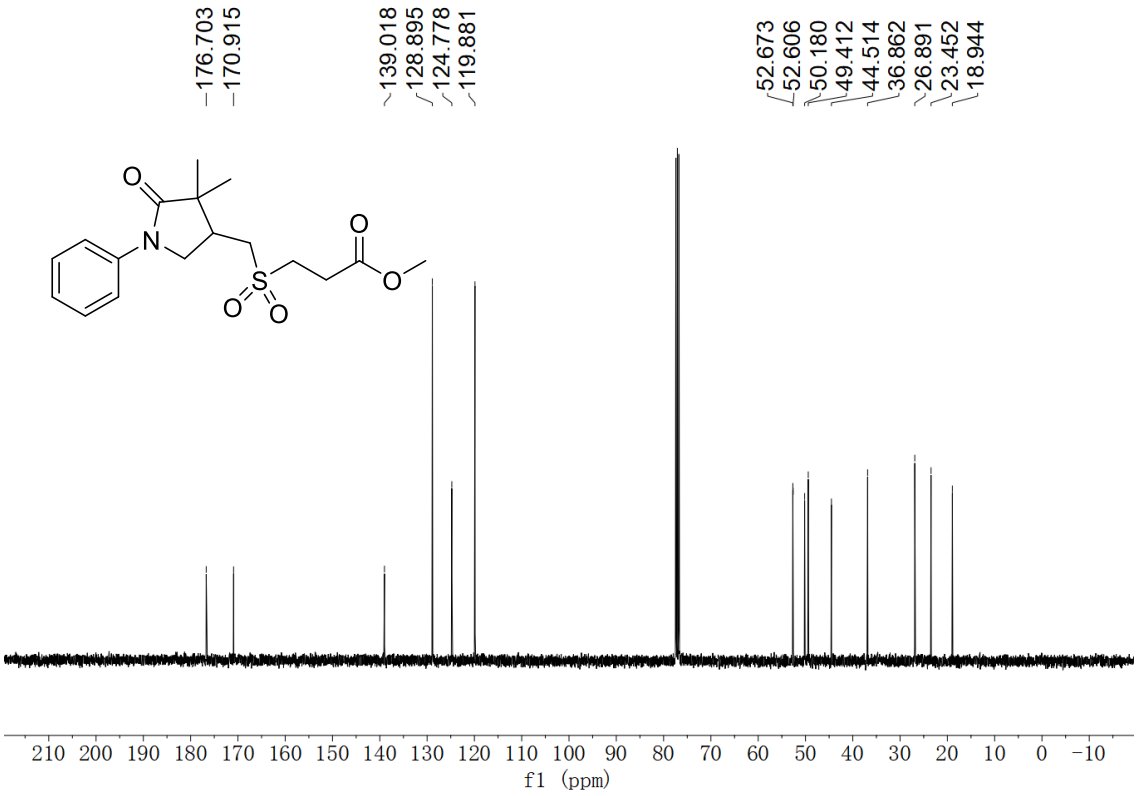


Figure S73 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-5-oxo-1-(p-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ba):

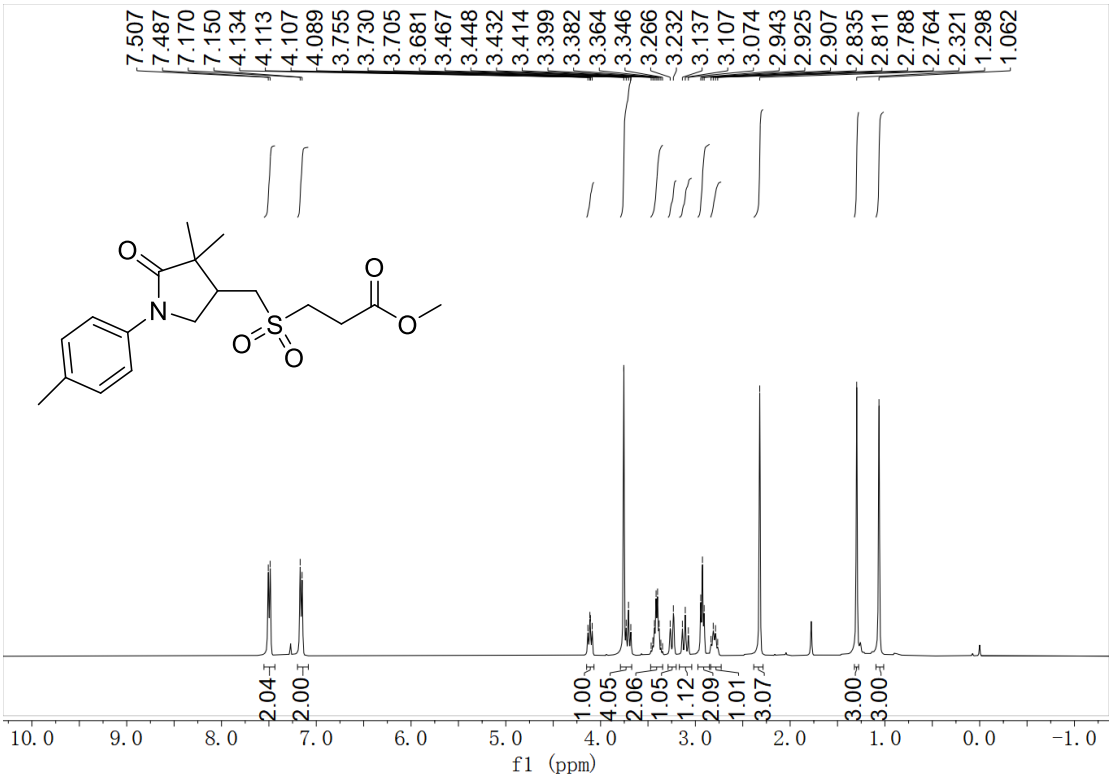


Figure S74 ^{1}H NMR (400 MHz, $CDCl_3$)

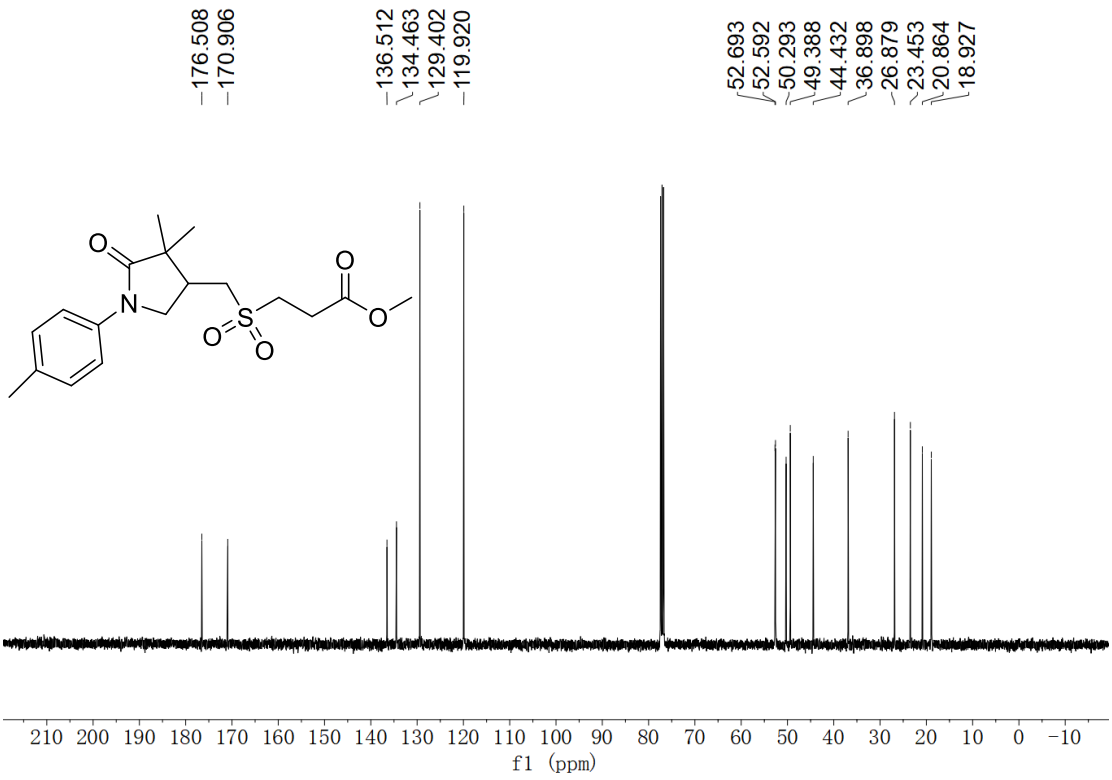


Figure S75 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(4-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ca):

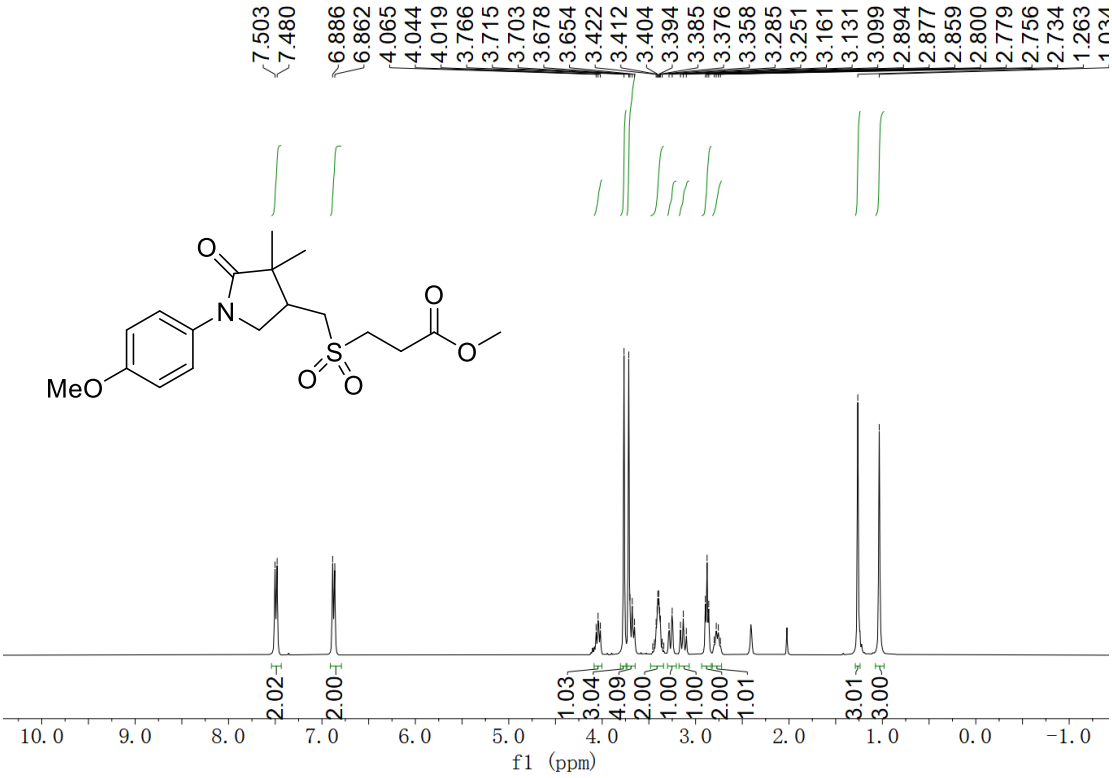


Figure S76 ^{1}H NMR (400 MHz, $CDCl_3$)

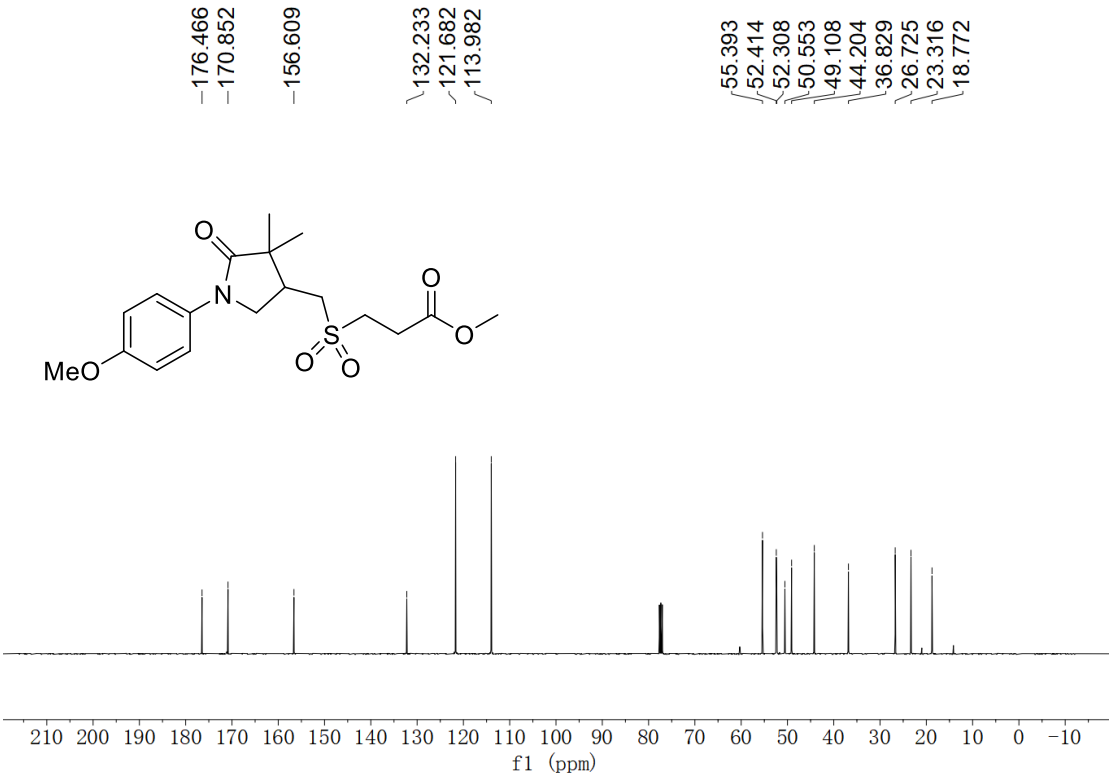


Figure S77 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(4-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl) propanoate (5da):

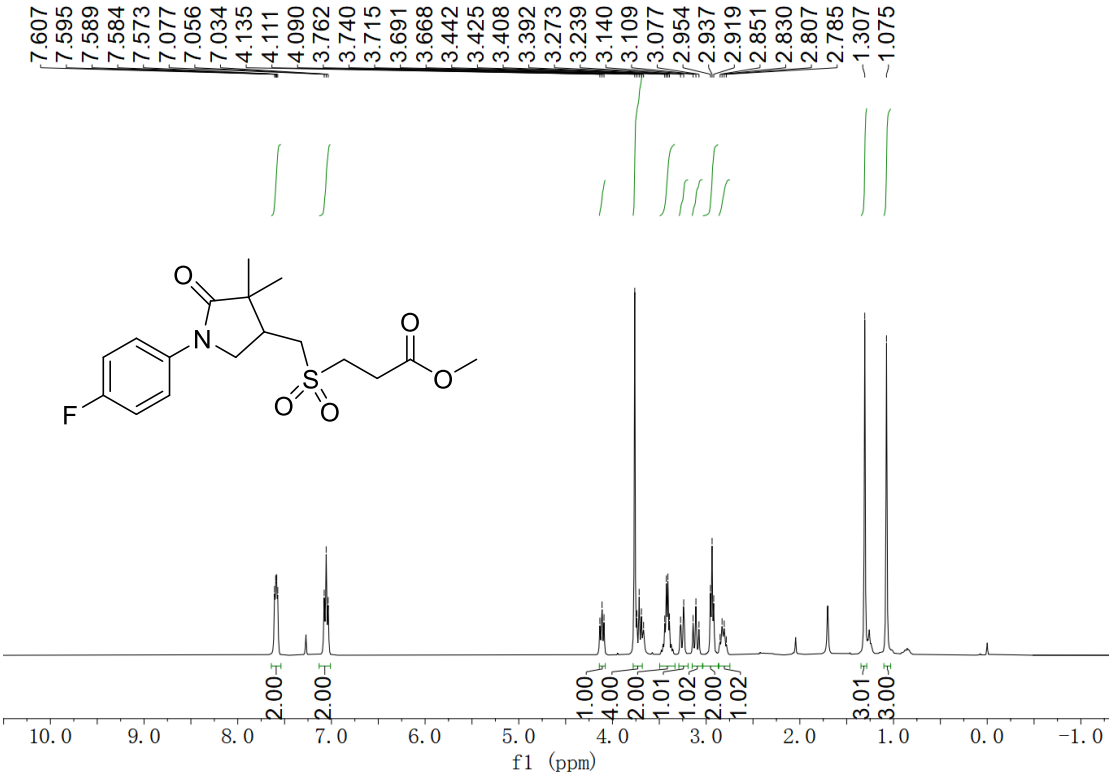


Figure S78 ^{1}H NMR (400 MHz, $CDCl_3$)

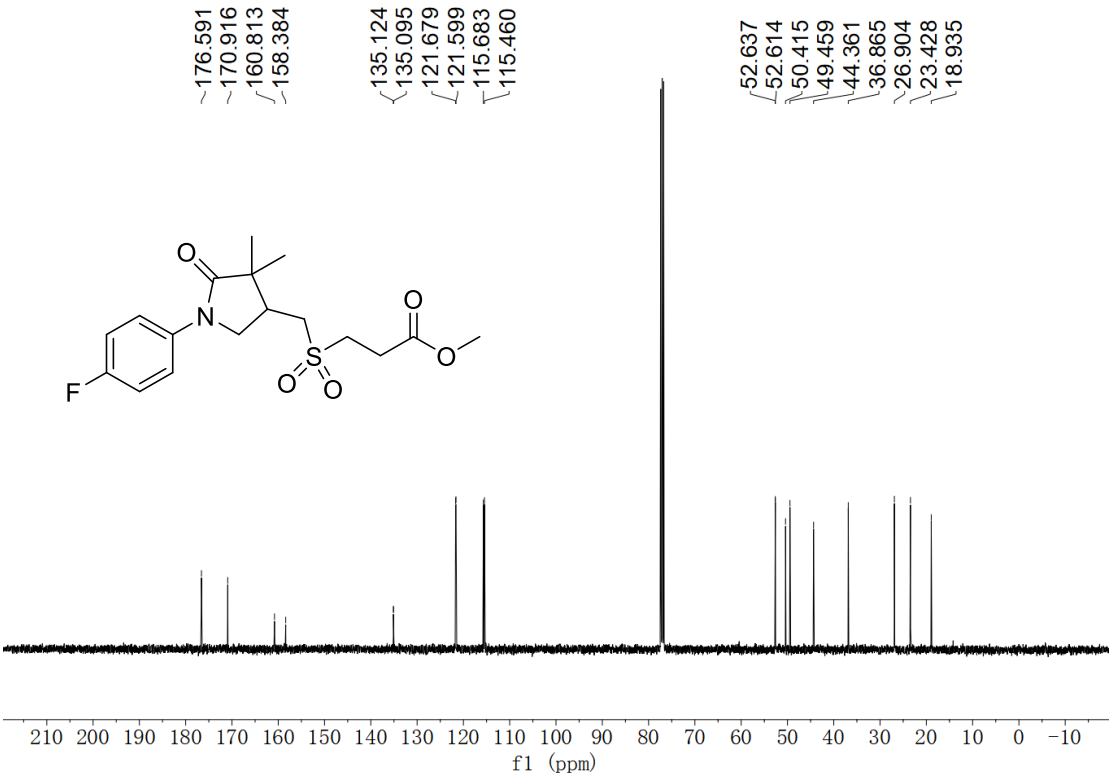


Figure S79 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(4-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ea):

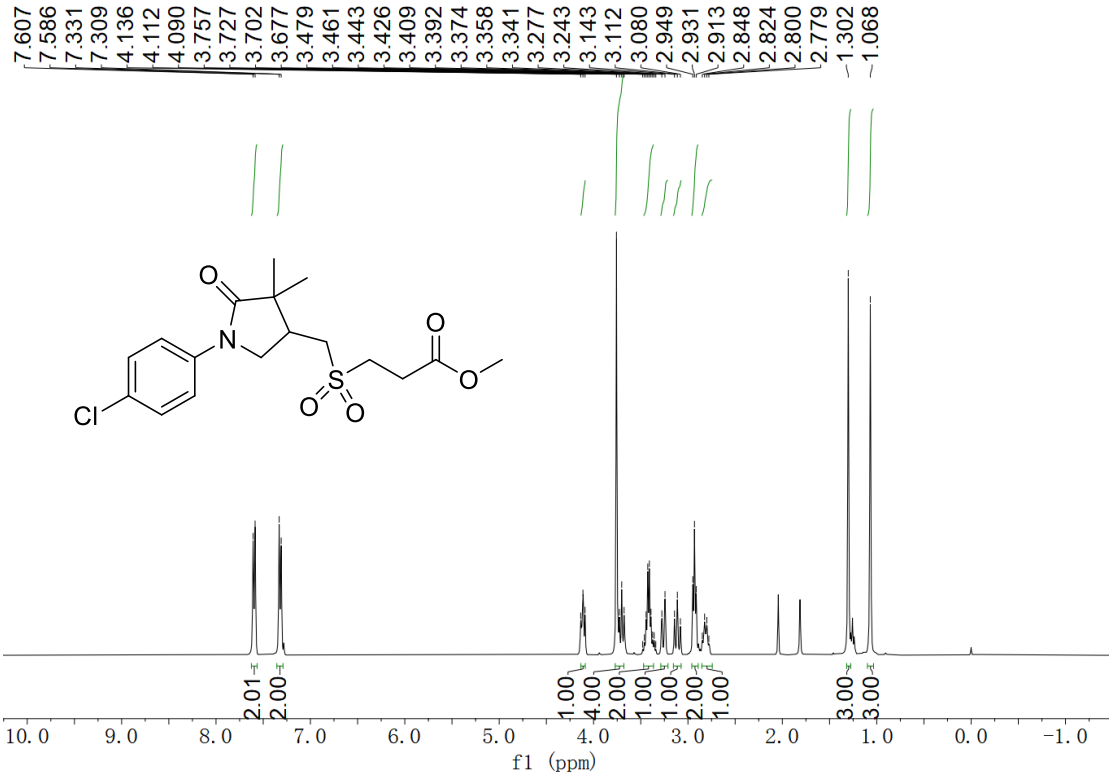


Figure S80 ^{1}H NMR (400 MHz, $CDCl_3$)

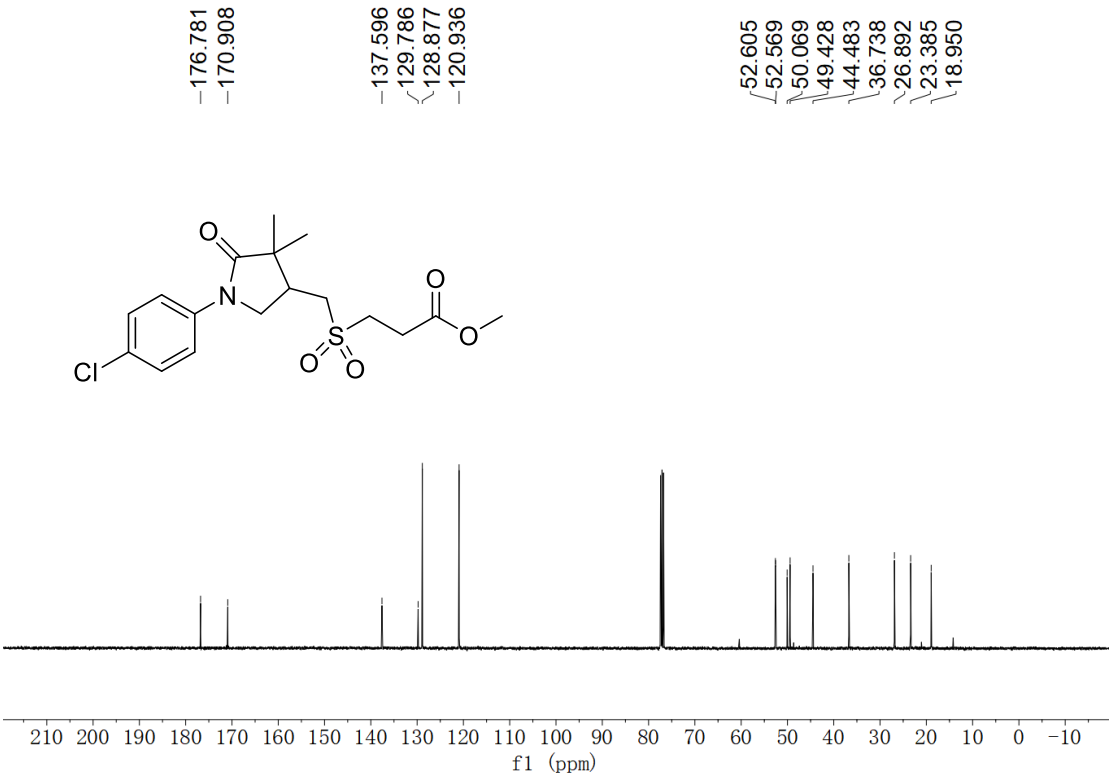


Figure S81 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(4-bromophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5fa):

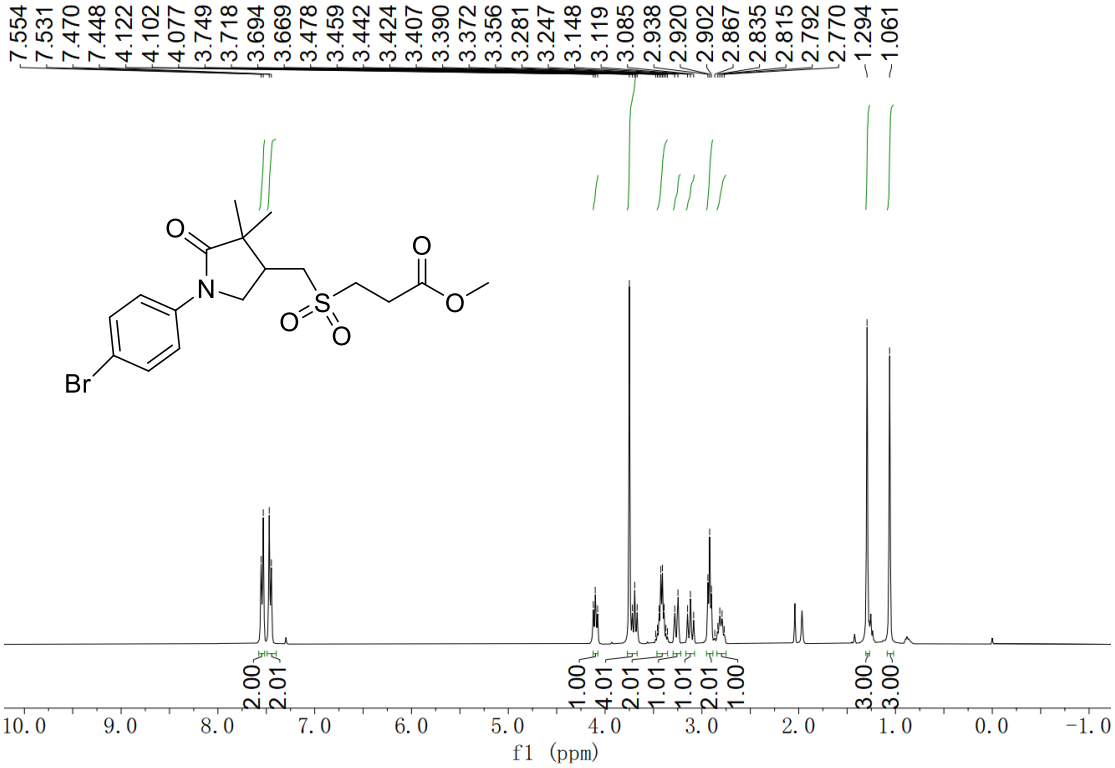


Figure S82 ^{1}H NMR (400 MHz, $CDCl_3$)

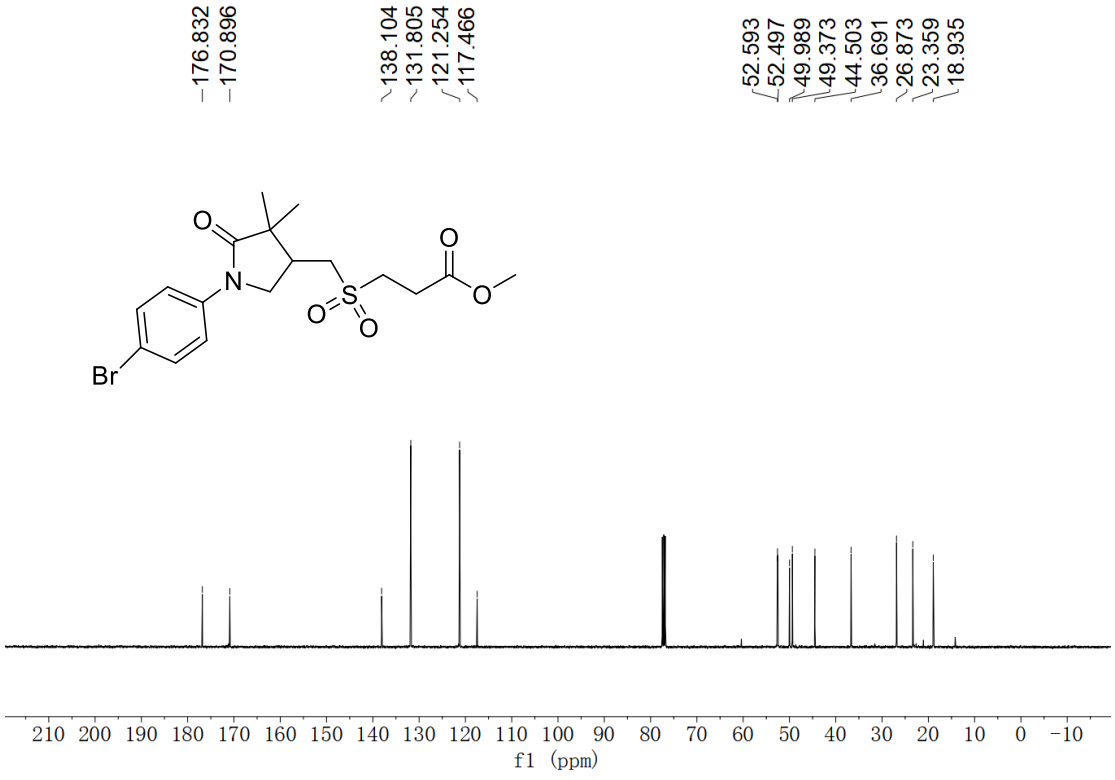


Figure S83 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-5-oxo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ga):

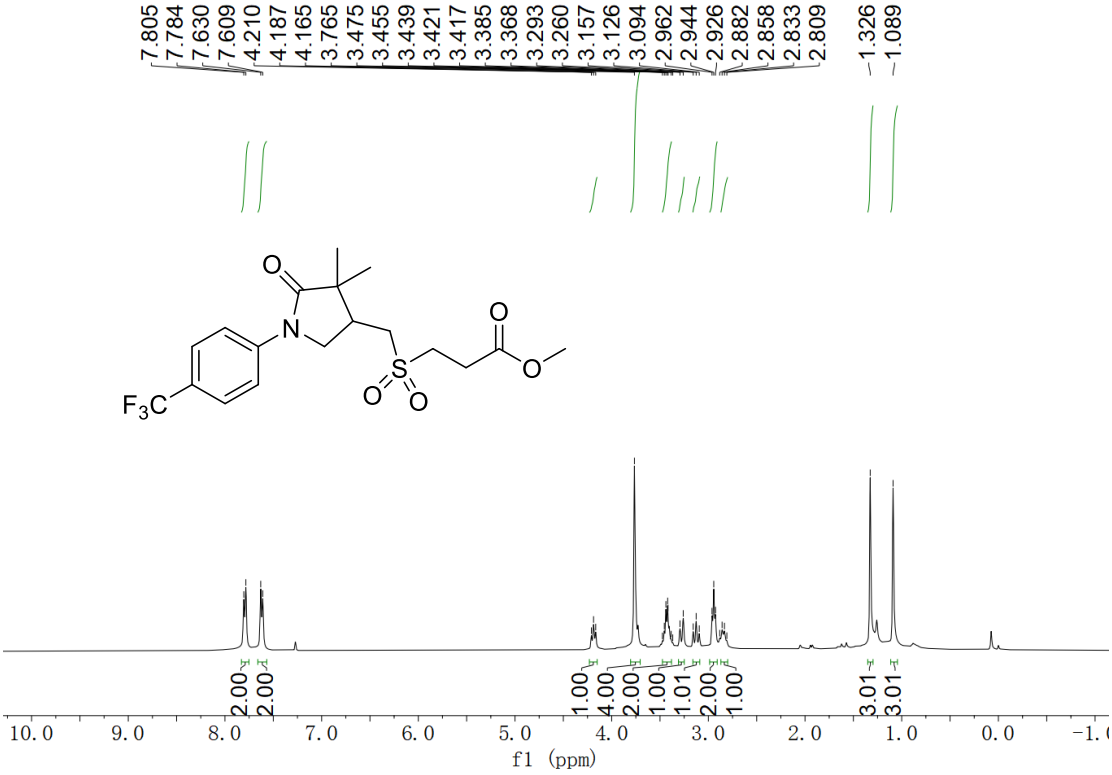


Figure S84 ^{1}H NMR (400 MHz, $CDCl_3$)

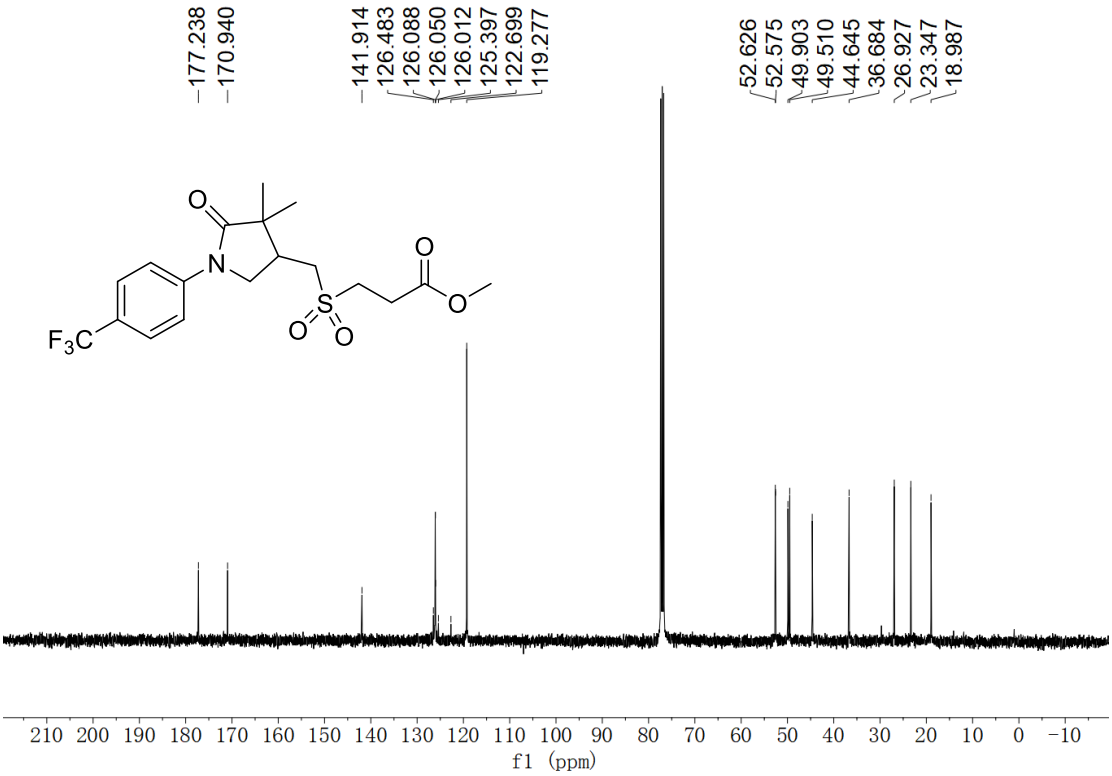


Figure S85 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-5-oxo-1-(o-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ha):

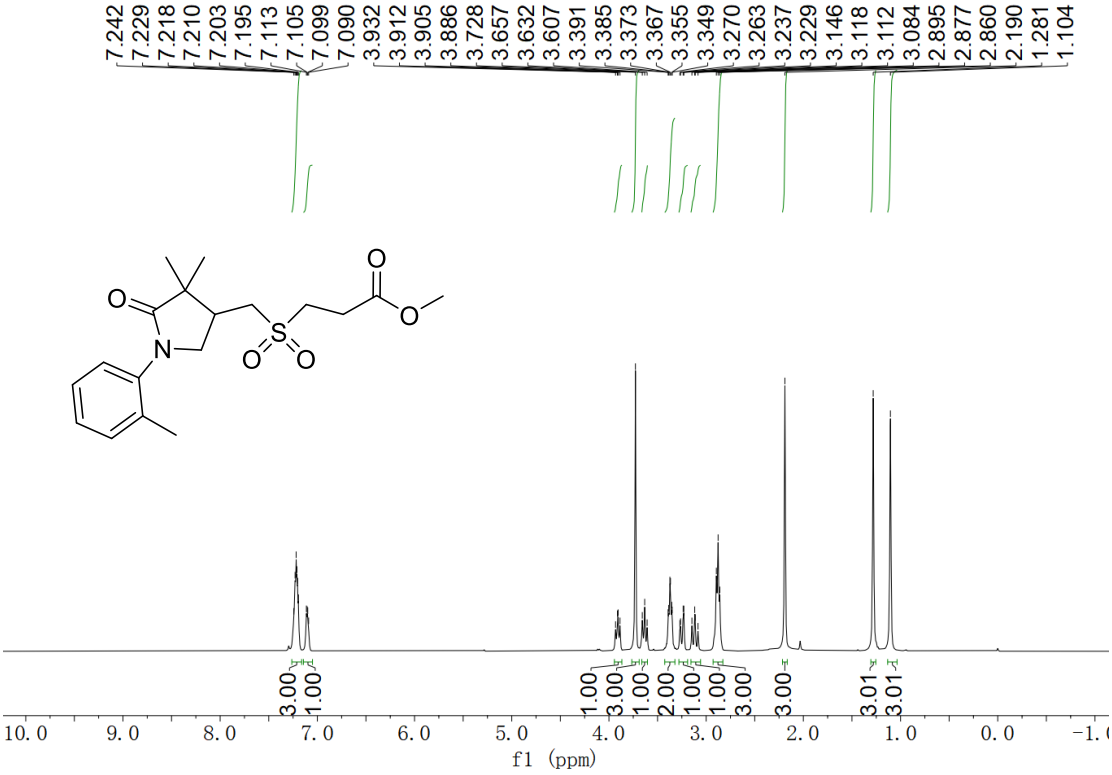


Figure S86 ^{1}H NMR (400 MHz, $CDCl_3$)

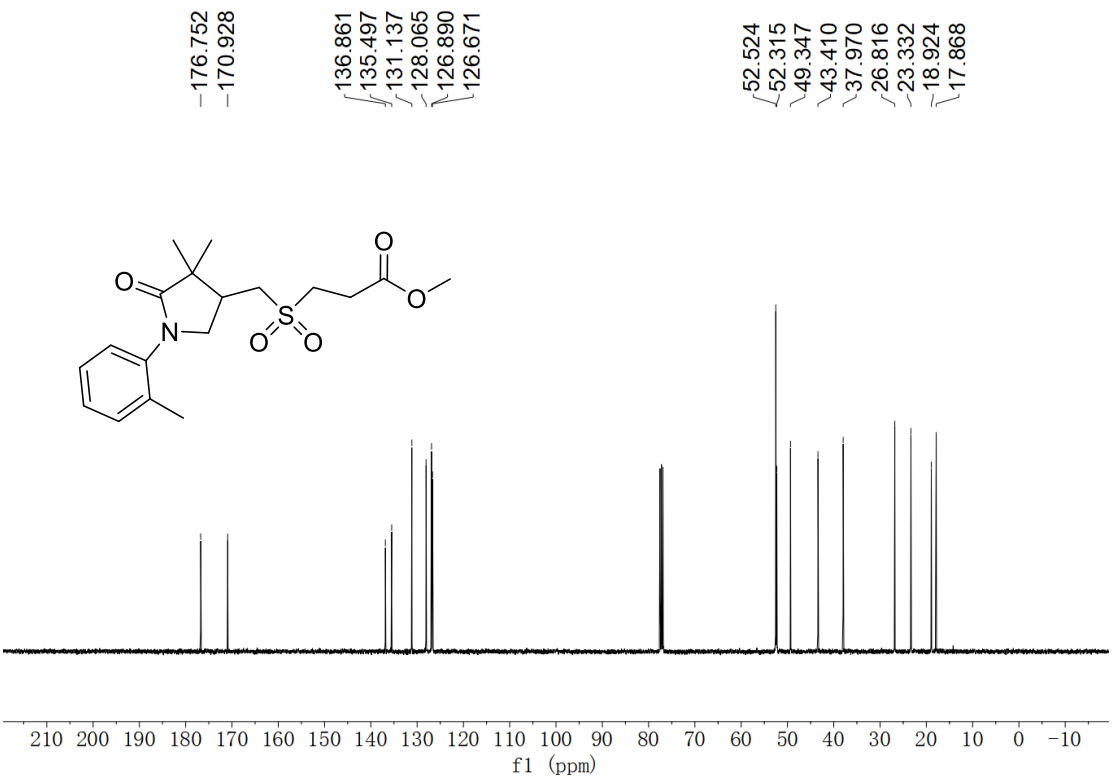


Figure S87 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(2-fluorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl) propanoate (5ia):

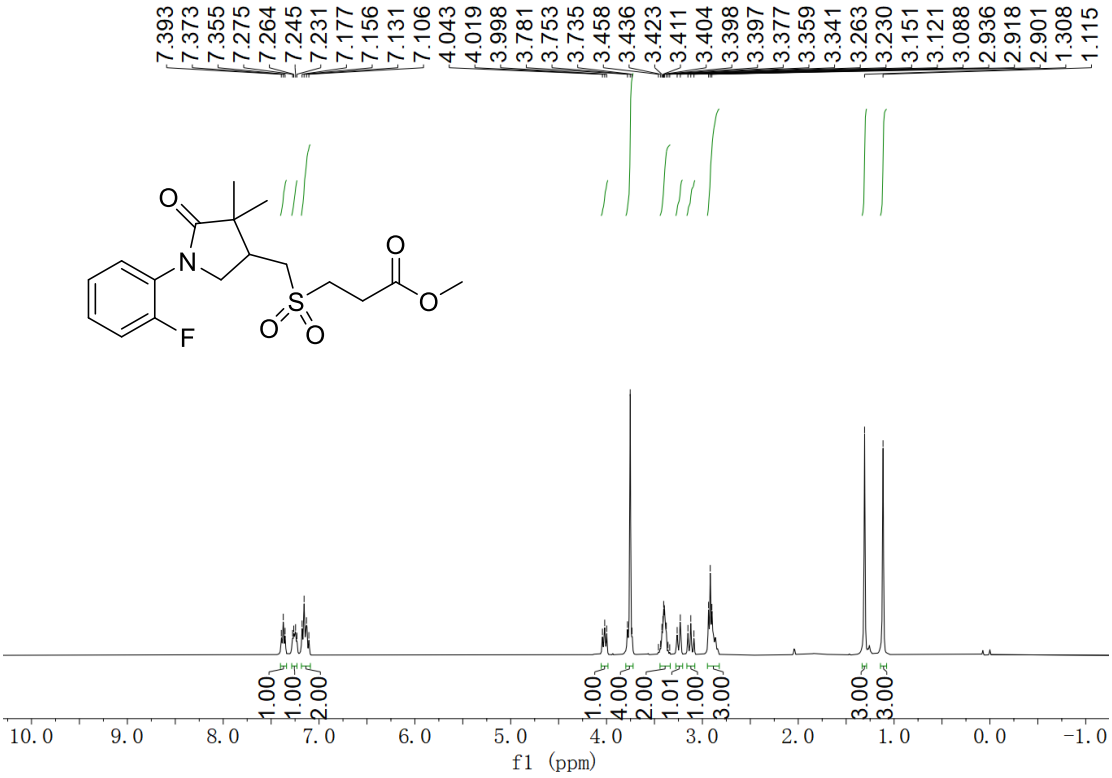


Figure S88 ^{1}H NMR (400 MHz, $CDCl_3$)

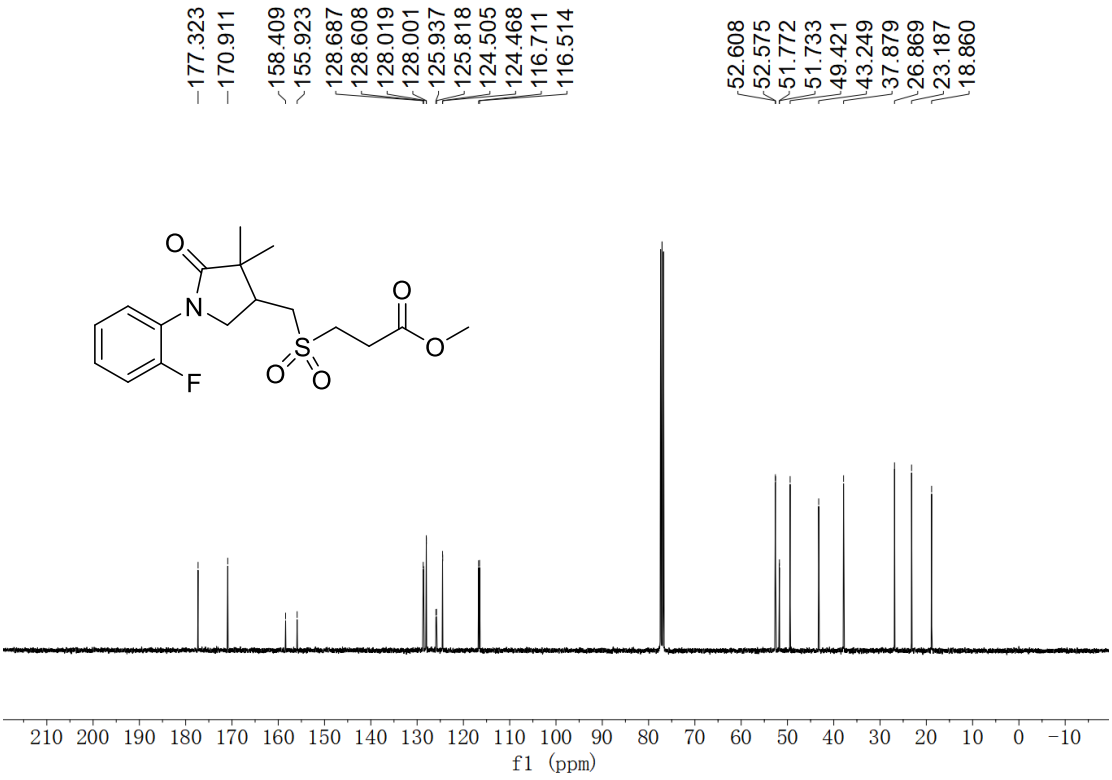


Figure S89 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-5-oxo-1-(m-tolyl)pyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ja):

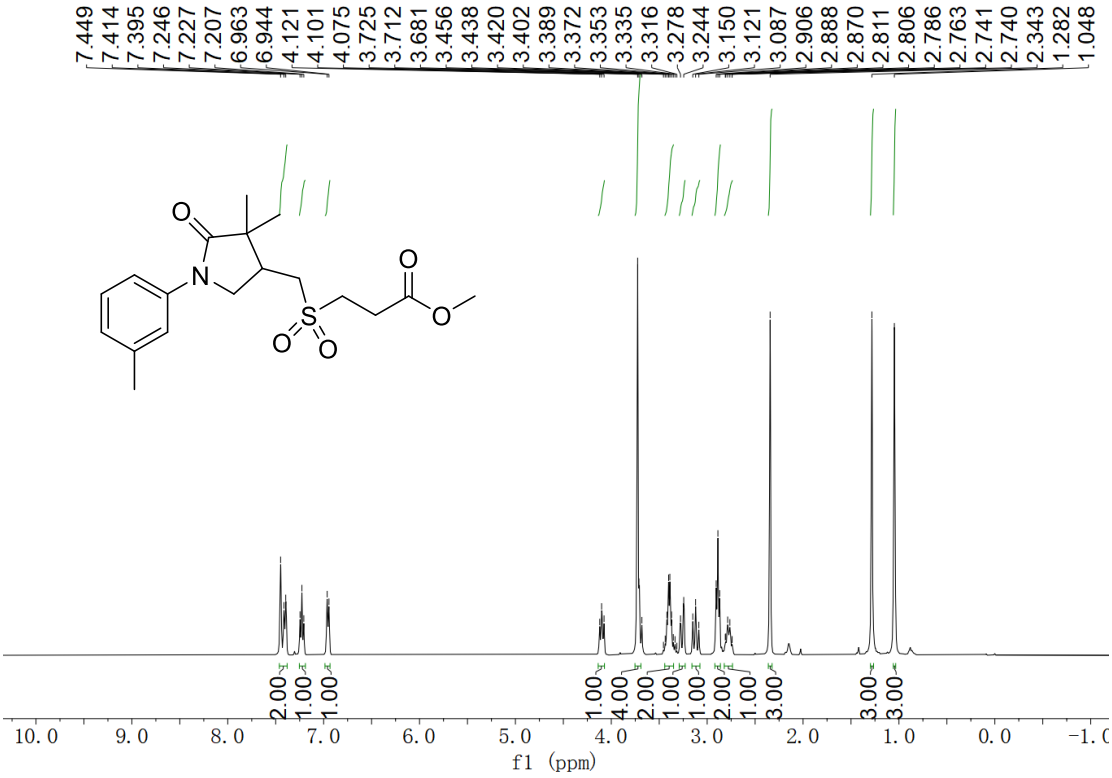


Figure S90 ^{1}H NMR (400 MHz, $CDCl_3$)

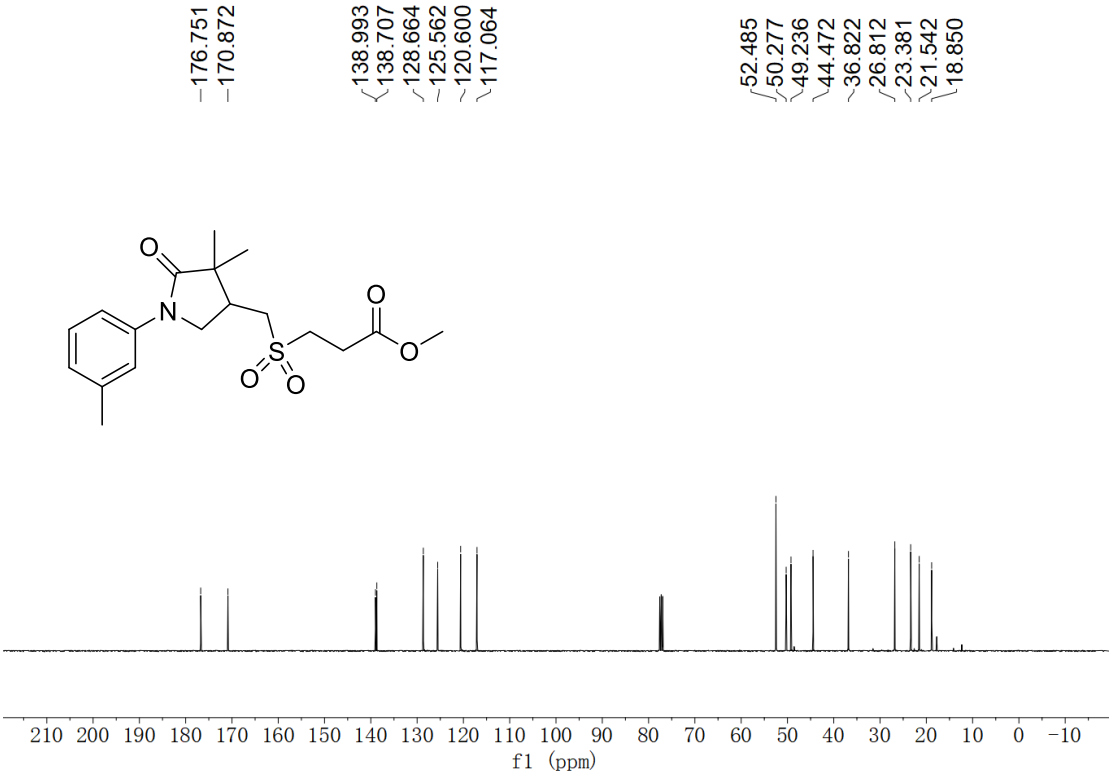


Figure S91 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(3-methoxyphenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ka):

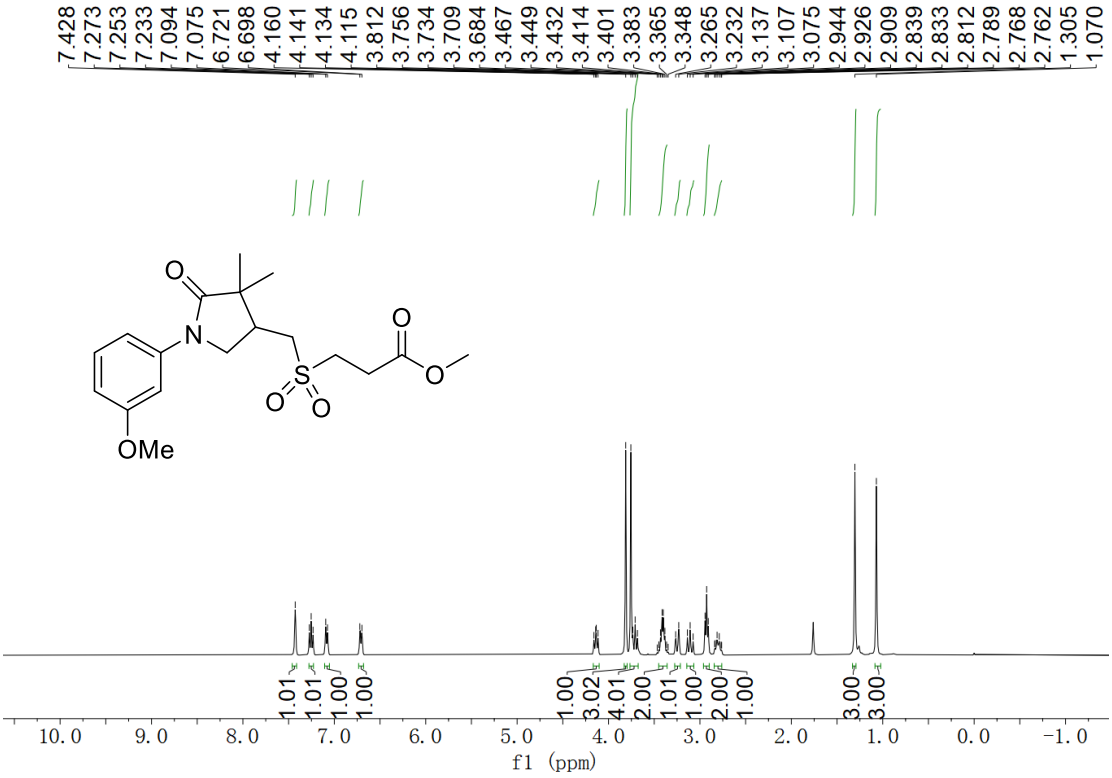


Figure S92 ^{1}H NMR (400 MHz, $CDCl_3$)

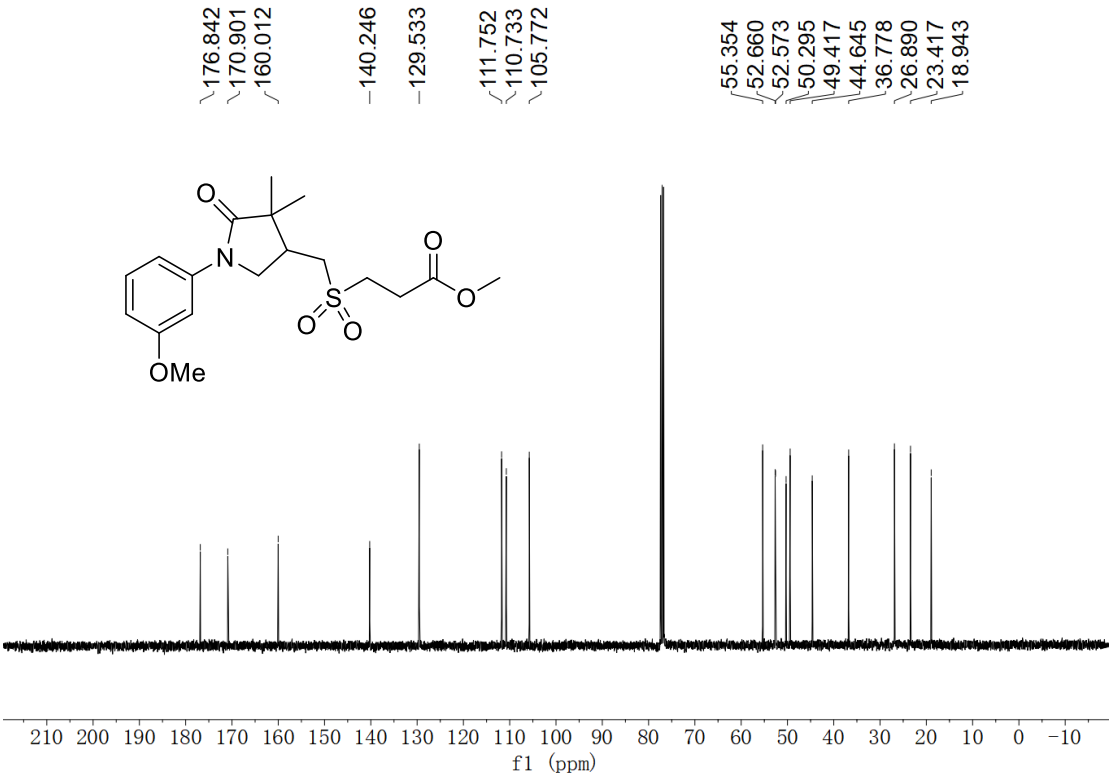


Figure S93 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-(3-chlorophenyl)-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5la):

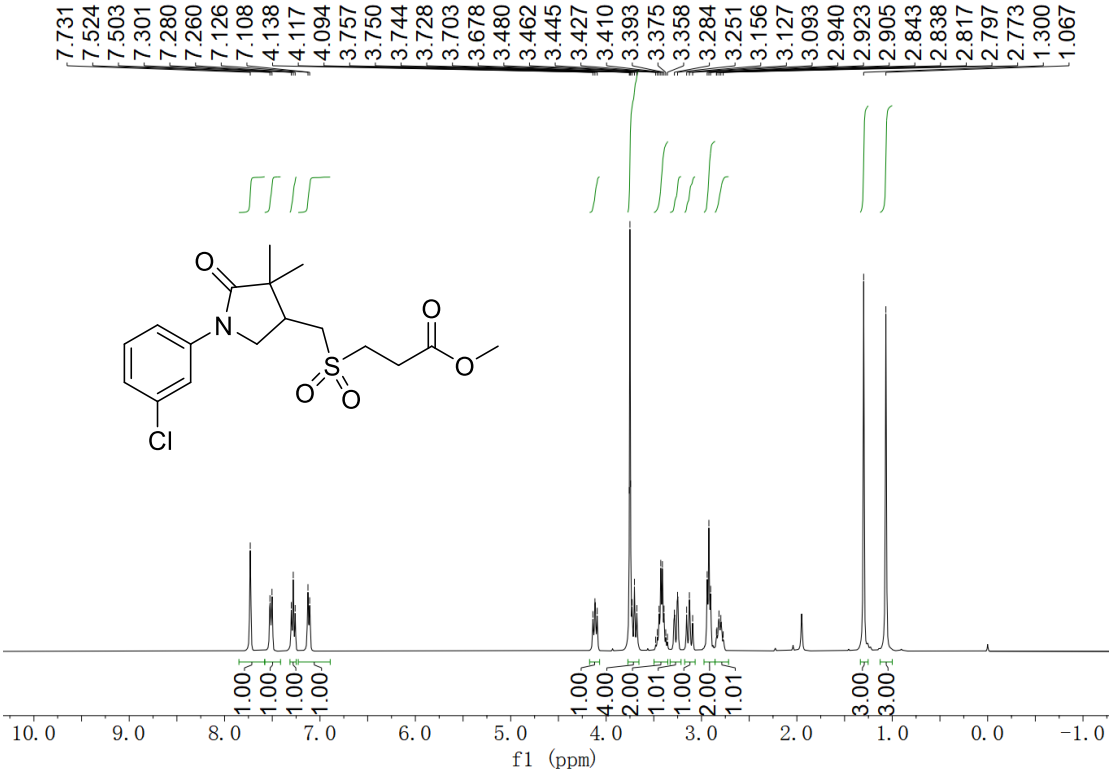


Figure S94 ^{1}H NMR (400 MHz, $CDCl_3$)

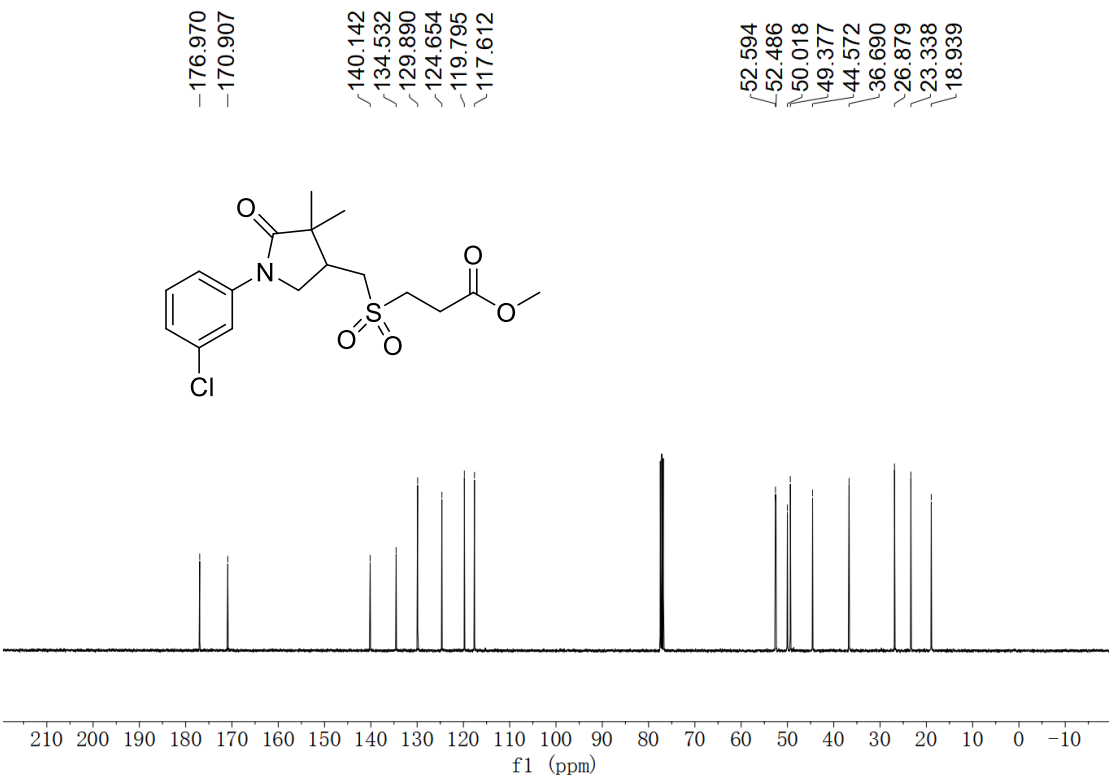


Figure S95 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4,4-dimethyl-1-(naphthalen-1-yl)-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ma):

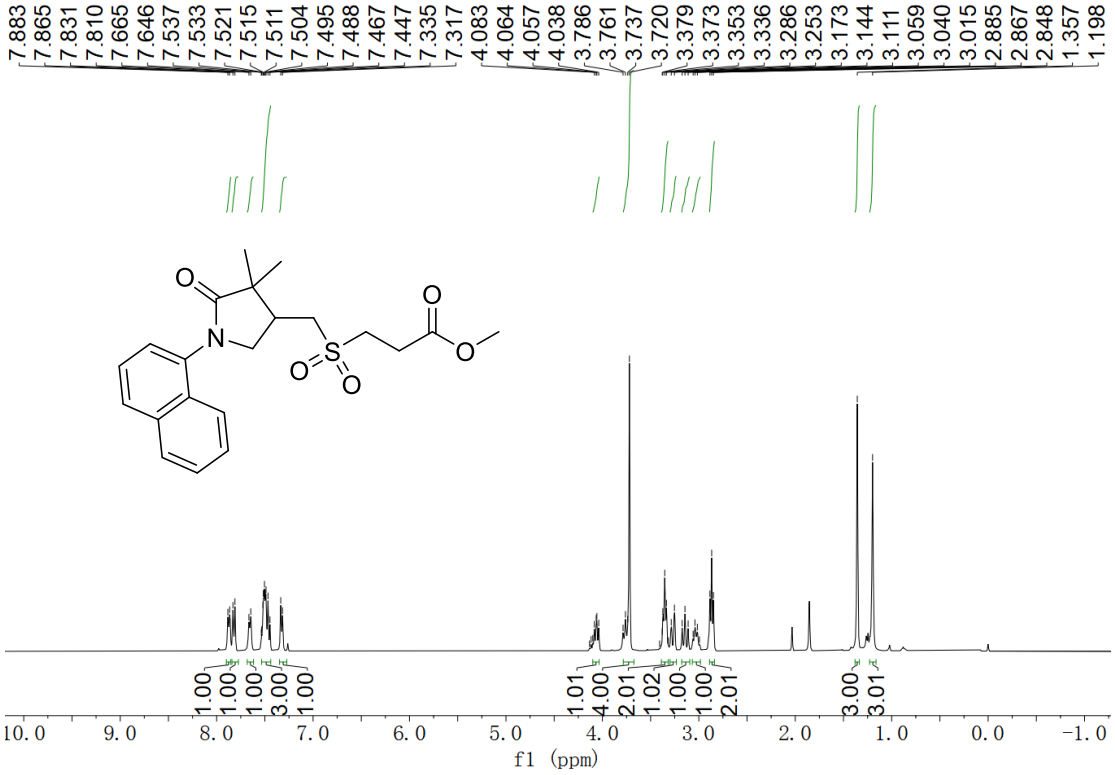


Figure S96 ^{1}H NMR (400 MHz, $CDCl_3$)

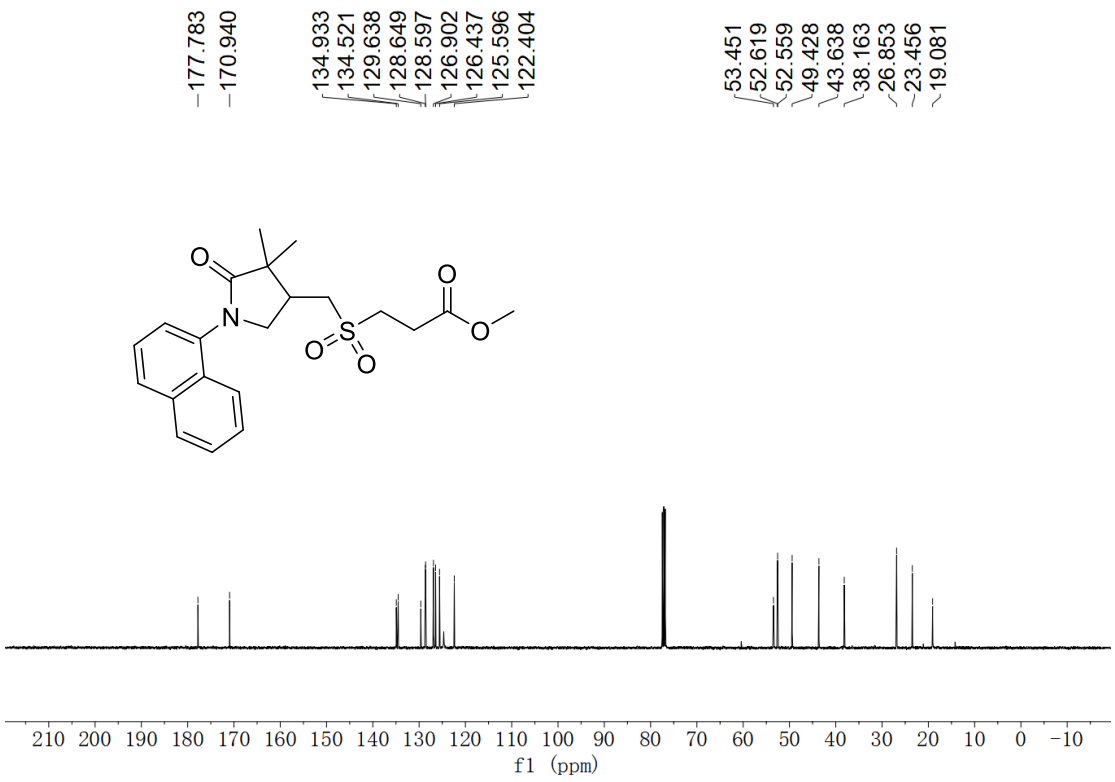


Figure S97 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((4-methyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5na):

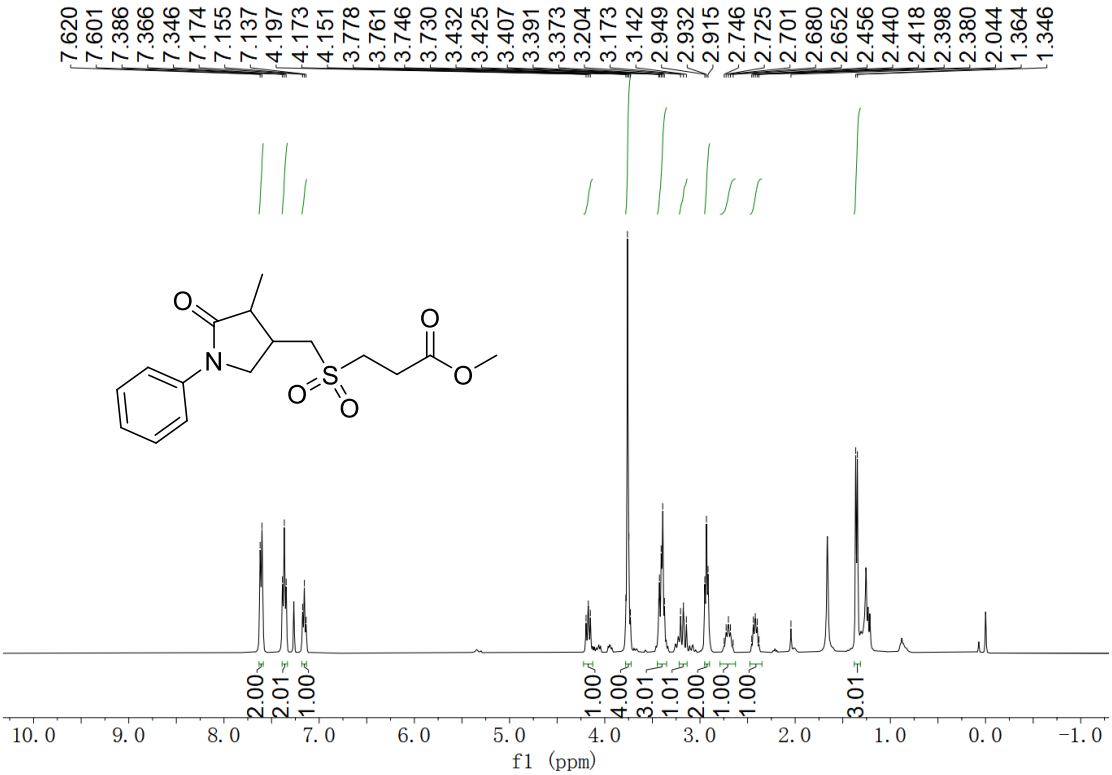


Figure S98 ^{1}H NMR (400 MHz, $CDCl_3$)

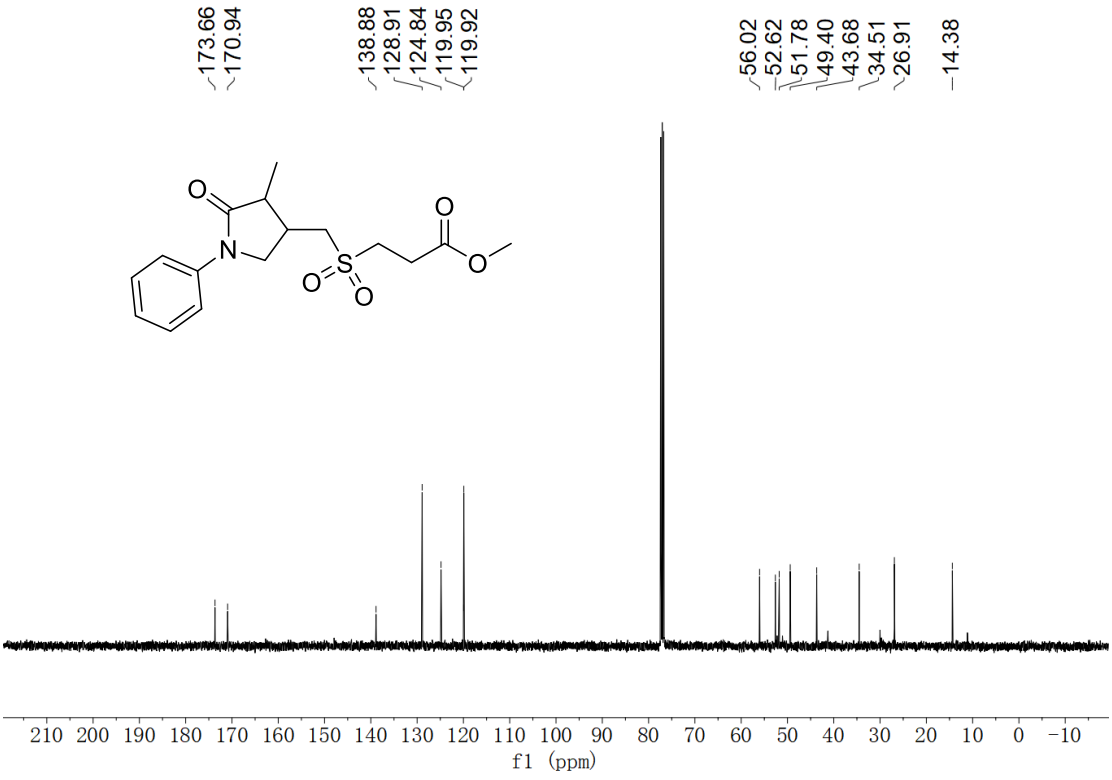


Figure S99 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((3,4,4-trimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5oa):

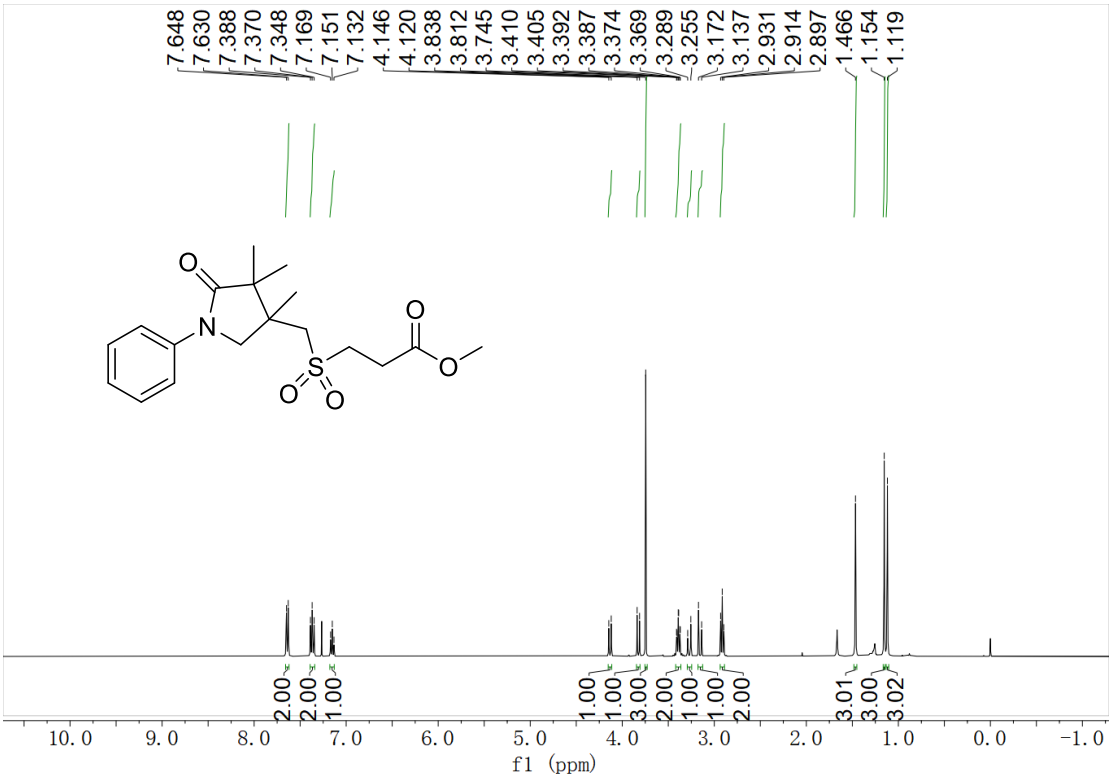


Figure S100 ^{1}H NMR (400 MHz, $CDCl_3$)

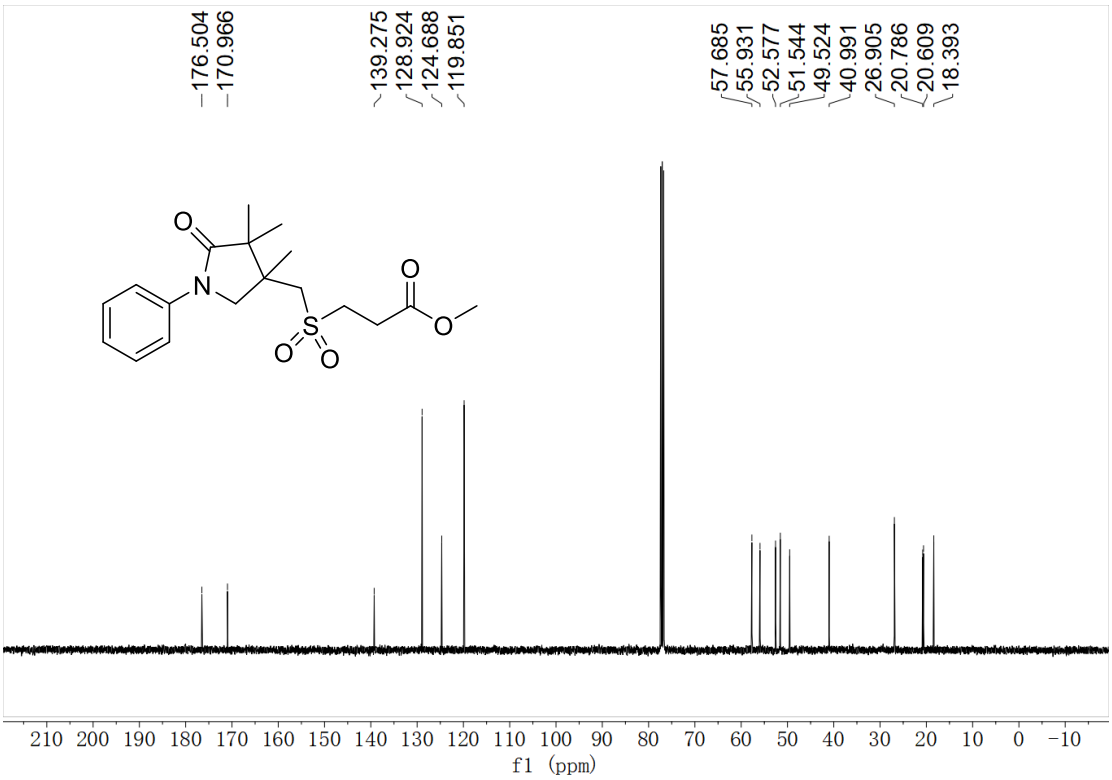


Figure S101 ^{13}C NMR (100 MHz, $CDCl_3$)

methyl 3-(((1-benzyl-4,4-dimethyl-5-oxopyrrolidin-3-yl)methyl)sulfonyl)propanoate (5pa):

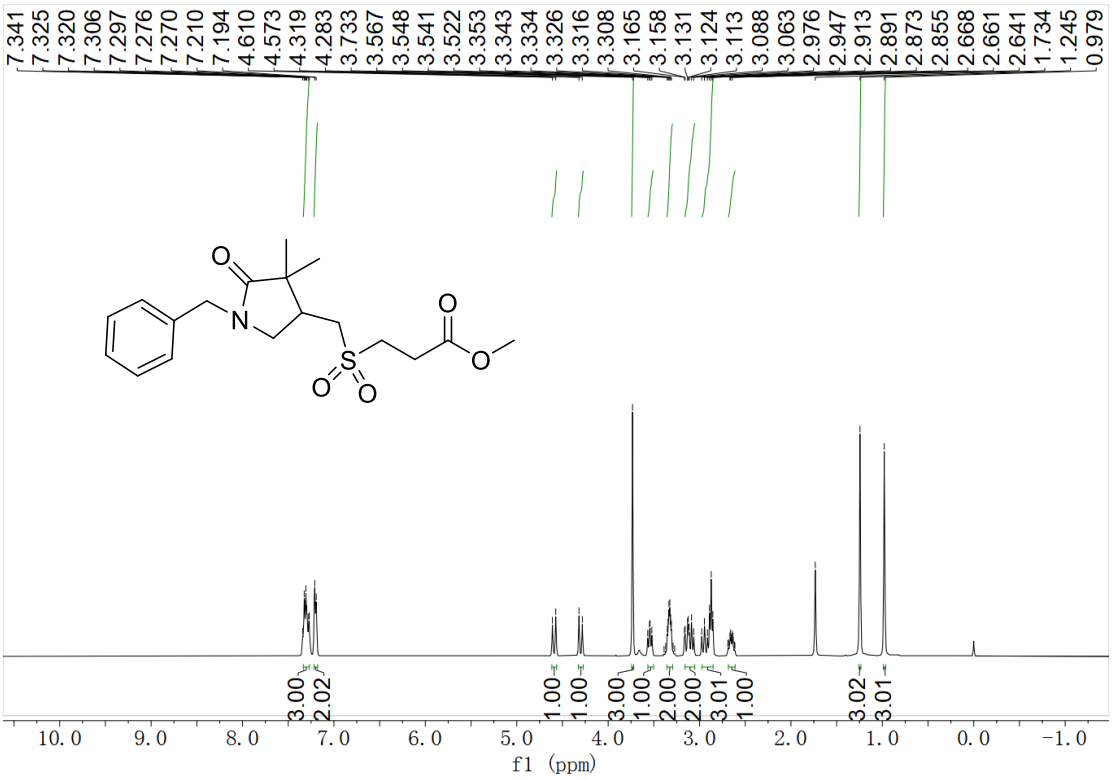


Figure S102 ^{1}H NMR (400 MHz, $CDCl_3$)

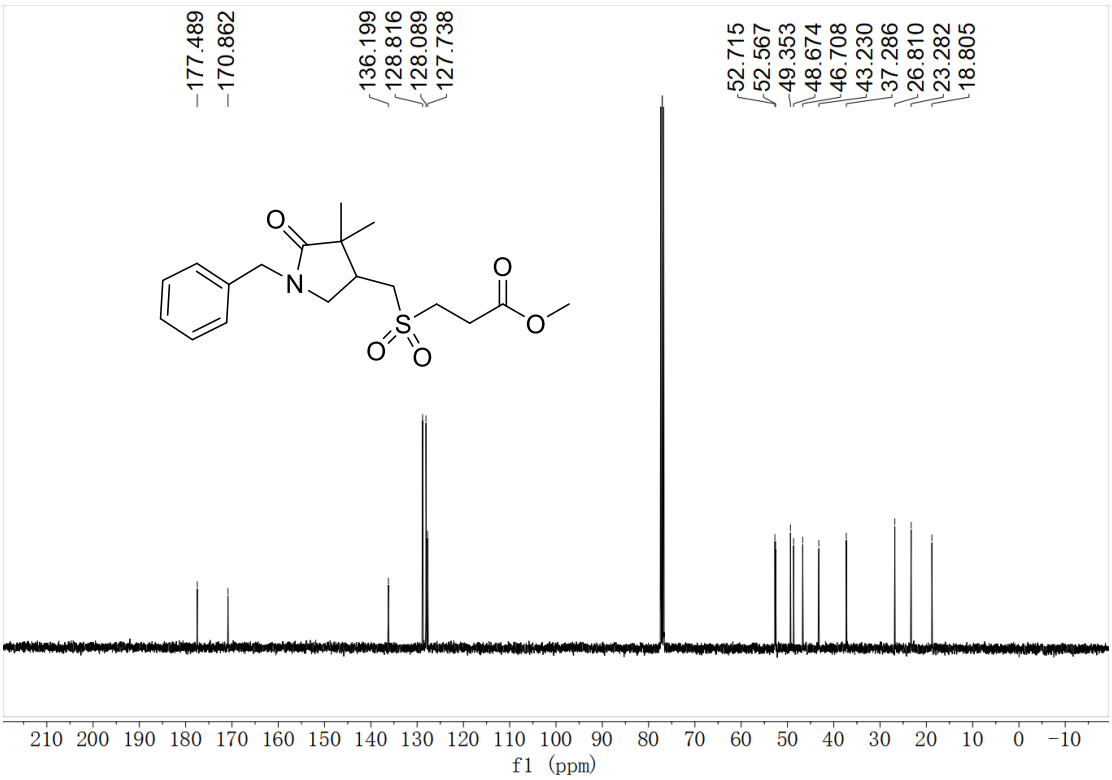


Figure S103 ^{13}C NMR (100 MHz, $CDCl_3$)

butyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ac):

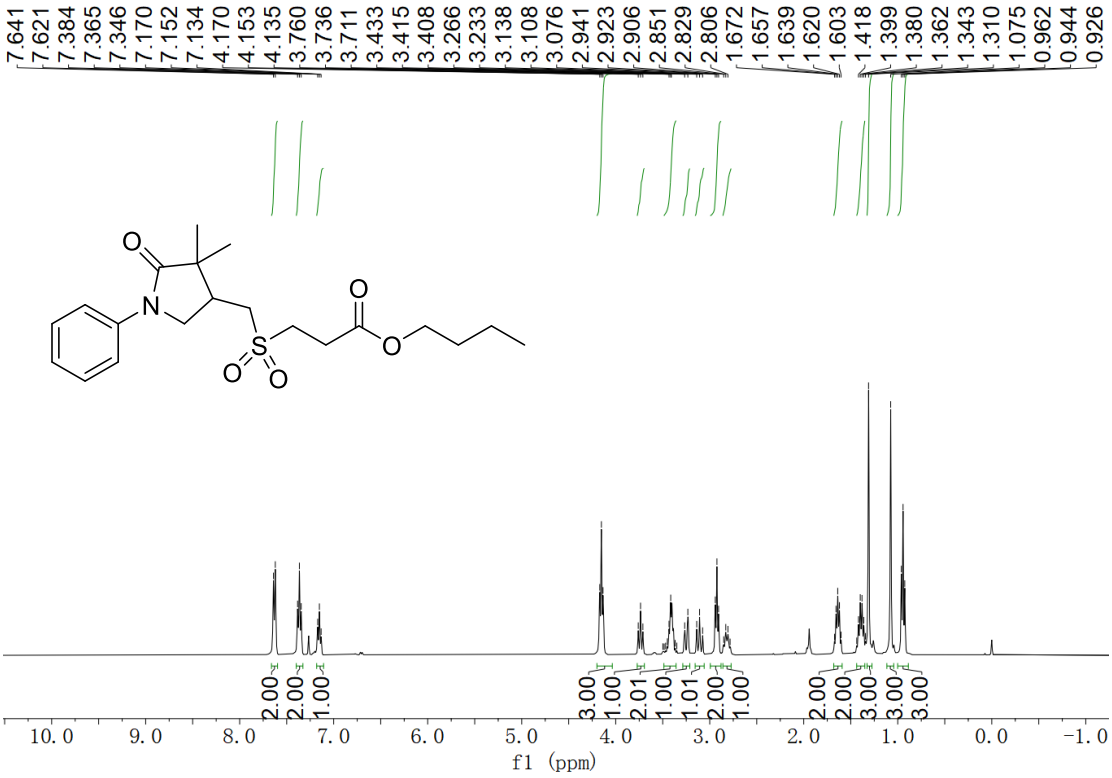


Figure S104 ^{1}H NMR (400 MHz, $CDCl_3$)

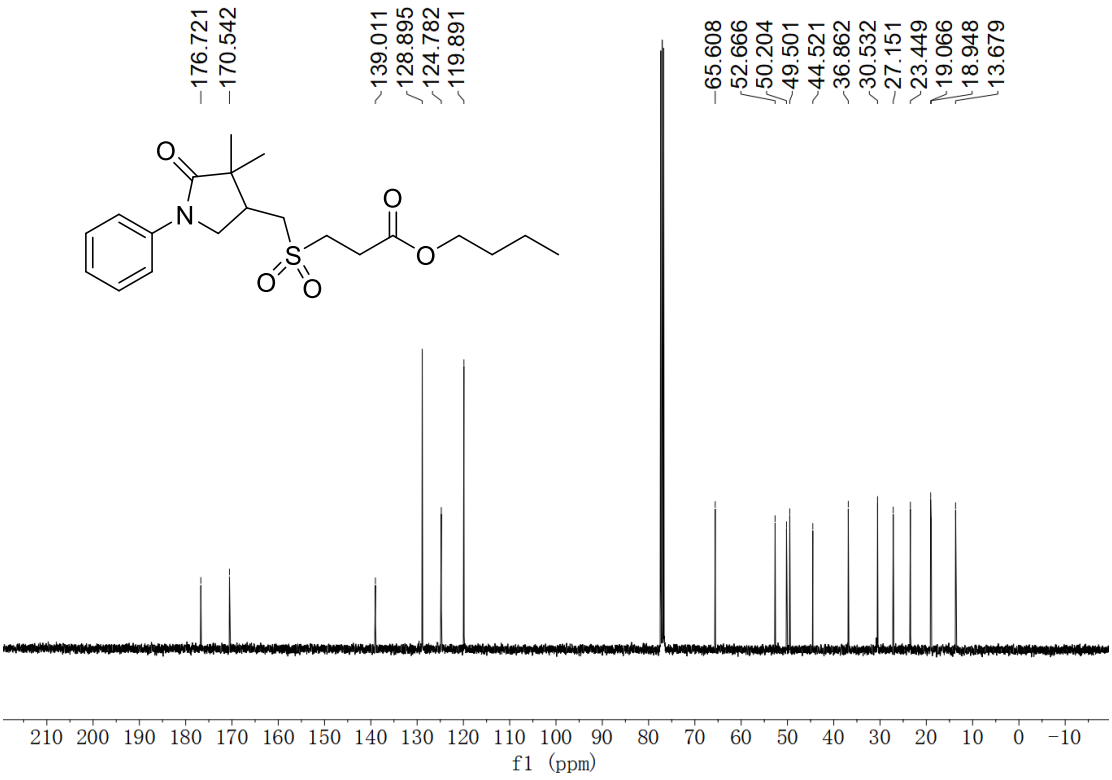


Figure S105 ^{13}C NMR (100 MHz, $CDCl_3$)

cinnamyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5am):

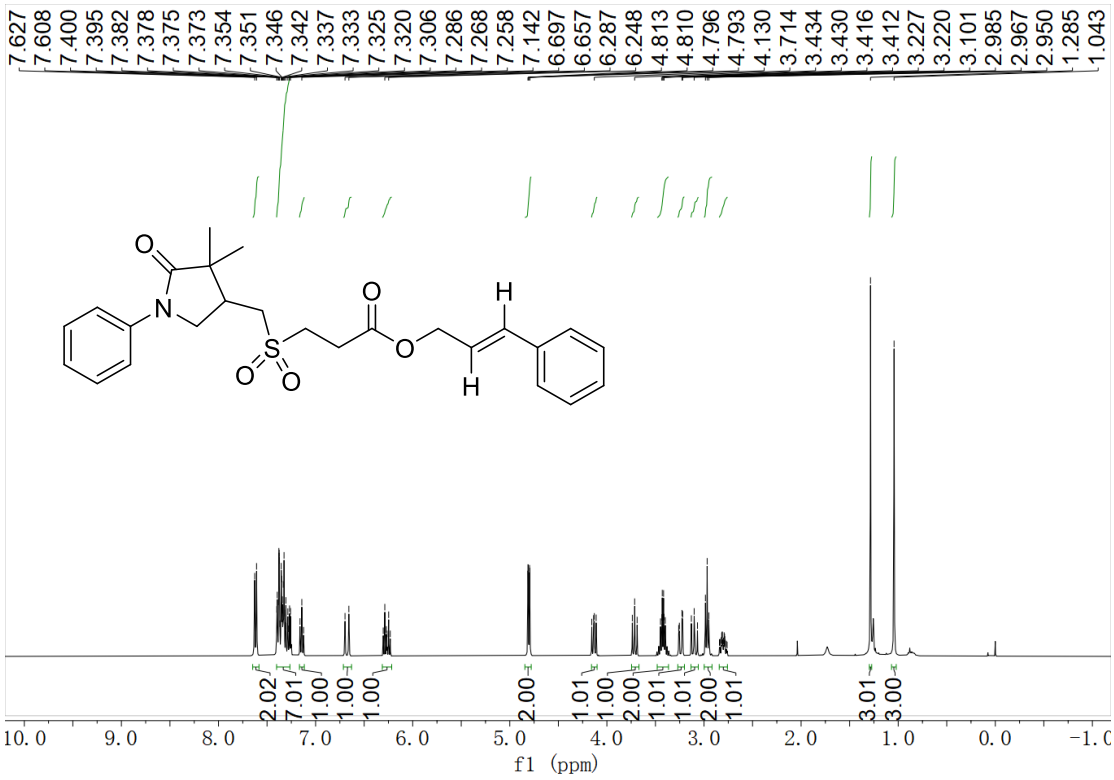


Figure S106 ^{1}H NMR (400 MHz, $CDCl_3$)

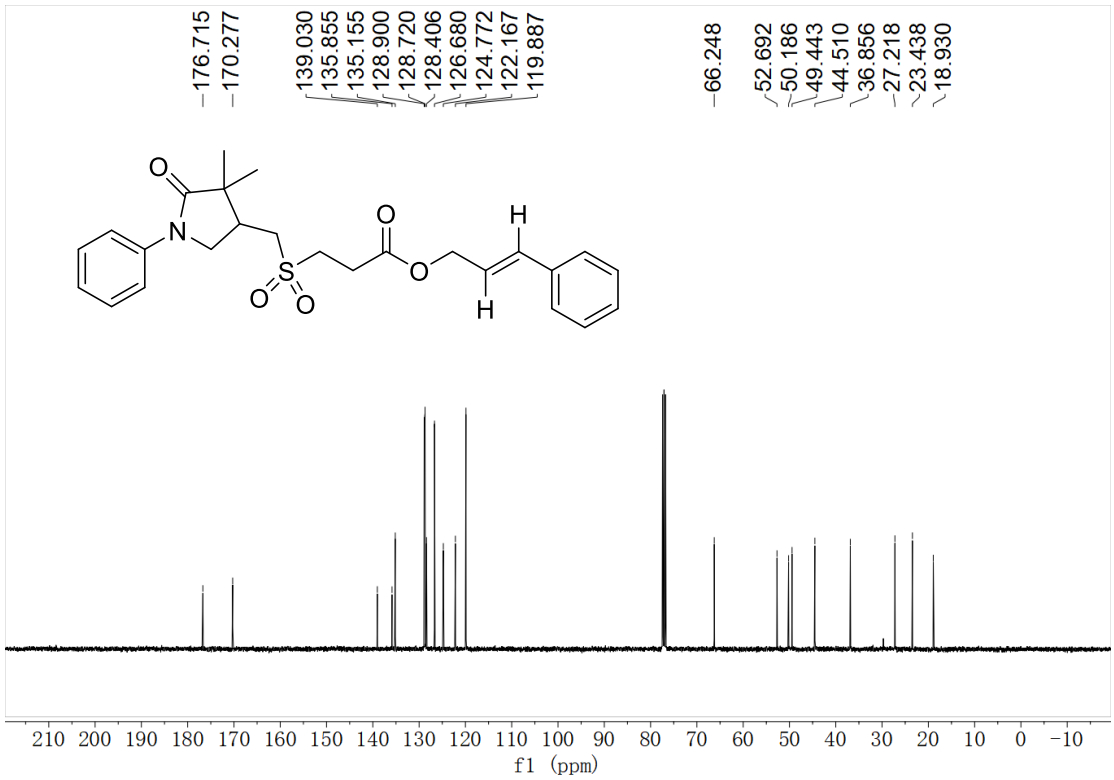


Figure S107 ^{13}C NMR (100 MHz, $CDCl_3$)

phenyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ae):

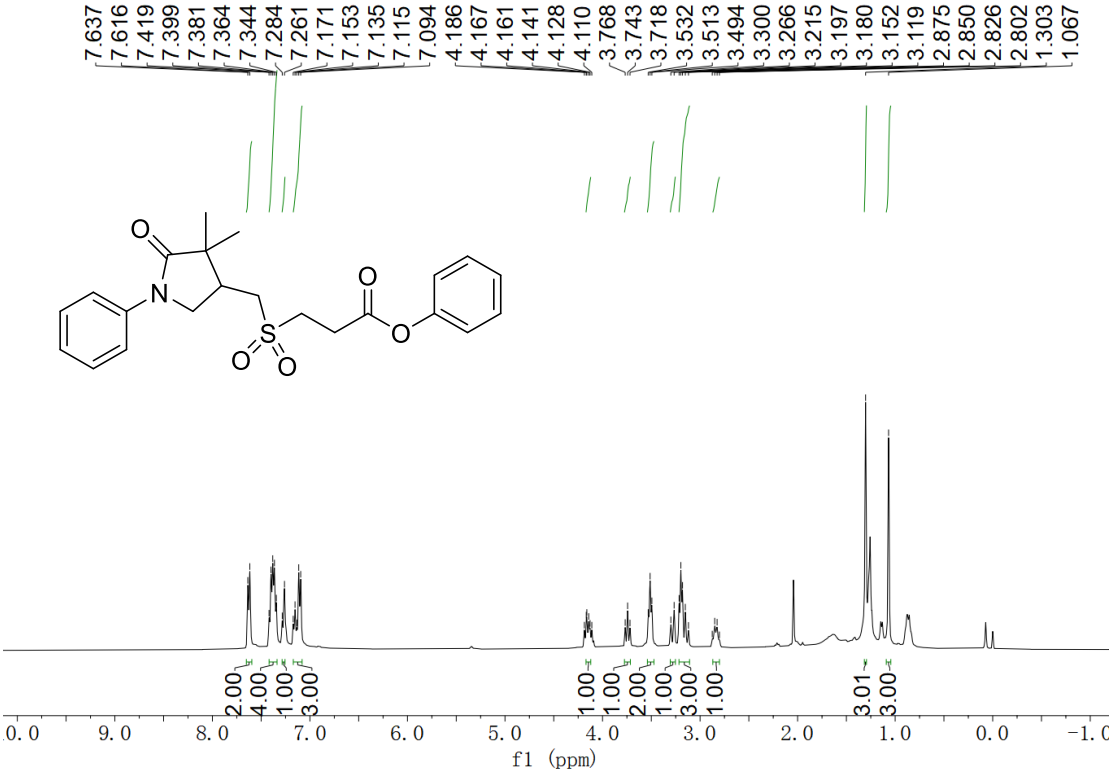


Figure S108 ^{1}H NMR (400 MHz, $CDCl_3$)

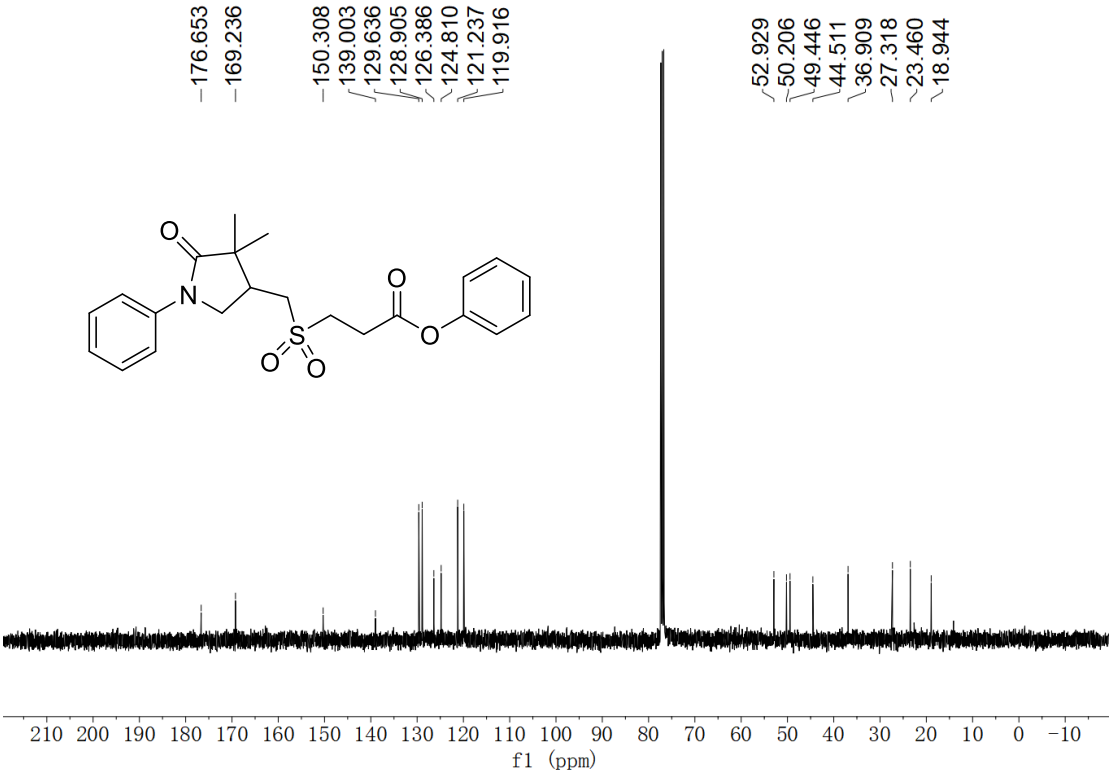


Figure S109 ^{13}C NMR (100 MHz, $CDCl_3$)

3,3-dimethyl-1-phenyl-4-(((2-(pyridin-2-yl)ethyl)sulfonyl)methyl)pyrrolidin-2-one (5ag):

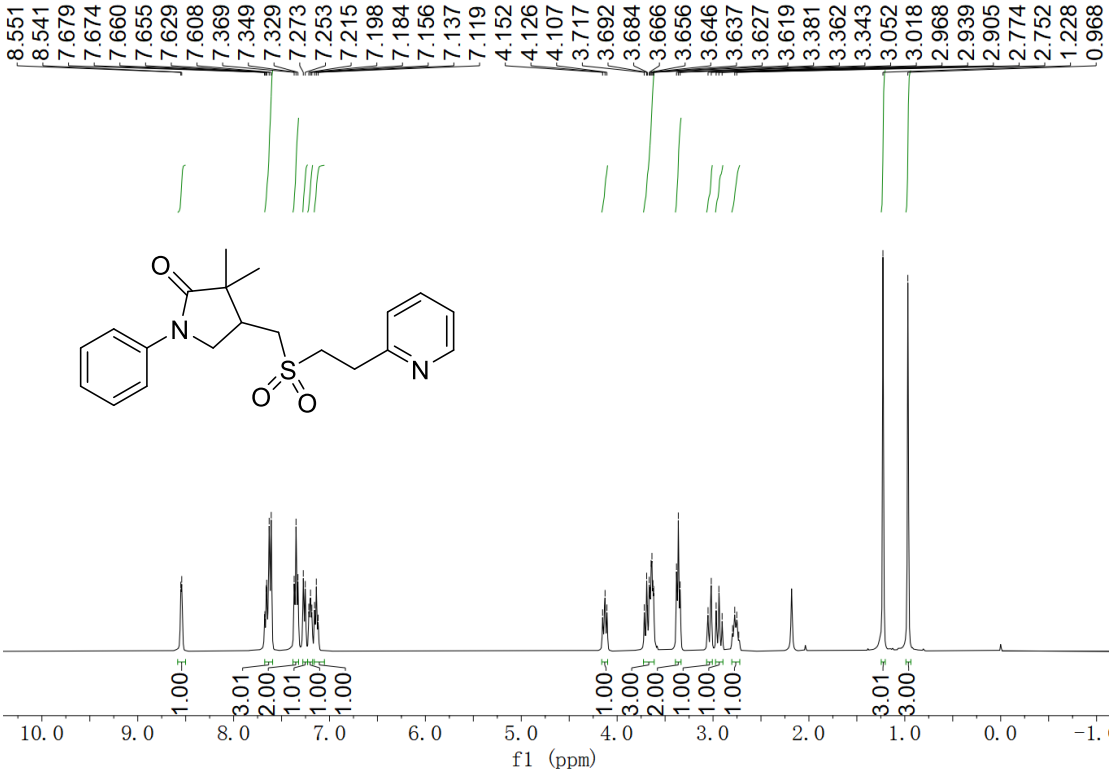


Figure S110 ^{1}H NMR (400 MHz, $CDCl_3$)

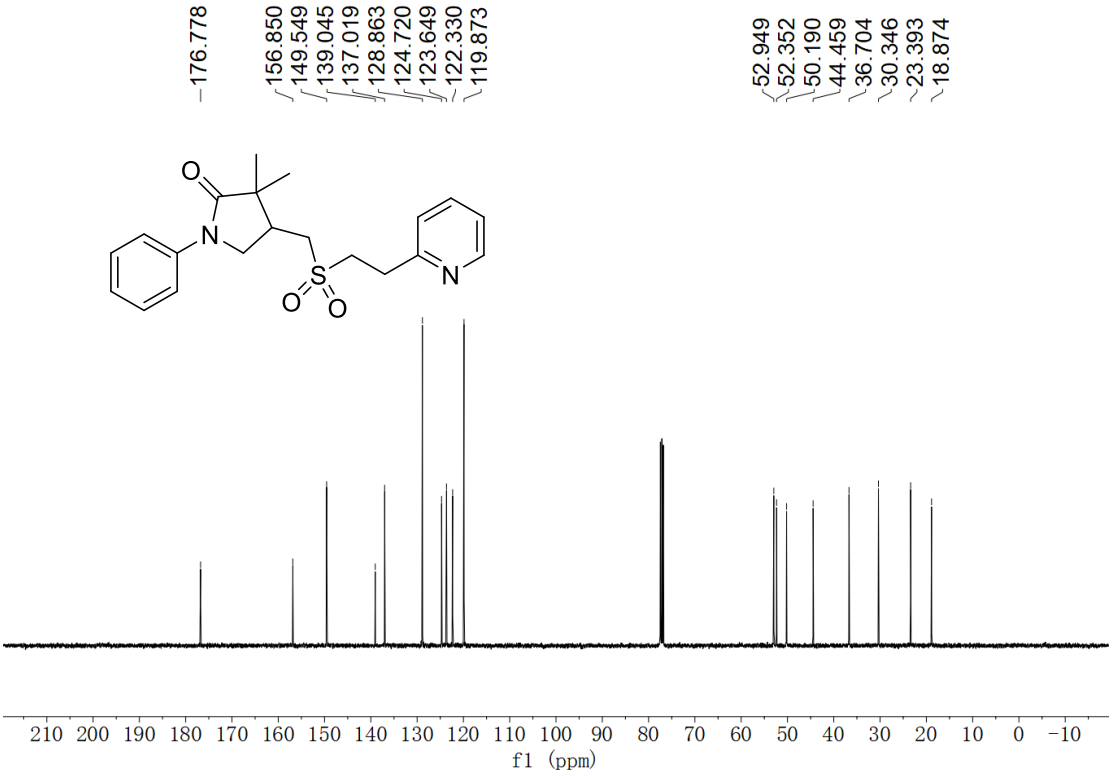


Figure S111 ^{13}C NMR (100 MHz, $CDCl_3$)

3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)-N,N-dimethylpropanamide (5ah):

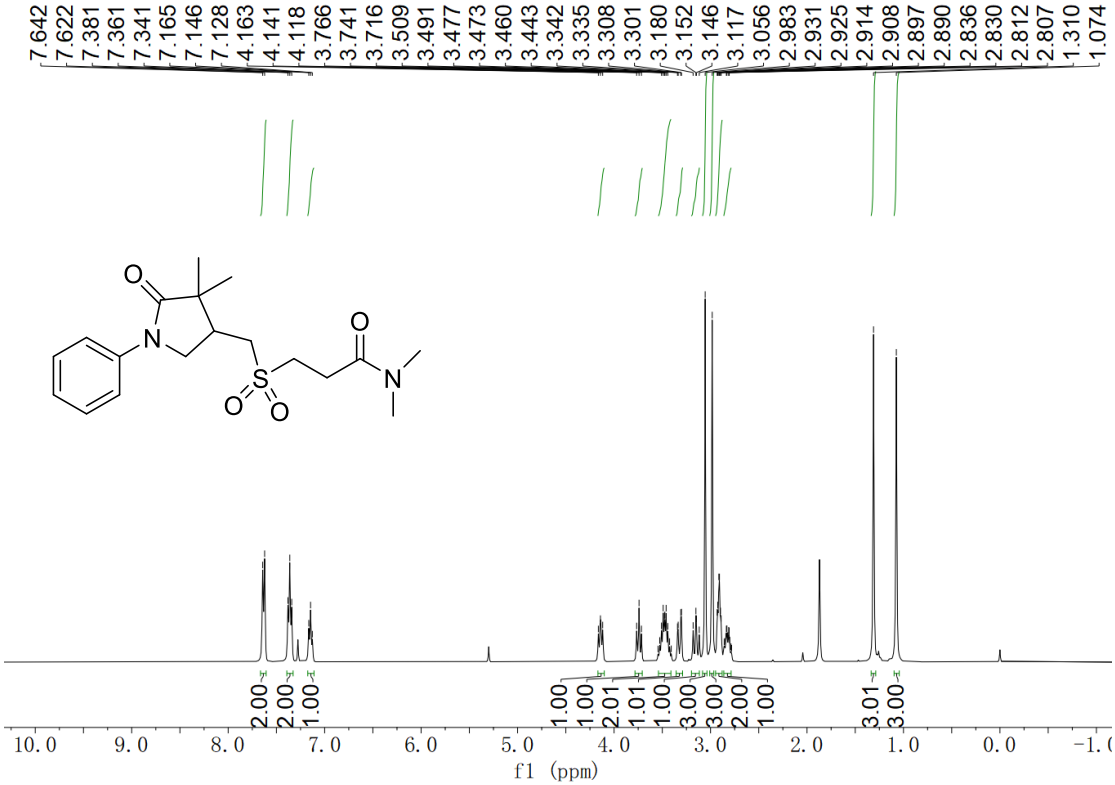


Figure S112 ^{1}H NMR (400 MHz, $CDCl_3$)

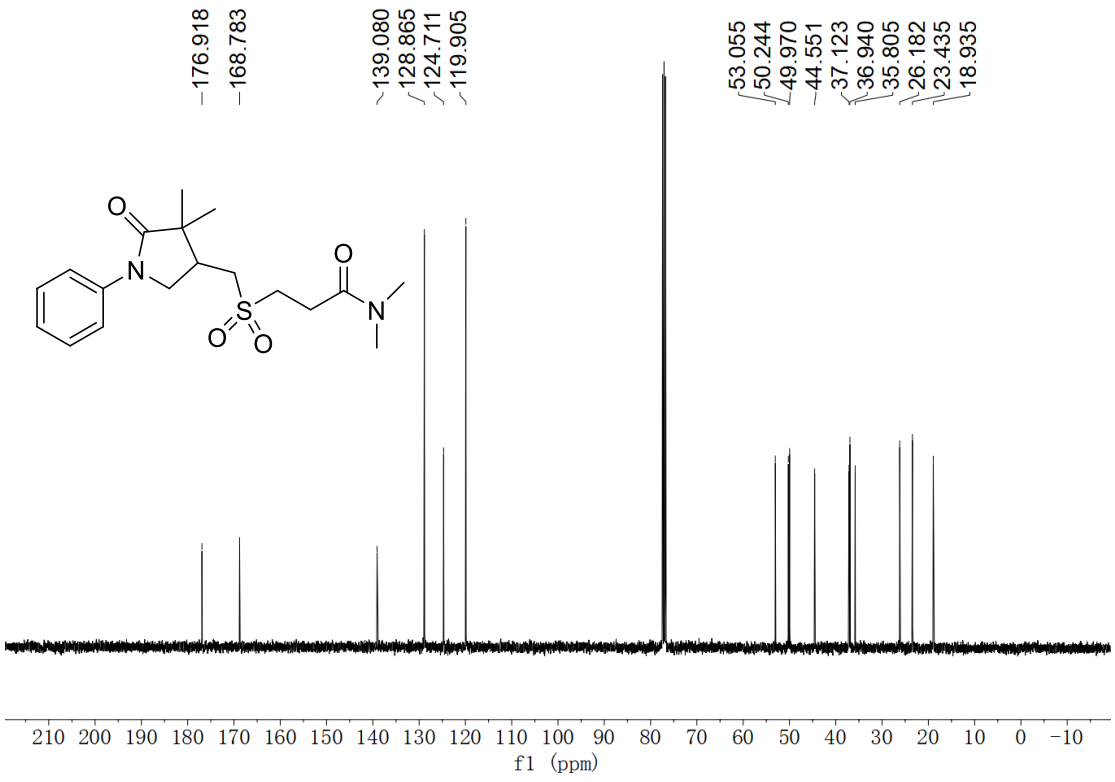


Figure S113 ^{13}C NMR (100 MHz, $CDCl_3$)

3,3-dimethyl-1-phenyl-4-(((2-(phenylsulfonyl)ethyl)sulfonyl)methyl)pyrrolidine-2-one (5ai):

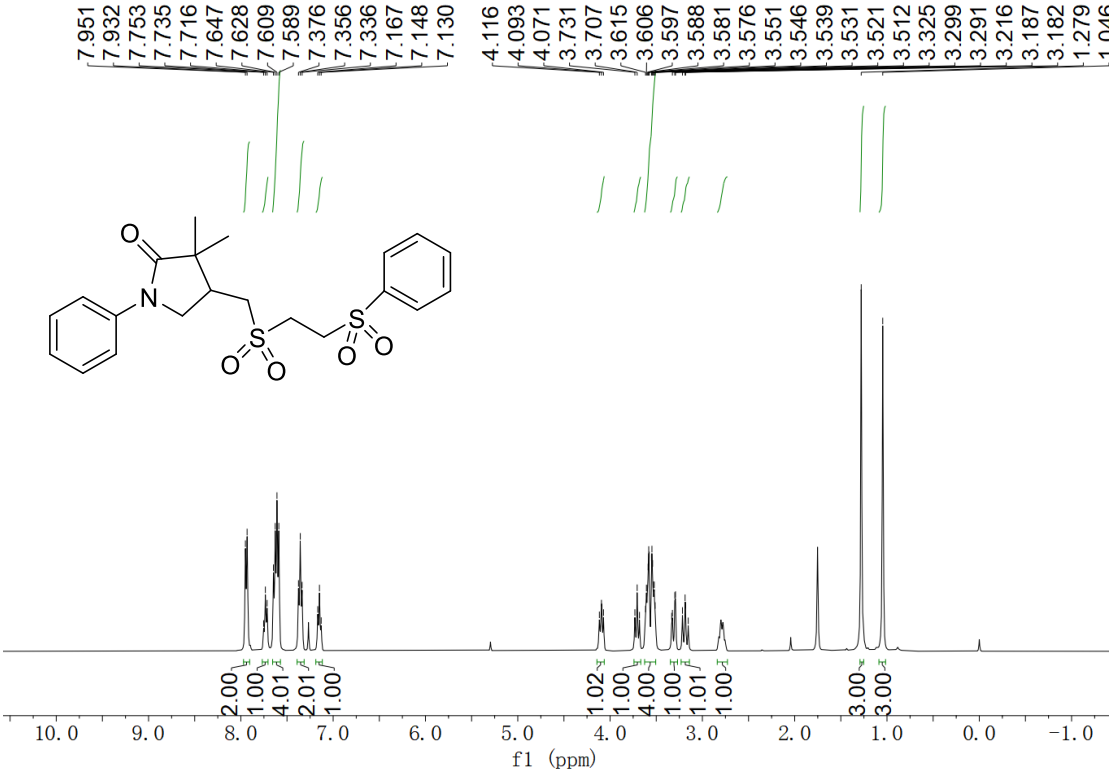


Figure S114 ^{1}H NMR (400 MHz, $CDCl_3$)

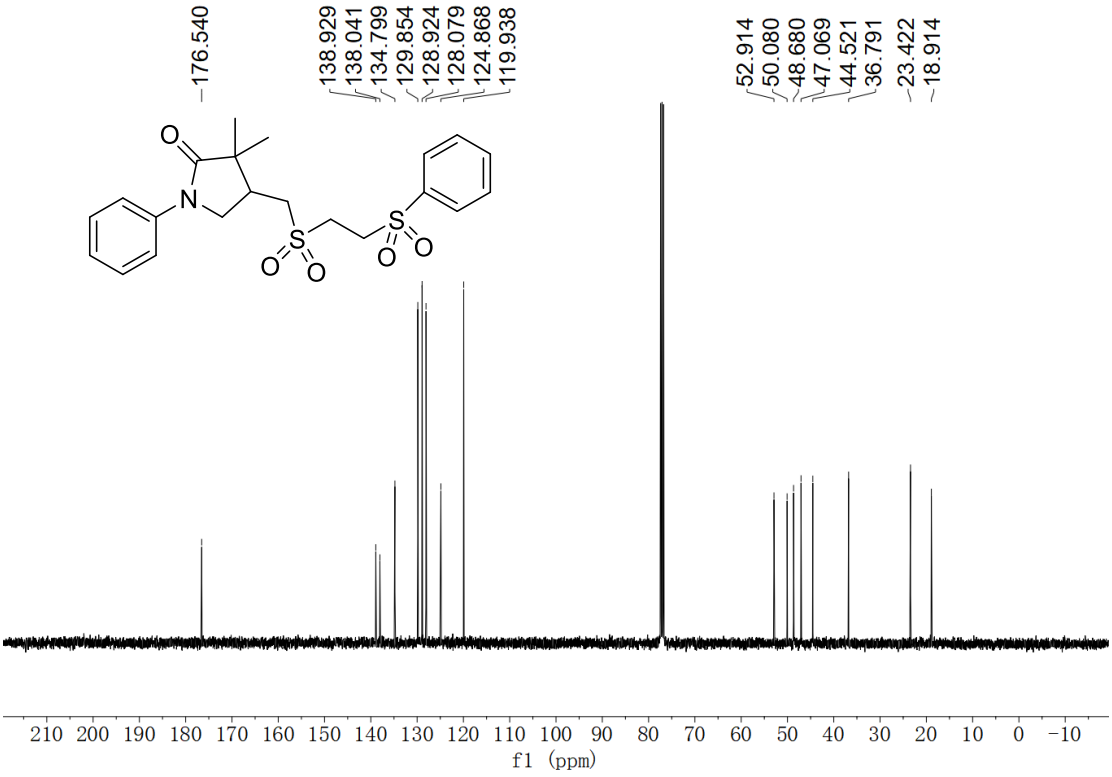


Figure S115 ^{13}C NMR (100 MHz, $CDCl_3$)

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propanoate (5ak):

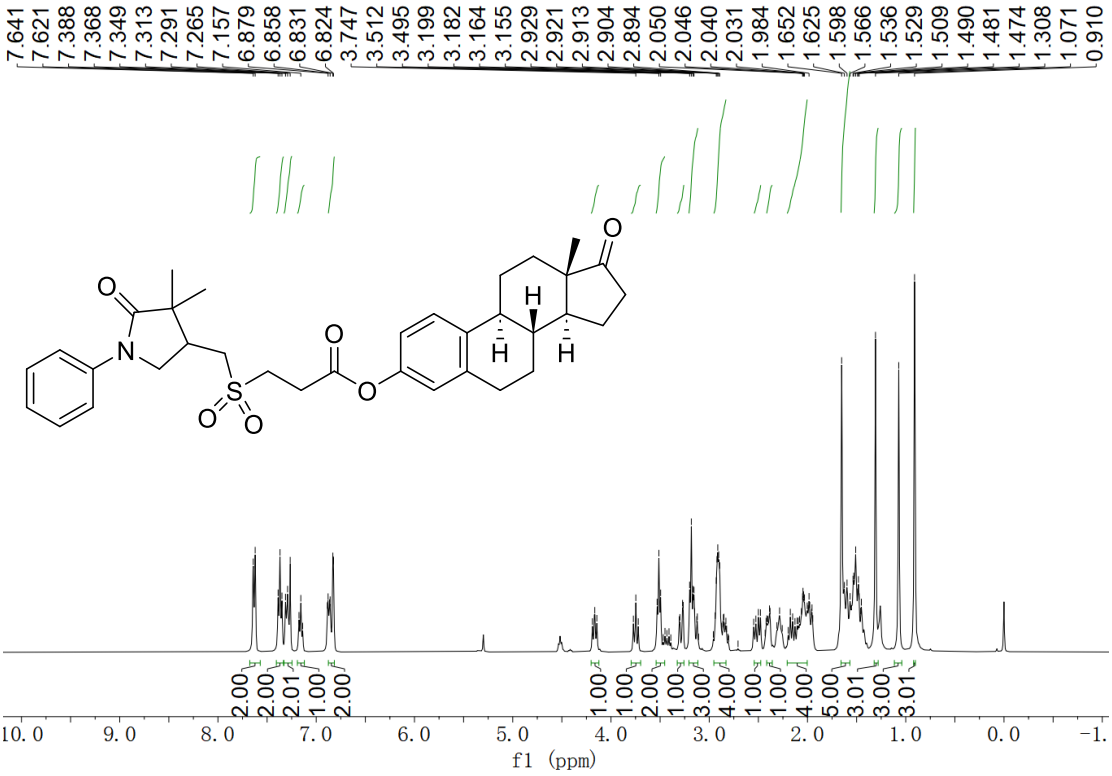


Figure S116 ^{1}H NMR (400 MHz, $CDCl_3$)

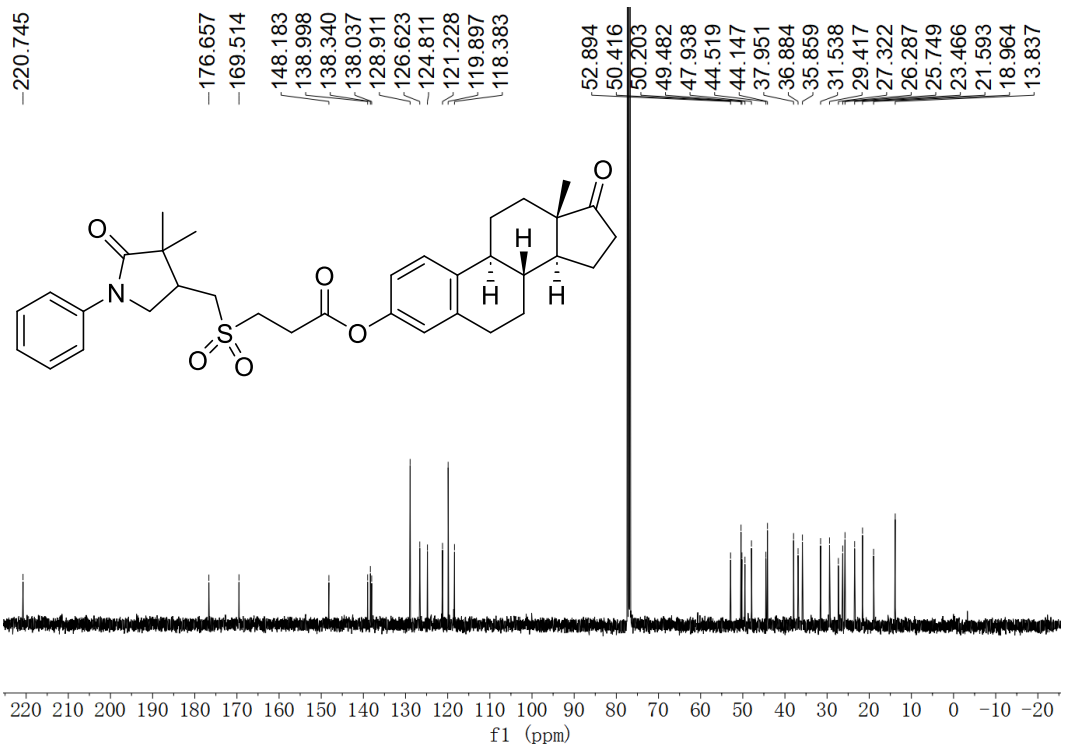


Figure S117 ^{13}C NMR (100 MHz, $CDCl_3$)

((5R)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl) methyl 3-(((4,4-dimethyl-5-oxo-1-phenylpyrrolidin-3-yl)methyl)sulfonyl)propano ate (5al):

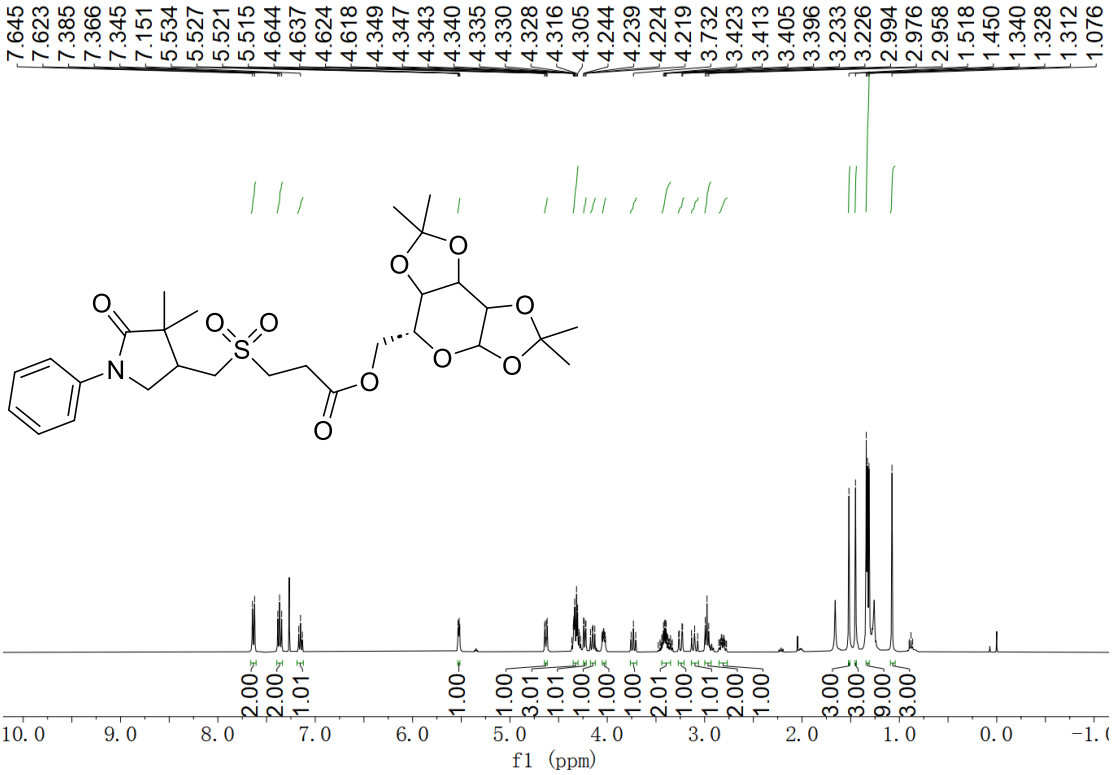


Figure S118 ^{1}H NMR (400 MHz, $CDCl_3$)

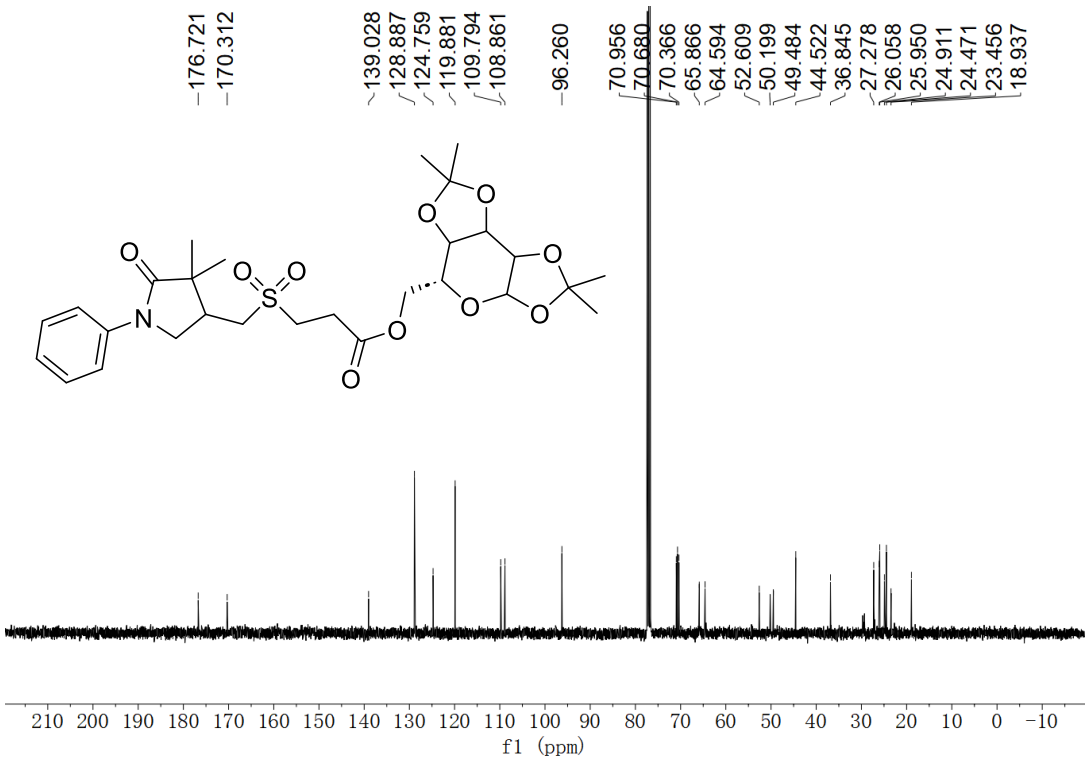


Figure S119 ^{13}C NMR (100 MHz, $CDCl_3$)

(Z)-4-(((cyclopropylmethyl)sulfonyl)methylene)-3,3-dimethyl-1-phenylpyrrolidin-2-one (8aa):

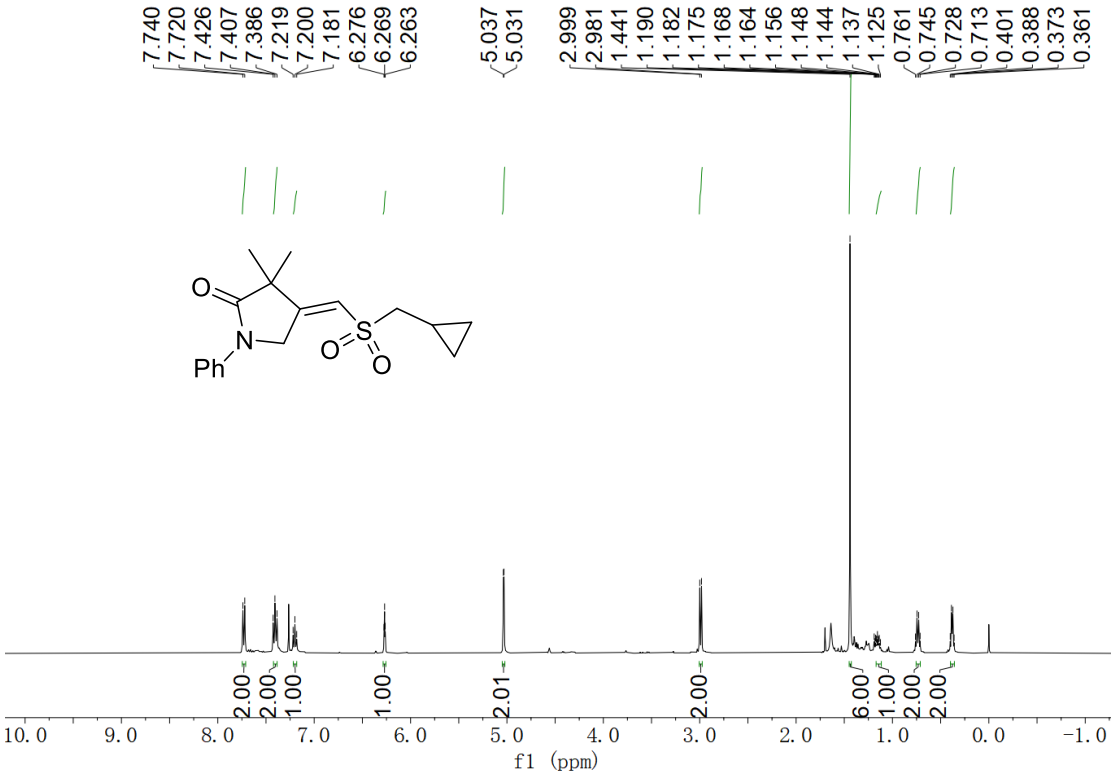


Figure S118 ^{1}H NMR (400 MHz, $CDCl_3$)

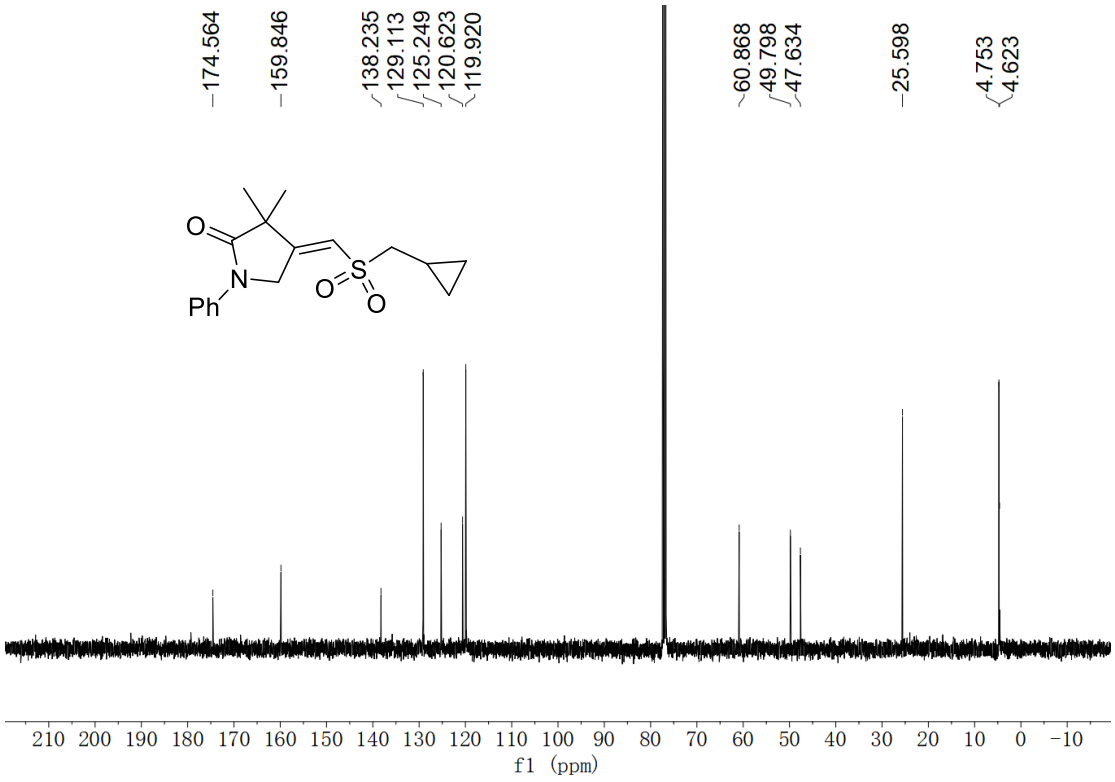


Figure S119 ^{13}C NMR (100 MHz, $CDCl_3$)