Electronic Supplementary Material (ESI) for RSC Advances

An Environmentally Benign Approach for the Synthesis of 3,3'-Pyrrolidonyl Spirooxindole Derivatives *via* Domino Knoevenagel/Michael/Cyclization Multicomponent Reactions

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Supporting Information

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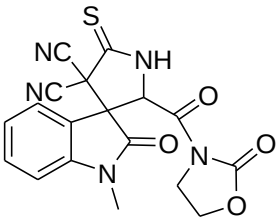
General Comments.

Solvents were dried and distilled prior to use according to the standard methods. Unless otherwise indicated, all materials were obtained from commercial sources, and used as purchased without dehydration. Flash column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H NMR, ^{13}C NMR spectra were recorded in DMSO at Bruker AV 400 MHz spectrometers, TMS served as internal standard (δ = 0 ppm). Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). The crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Mass spectra were recorded on a LCQ advantage spectrometer with ESI resource. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were determined on a T-4 melting point apparatus (uncorrected).

Typical reaction procedure for the synthesis of 3,3'-pyrrolidinyl-spirooxindole:

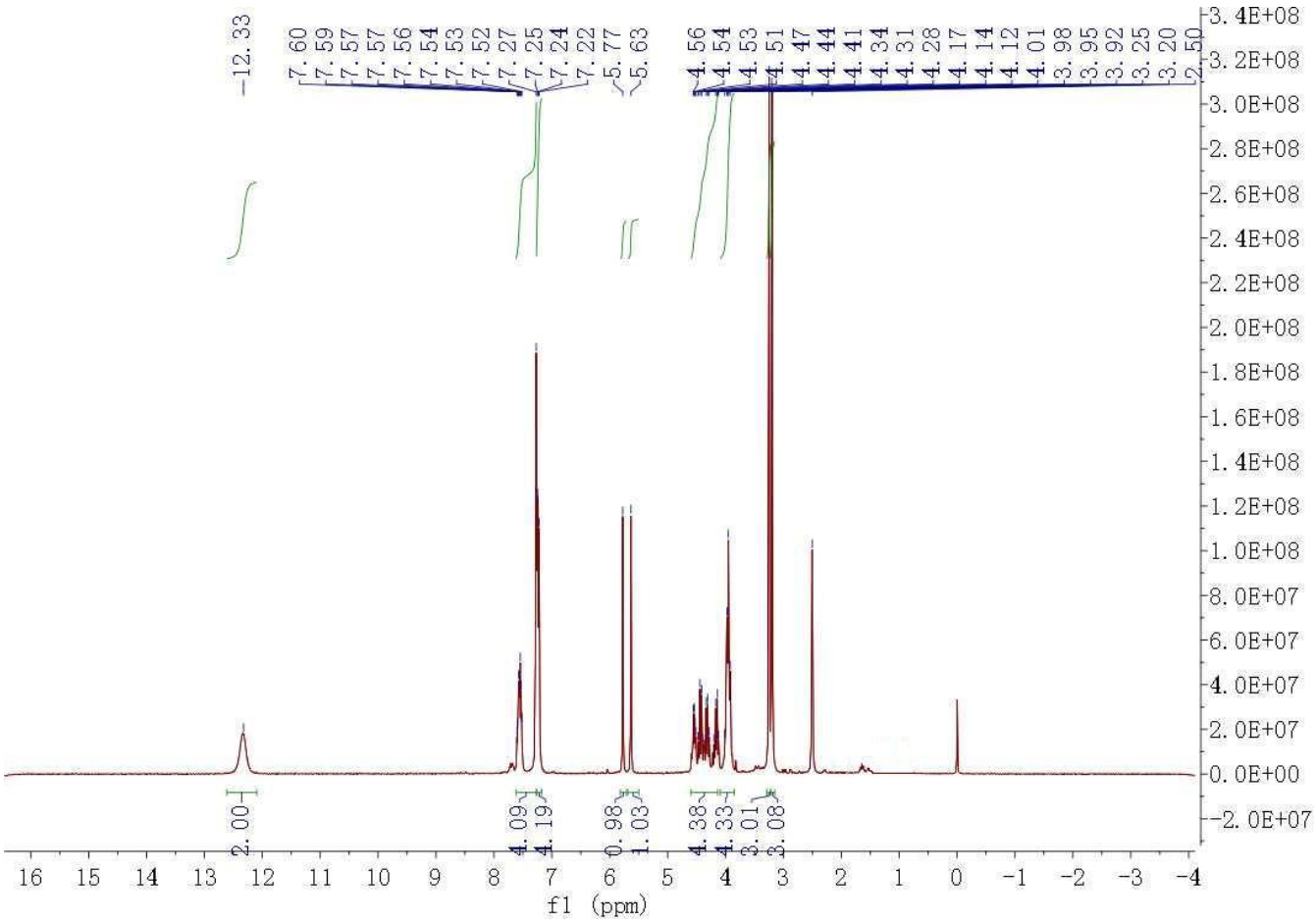
A solution of isatin **1** (0.3 mmol), TEA (0.03 mmol) and malononitrile **2** (0.3 mmol) in 5 ml H_2O was stirred at room temperature. After the reaction was completed (monitored by TLC), α-isothiocyanato imide **3** (0.33 mmol) was added and the mixture was sonicated for 1 min in ultrasound bath, then allowed to further stirred at room temperature. After complete consumption of the dicyanoalkene, as indicated by TLC (ethyl acetate/hexane = 3:1), the solvent was evaporated. The residue was purified by column chromatography over silica gel (ethyl acetate/hexane=3:1) to afford product as a colorless powder.

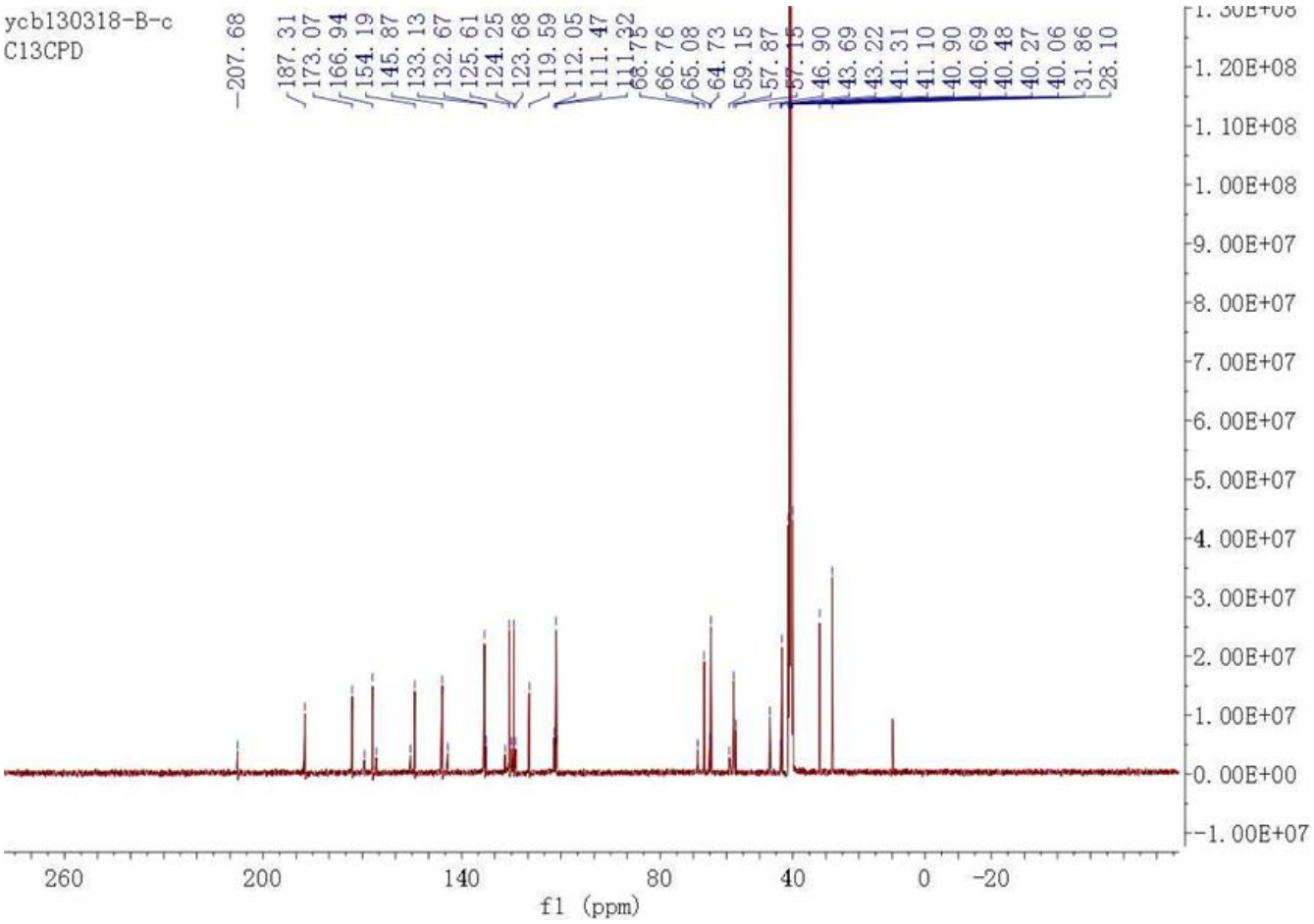
1-Methyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



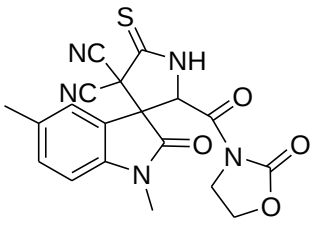
Major diastereoisomer **4a**: white solid. mp 151-153 °C; ^{1}H NMR (300 MHz, DMSO): δ 12.33 (br, 1H), 7.26-7.62 (m, 4H), 5.77 (s, 1H), 4.15-4.66 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 187.31, 173.07, 166.94, 154.19, 145.87, 133.13, 125.61, 124.25, 119.59, 112.05, 111.47, 66.76, 64.73, 57.87, 43.22, 31.86, 28.10. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{13}N_5O_4SNa$: 418.0580, found: 418.0583.

Minor diastereoisomer **4a'**: ^{1}H NMR (300 MHz, DMSO): δ 12.33 (br, 1H), 7.13-7.25 (m, 4H), 5.63 (s, 1H), 3.85-4.11 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 187.31, 169.38, 165.79, 155.41, 144.20, 132.67, 126.88, 124.88, 123.68, 112.05, 111.32, 68.75, 65.08, 59.15, 43.69, 31.86, 28.10.



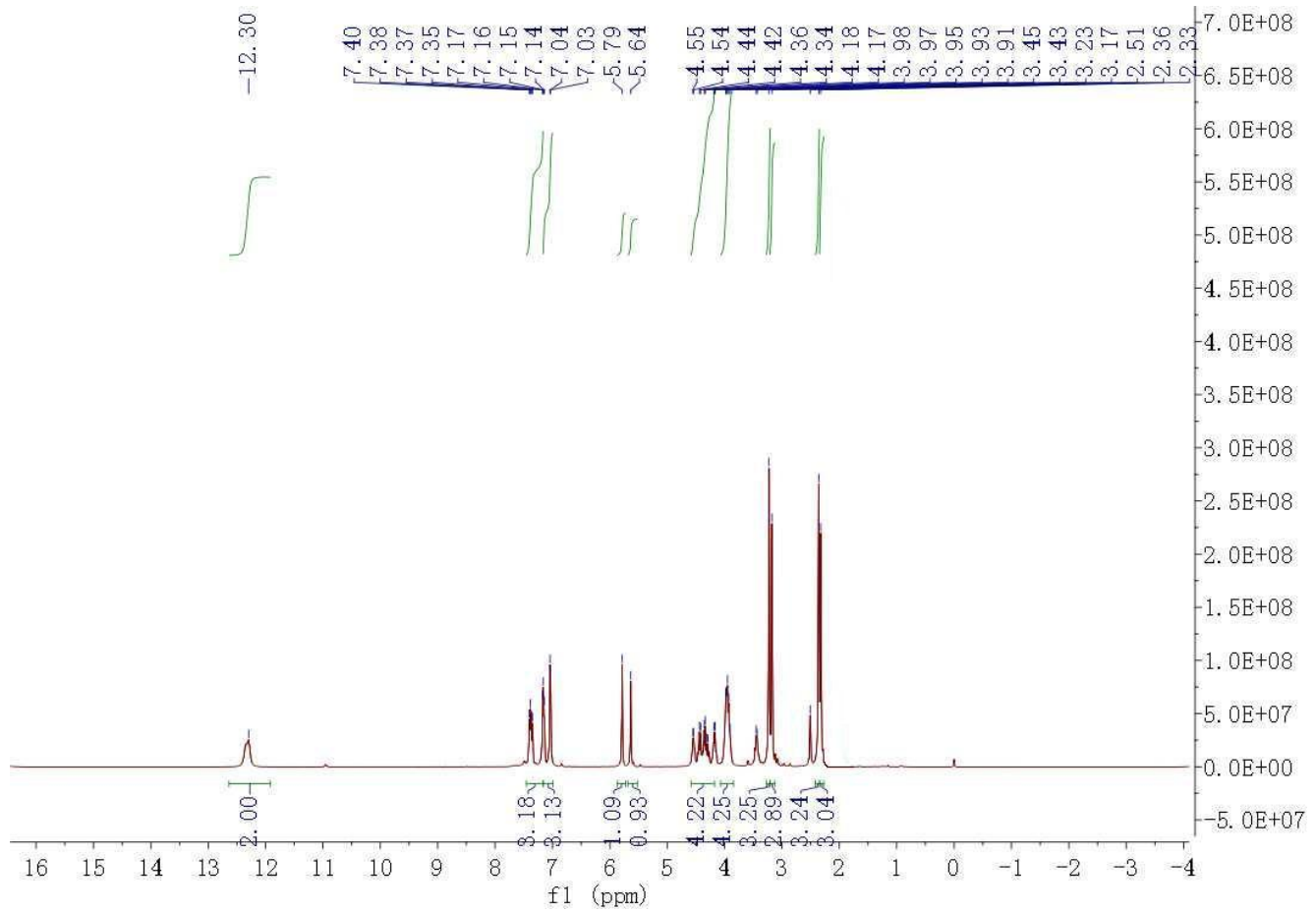


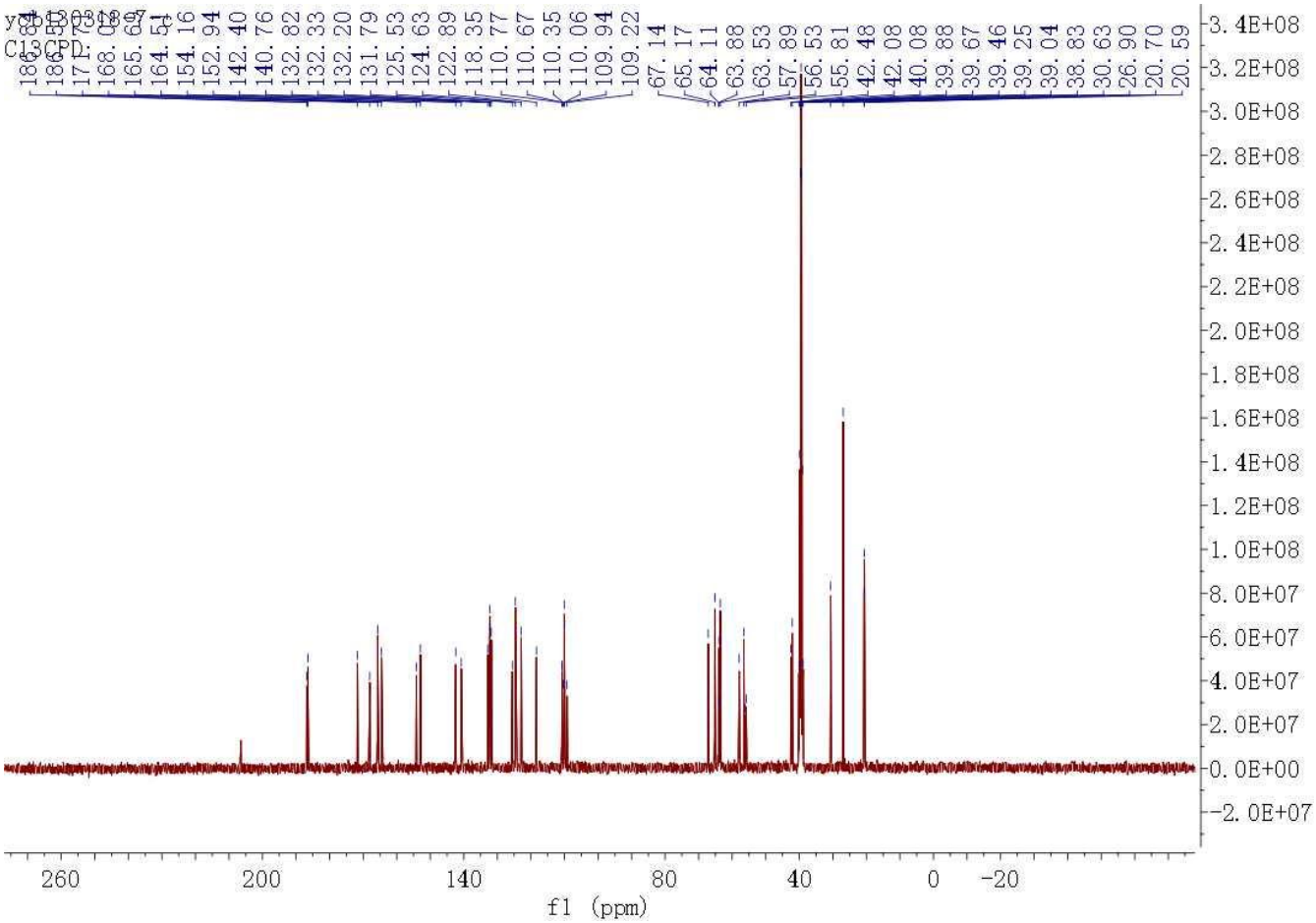
1,5-Dimethyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4', 4'-dicarbonitrile



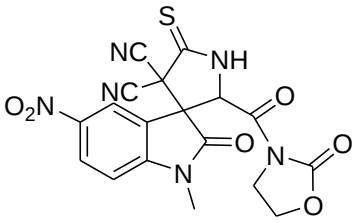
Major diastereoisomer **4b**: white solid. mp 165-168 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.30 (br, 1H), 7.16-7.45 (m, 3H), 5.79 (s, 1H), 4.13-4.59 (dt, J = 8.0 Hz, J = 4.0 Hz, 4H), 3.23 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.50, 171.71, 165.69, 152.94, 142.40, 132.33, 132.20,124.63, 122.89, 110.67, 110.35, 110.06, 65.17, 63.53, 56.53, 55.81, 42.08, 26.90, 20.59. HRMS calculated $[M+Na]^{+}$ for $C_{19}H_{15}N_5O_4SNa$: 432.0737, found: 432.0740.

Minor diastereoisomer **4b'**: ^{1}H NMR (400 MHz, DMSO): δ 12.30 (br, 1H), 7.00-7.15 (m, 3H), 5.64 (s, 1H), 3.83-4.08 (dt, J = 8.0 Hz, J = 4.0 Hz, 4H), 3.17 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.84, 168.02, 164.51, 154.16, 140.76, 132.82, 131.79, 125.53, 118.35, 110.77, 109.94, 109.22, 67.14, 63.88, 57.89, 56.11, 42.48, 30.63, 20.70.



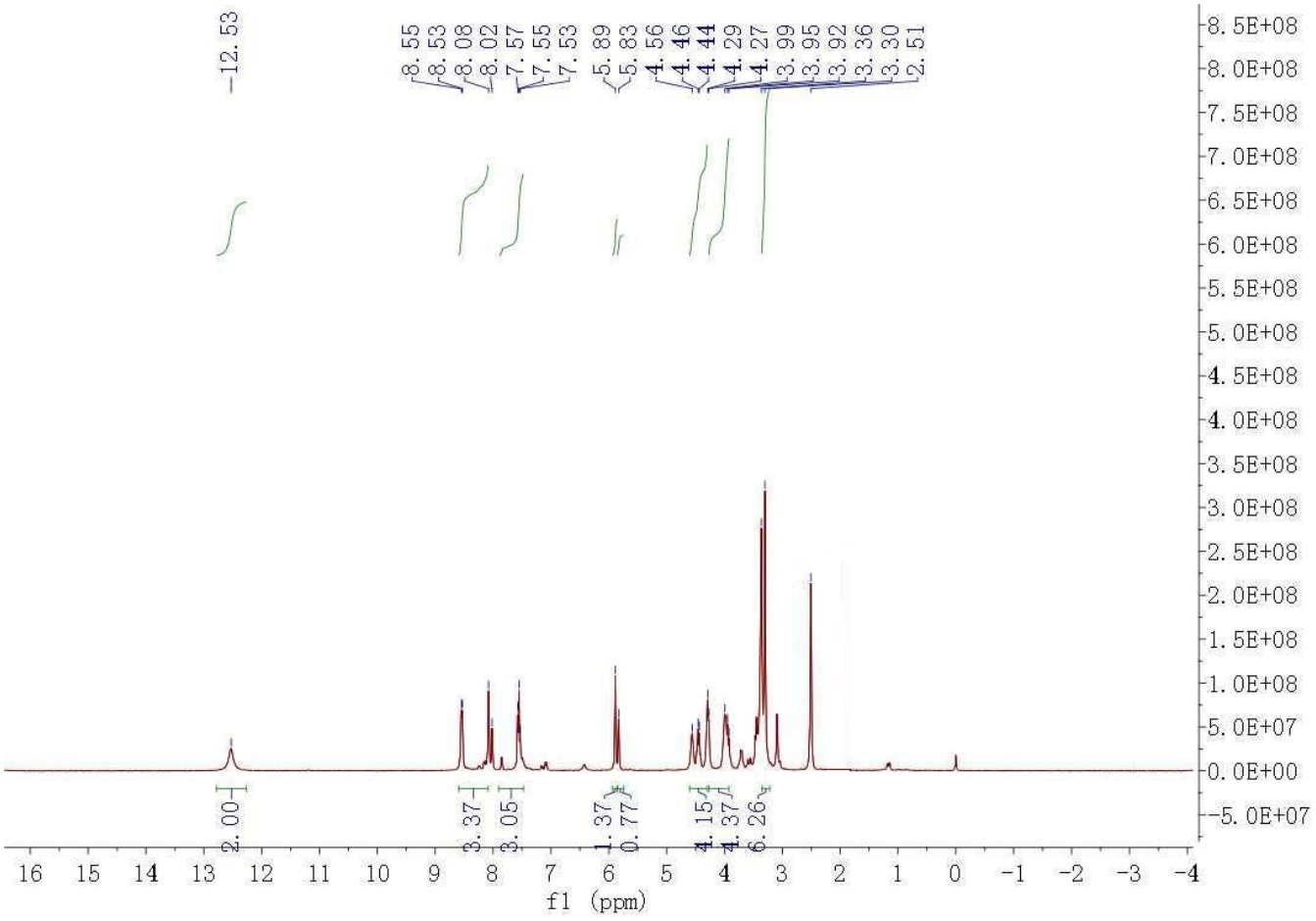


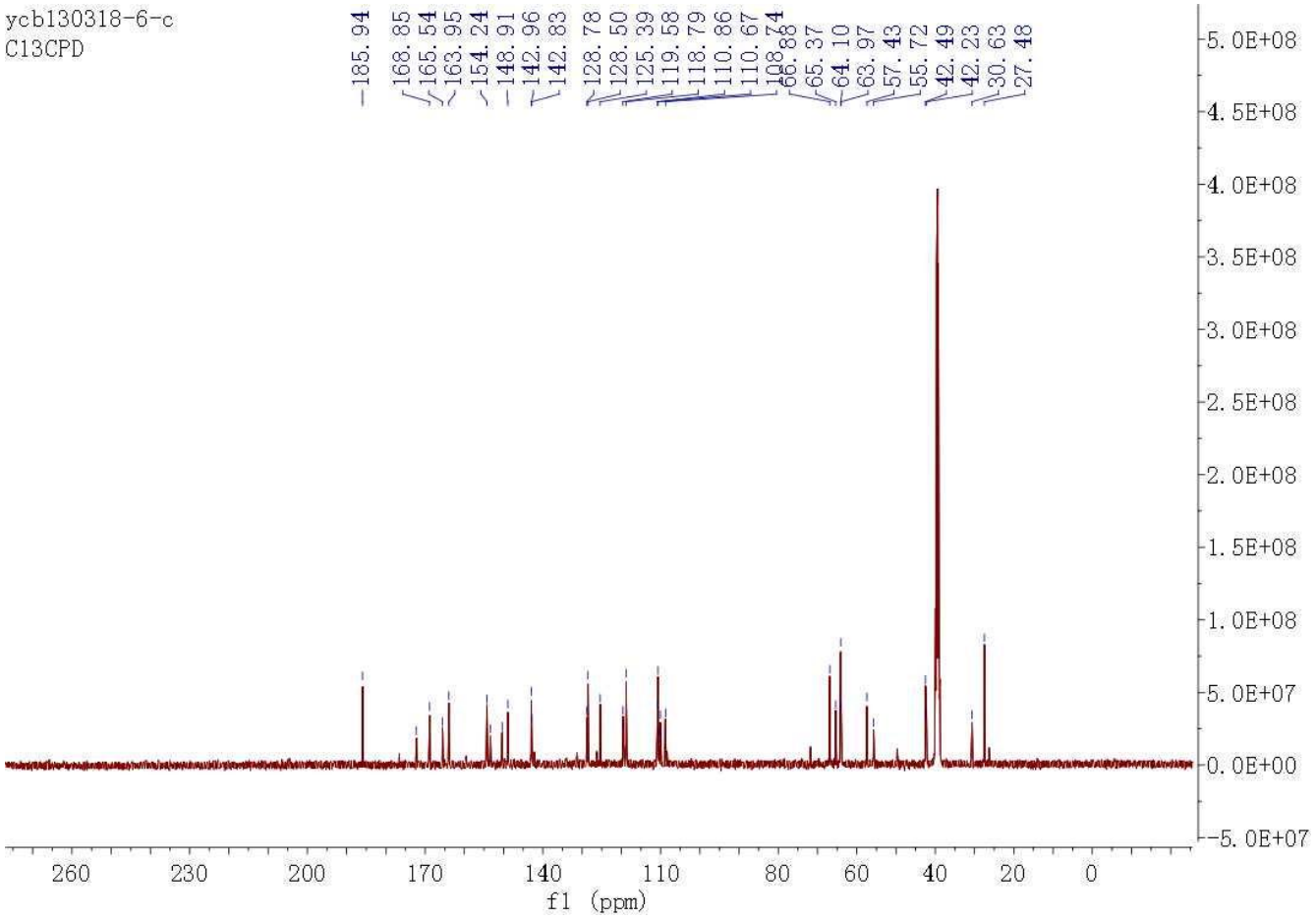
1-Methyl-5-nitro-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



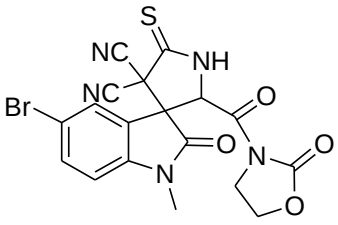
Major diastereoisomer **4c**: white solid; mp 161-163 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.53 (br, 1H), 8.03-8.57 (m, 3H), 5.89 (s, 1H), 4.26-4.62 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 185.94, 168.85, 163.95, 154.24, 148.91, 142.96, 128.50, 119.58, 118.79, 110.67, 108.74, 66.88, 64.10, 57.43, 42.49, 30.63, 27.48. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{12}N_6O_6SNa$: 463.0431, found: 463.0435.

Minor diastereoisomer **4c'**: ^{1}H NMR (400 MHz, DMSO): δ 12.53 (br, 1H), 7.42-7.88 (m, 3H), 5.83 (s, 1H), 3.91-4.23 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 185.94, 172.22, 165.54, 153.33, 150.36, 142.83, 128.78, 125.39, 119.44, 110.86, 110.05, 65.37, 63.97, 55.72, 42.23, 30.63, 27.48.



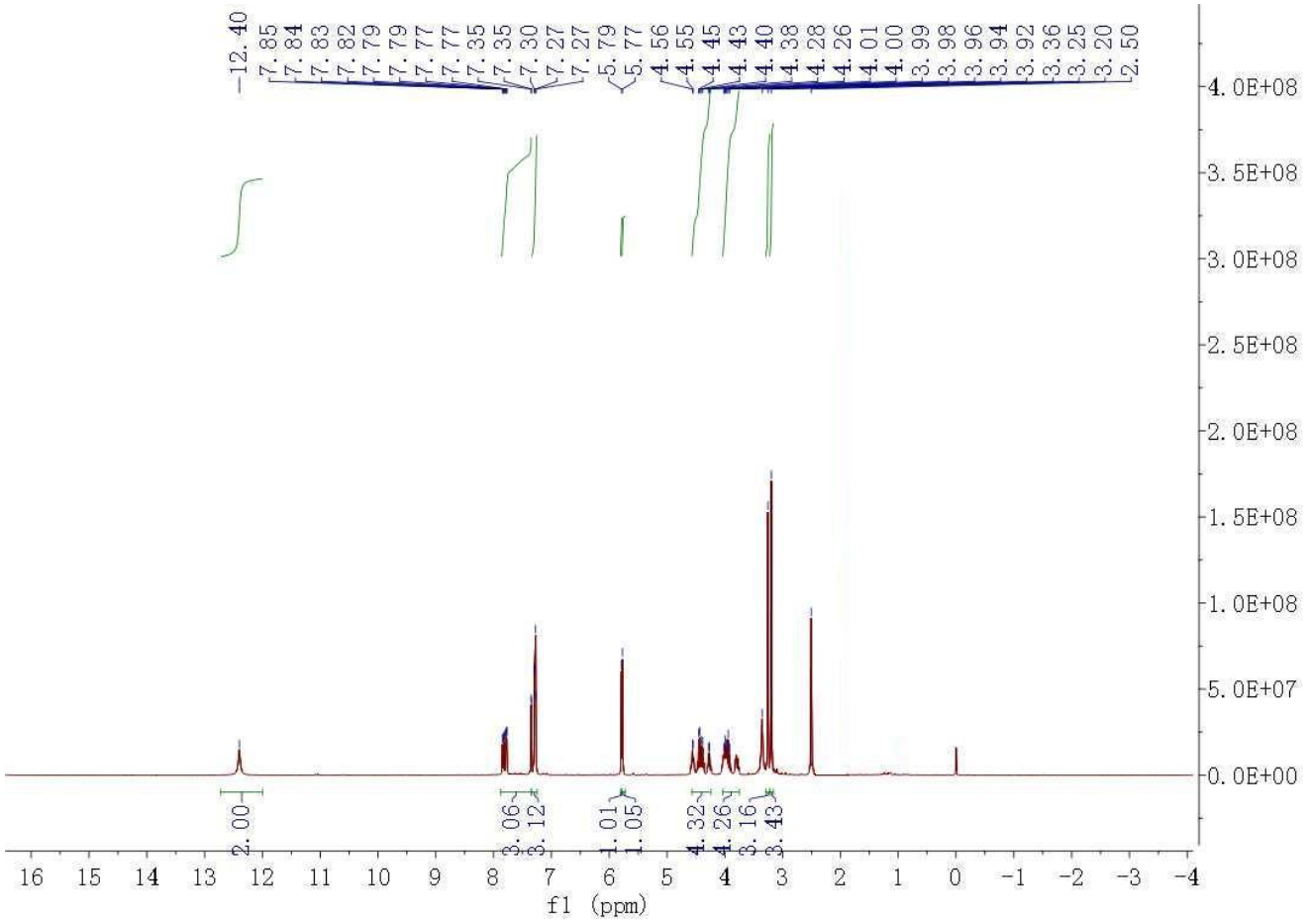


5-Bromo-1-methyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



Major diastereoisomer **4d**: white solid; mp 173-175 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.40 (br, 1H), 7.35-7.87 (m, 3H), 5.77 (s, 1H), 4.25-4.63 (dt, J = 7.7 Hz, J = 4.0 Hz, 4H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.17, 167.87, 164.19, 154.20, 142.52, 134.35, 126.86, 125.57, 114.92, 112.54, 110.53, 108.92, 66.88, 63.98, 57.72, 42.48, 30.66, 27.08. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{12}BrN_5O_4SNa$: 495.9686, found: 495.9689.

Minor diastereoisomer **4d'**: ^{1}H NMR (400 MHz, DMSO): δ 12.40 (br, 1H), 7.15-7.33 (m, 3H), 5.79 (s, 1H), 3.73-4.05 (dt, J = 7.7 Hz, J = 4.0 Hz, 4H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.07, 171.28, 165.62, 153.06, 144.22, 134.78, 127.15, 120.54, 114.15, 112.25, 110.45, 110.17, 65.34, 63.80, 56.10, 42.22, 30.66, 27.12.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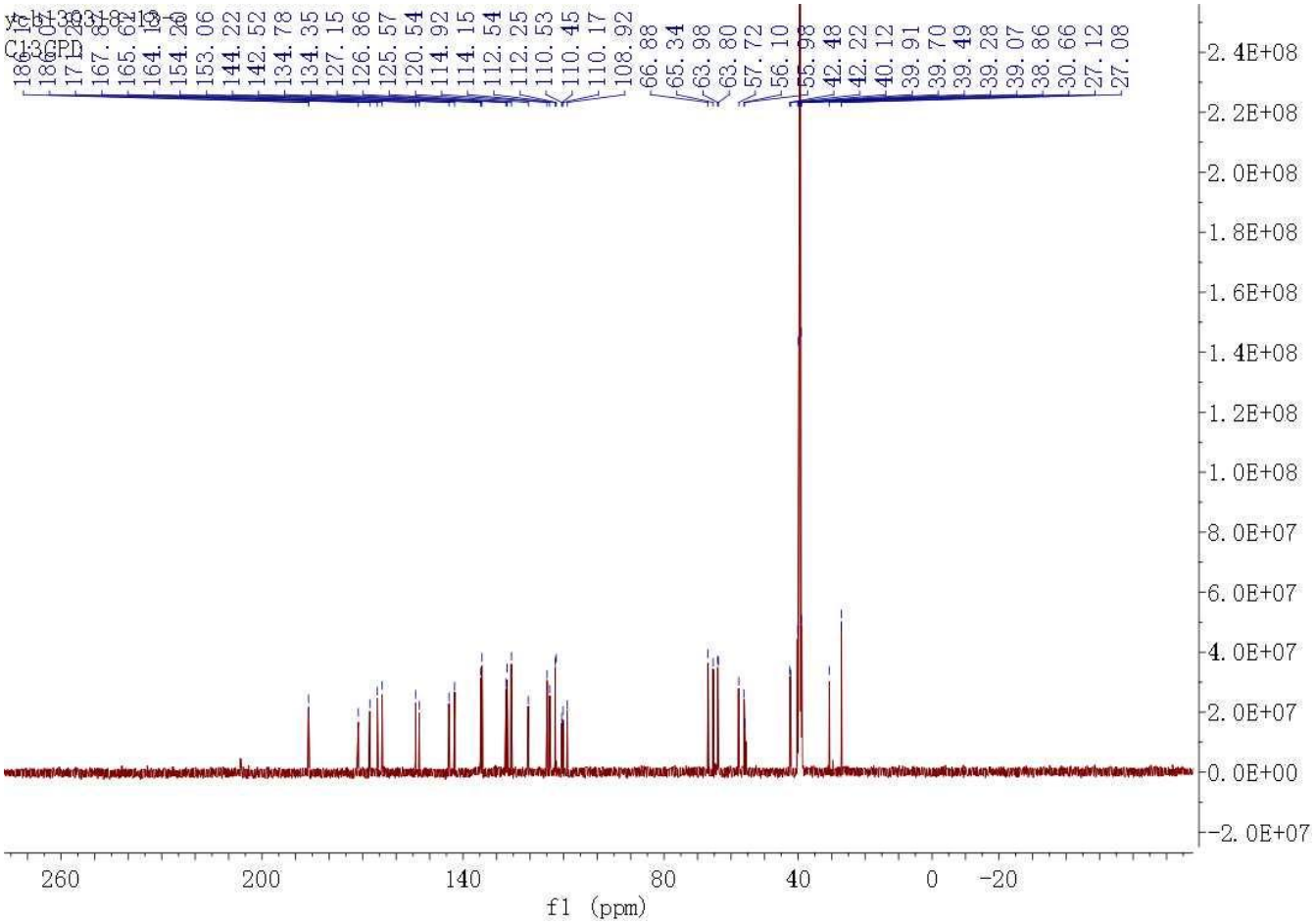
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39.49
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39.07
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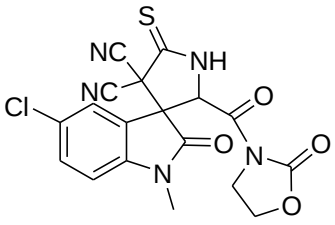
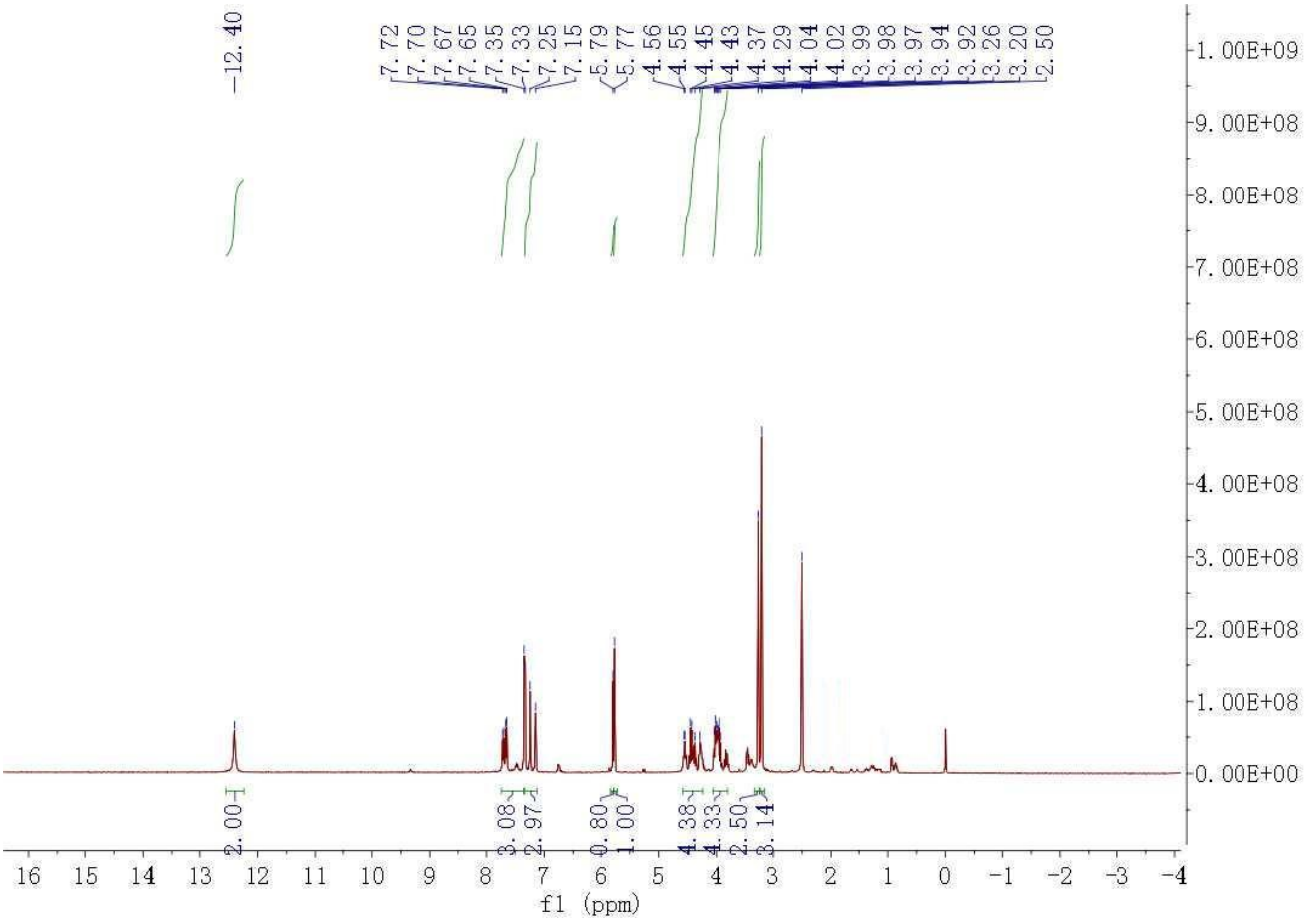
27.12
27.08
f1 (ppm)

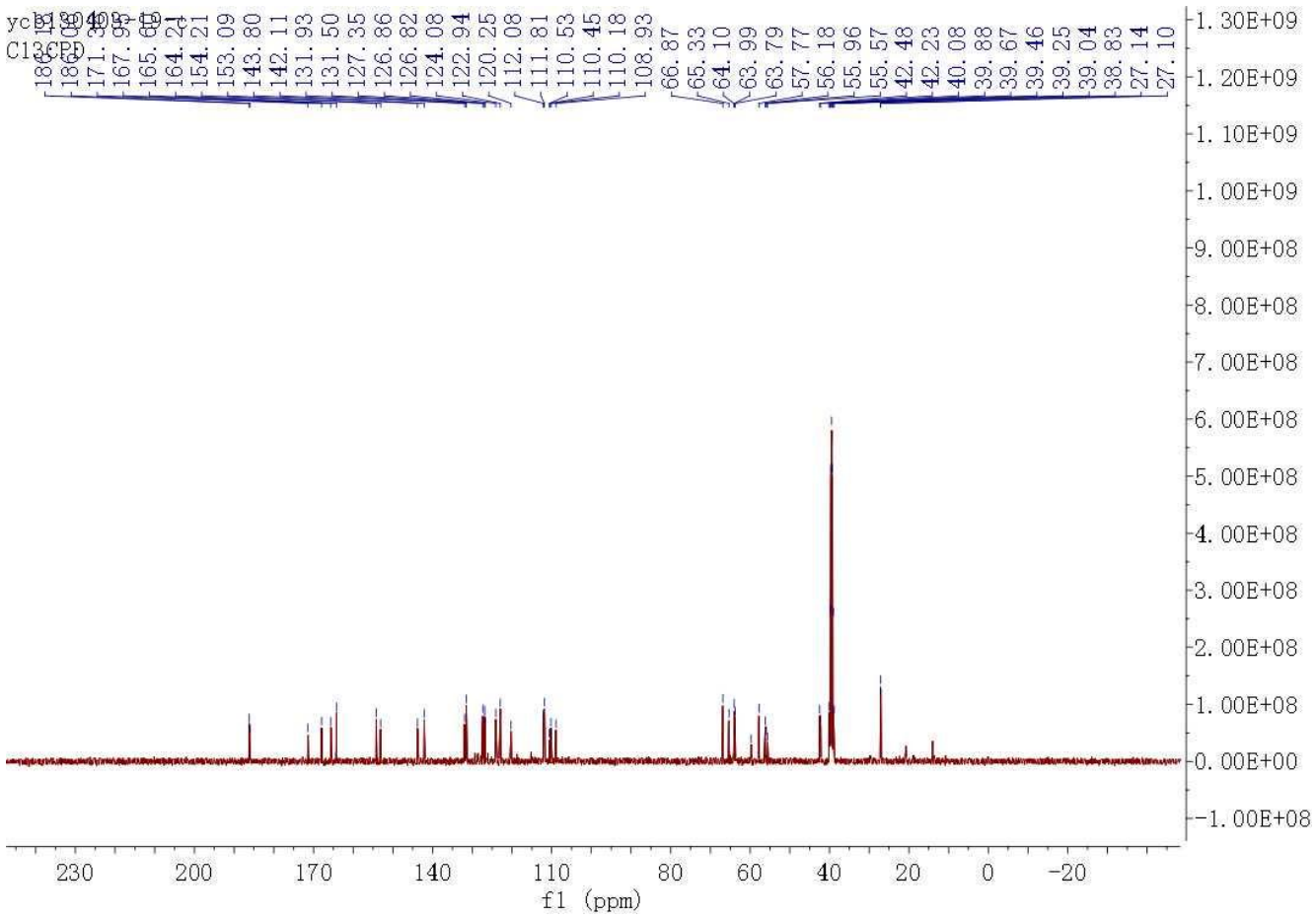
5-Chloro-1-methyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



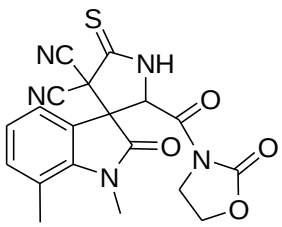
Major diastereoisomer **4e**: white solid; mp 158-161 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.40 (br, 1H), 7.34-7.78 (m, 3H), 5.77 (s, 1H), 4.24-4.59 (dt, J = 8.2 Hz, J = 4.2 Hz, 4H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.18, 167.95, 164.21, 154.21, 142.11, 131.50, 127.35, 126.82, 122.94, 111.81, 110.18, 66.87, 63.99, 57.77, 55.96, 42.48, 27.10. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{12}ClN_5O_4S$: 452.0191, found: 452.0195.

Minor diastereoisomer **4e'**: ^{1}H NMR (400 MHz, DMSO): δ 12.40 (br, 1H), 7.11-7.31 (m, 3H), 5.79 (s, 1H), 3.75-4.07 (dt, J = 8.2 Hz, J = 4.2 Hz, 4H), 3.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.06, 171.38, 165.60, 153.09, 143.80, 131.93, 126.84, 124.08, 112.08, 110.45, 108.93, 65.33, 63.79, 56.18, 55.57, 42.23, 27.14.



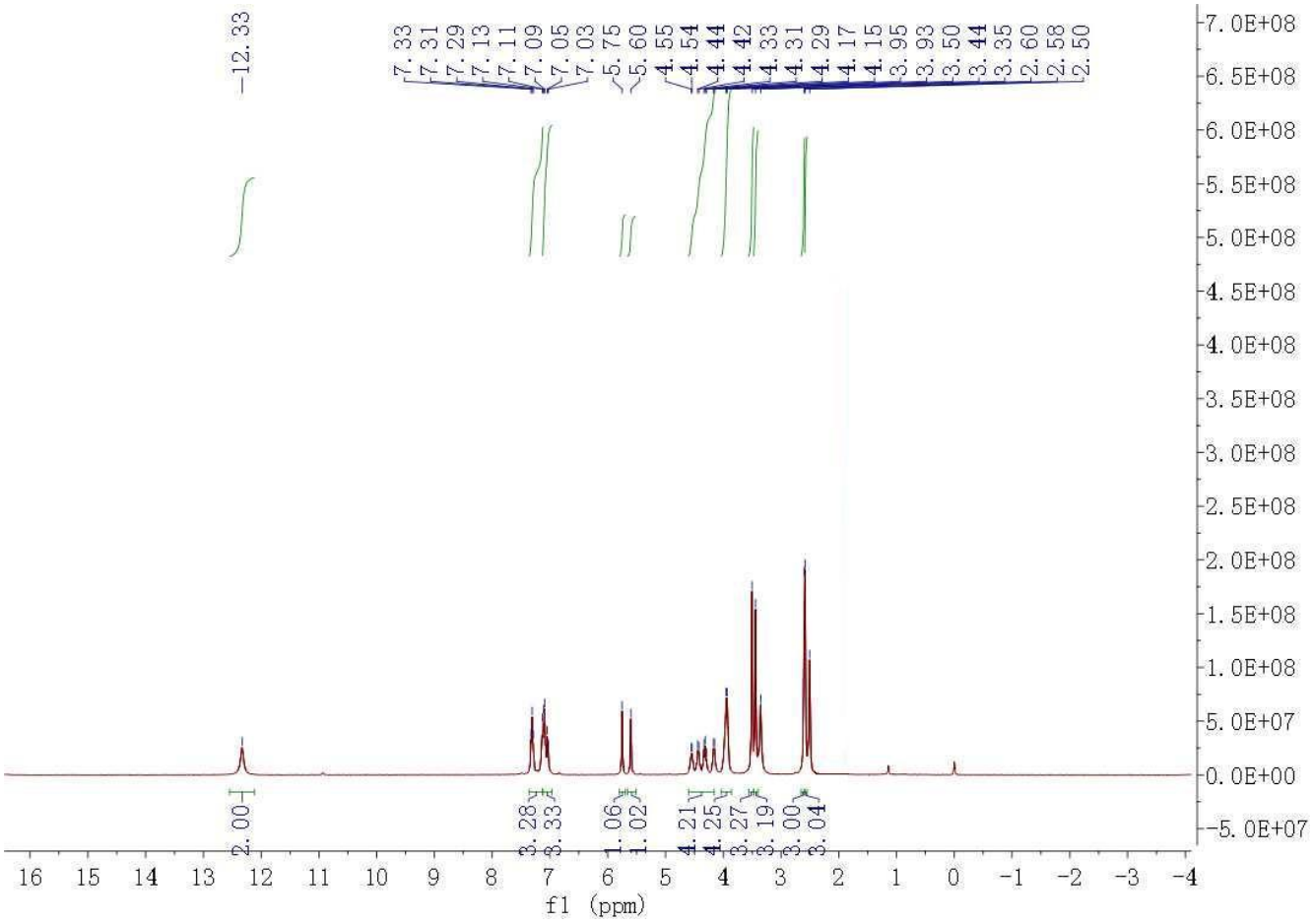


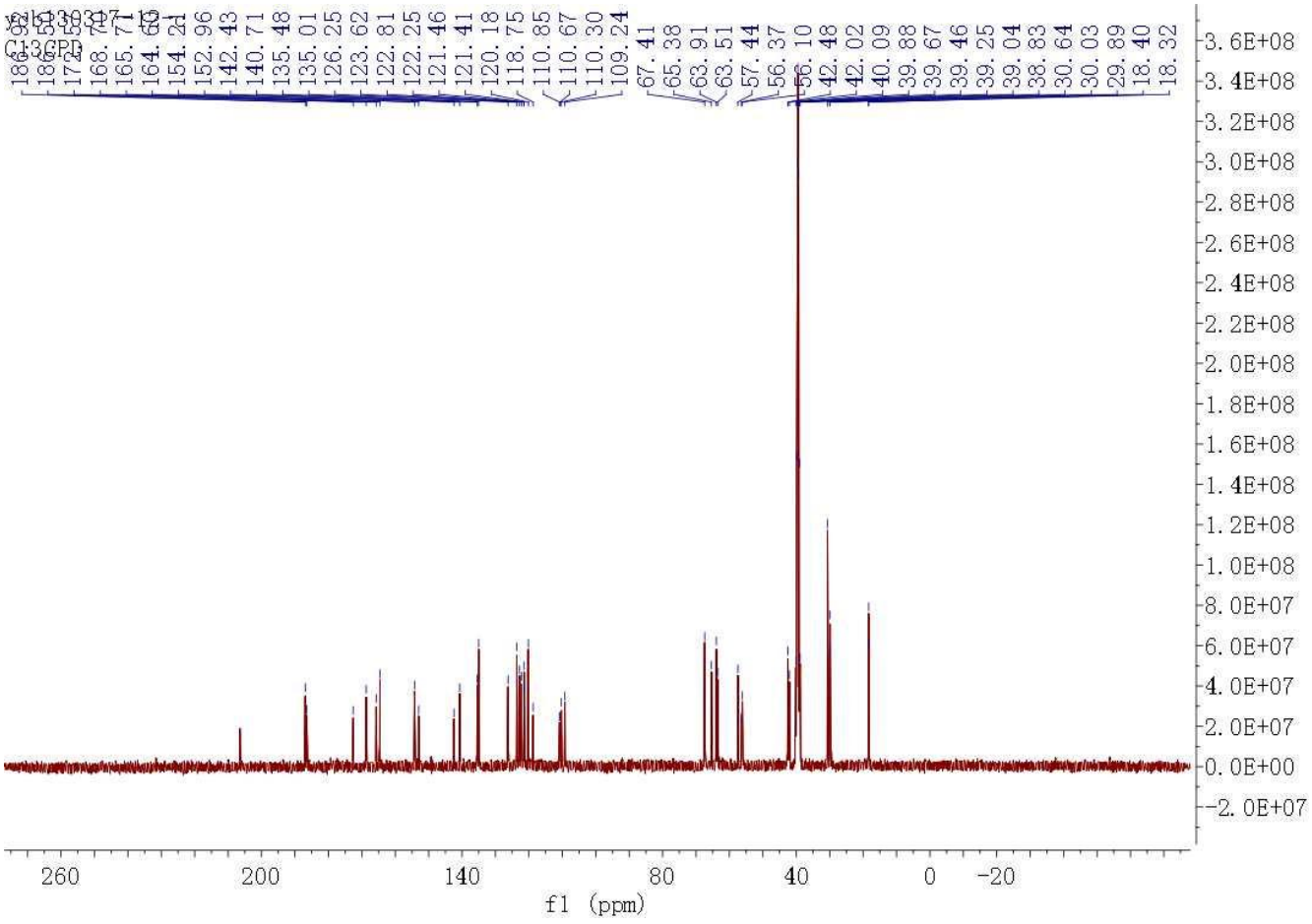
1,7-Dimethyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4', 4'-dicarbonitrile



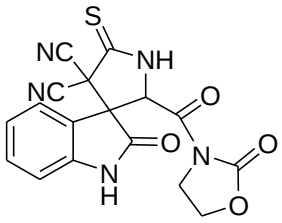
Major diastereoisomer **4f**: white solid; mp 166-168 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.33 (br, 1H), 7.13-7.36 (m, 3H), 5.75 (s, 1H), 4.13-4.61 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H), 3.50 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.92 , 168.70 , 164.60, 154.21, 140.71, 135.01, 123.62, 122.81, 121.41, 120.18, 110.30, 109.24, 67.41, 63.91, 57.44, 42.48, 30.64, 29.89, 18.32. HRMS calculated $[M+Na]^{+}$ for $C_{19}H_{15}N_5O_4SNa$: 432.0737, found: 432.0741.

Minor diastereoisomer **4f'**: ^{1}H NMR (400 MHz, DMSO): δ 12.33 (br, 1H), 6.85-7.11 (m, 3H), 5.60 (s, 1H), 3.76-4.08 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H), 3.44 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.50 , 172.57, 165.71, 152.96, 142.43, 135.48, 126.25, 122.25, 121.47, 118.75, 110.85, 110.67, 65.38, 63.51, 56.10, 42.02, 30.64, 30.03, 18.40.



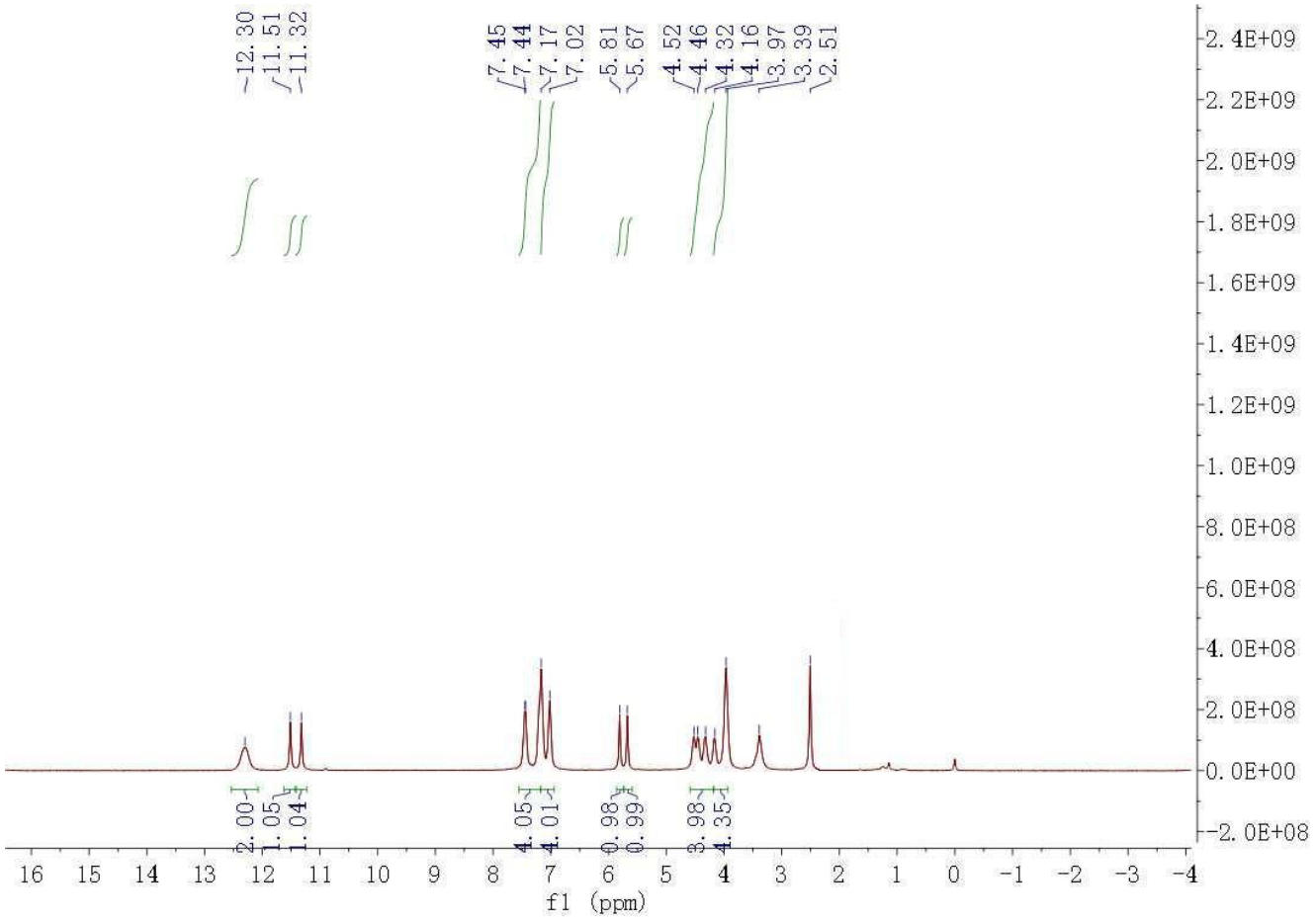


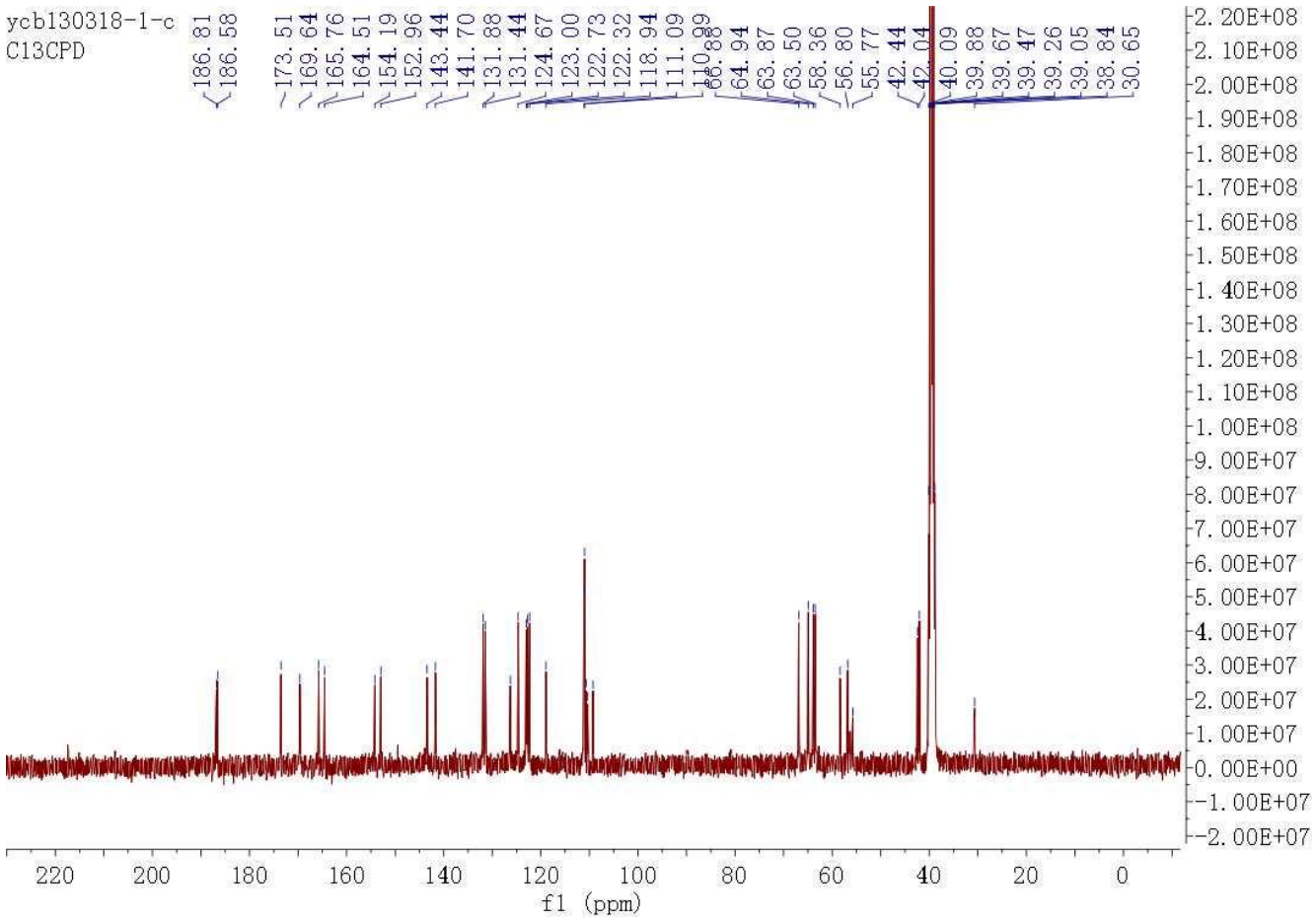
2-Oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



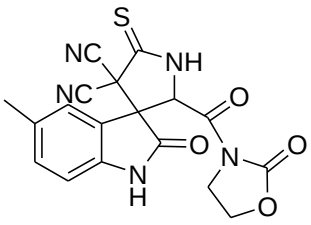
Major diastereoisomer **4g**: white solid; mp 171-173 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.30 (br, 1H), 11.51 (s, 1H), 7.17-7.55 (m, 4H), 5.81 (s, 1H), 4.26-4.60 (dt, J = 7.9 Hz, J = 4.1 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.81, 173.51, 165.76, 152.96, 141.70, 131.88, 124.67, 123.00, 122.73, 122.32, 118.94, 110.99, 64.94, 63.87, 56.80, 42.04, 30.65. HRMS calculated $[M+Na]^{+}$ for $C_{17}H_{11}N_5O_4SNa$: 404.0424, found: 404.0428.

Minor diastereoisomer **4g'**: ^{1}H NMR (400 MHz, DMSO): δ 12.30 (br, 1H), 11.32 (s, 1H), 6.93-7.17 (m, 4H), 5.67 (s, 1H), 3.74-4.60 (dt, J = 7.9 Hz, J = 4.1 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.58, 169.64, 164.51, 154.19, 143.44, 131.44, 126.29, 123.00, 122.73, 122.32, 118.94, 111.09, 66.88, 63.87, 58.36, 42.44, 30.65.



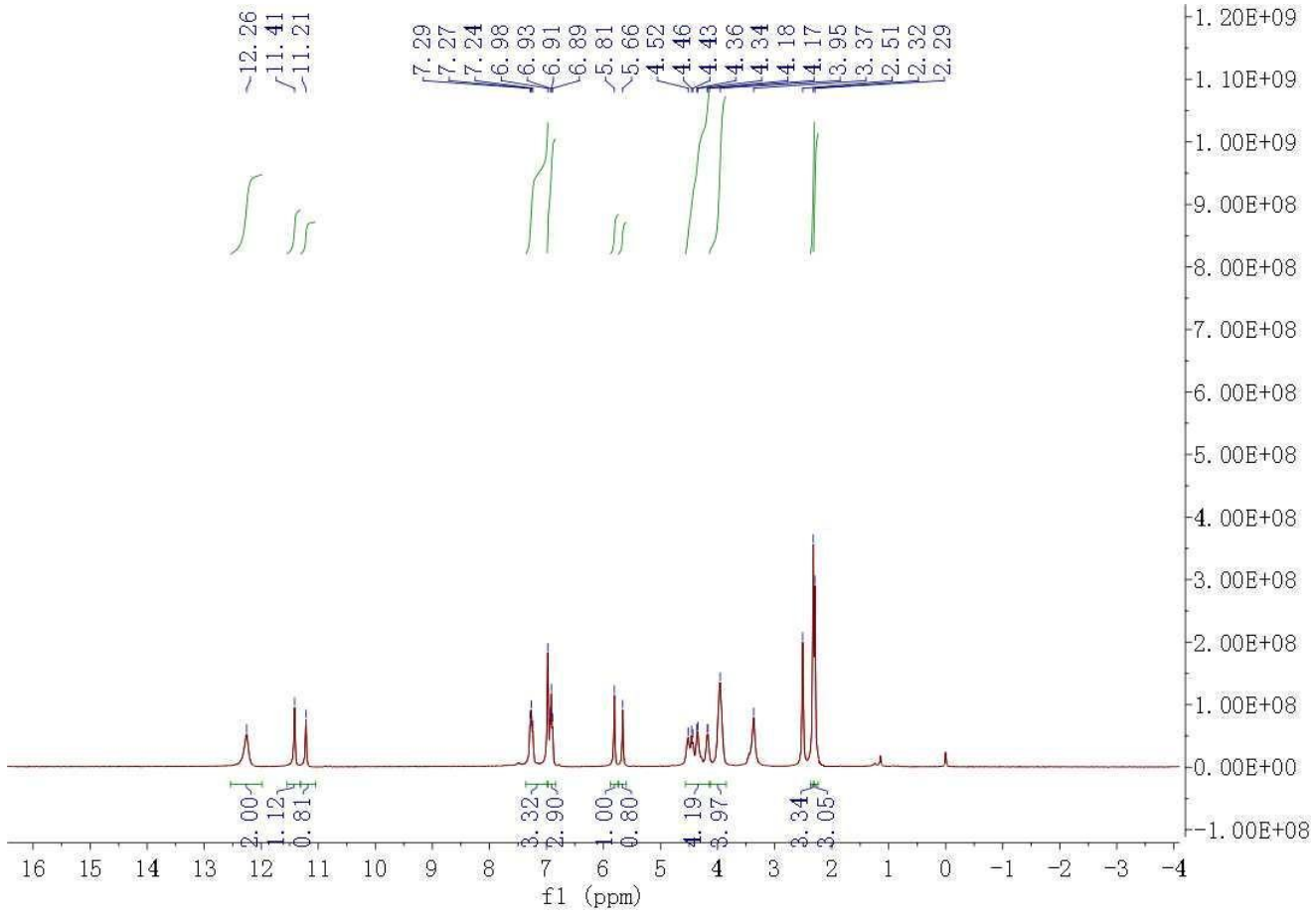


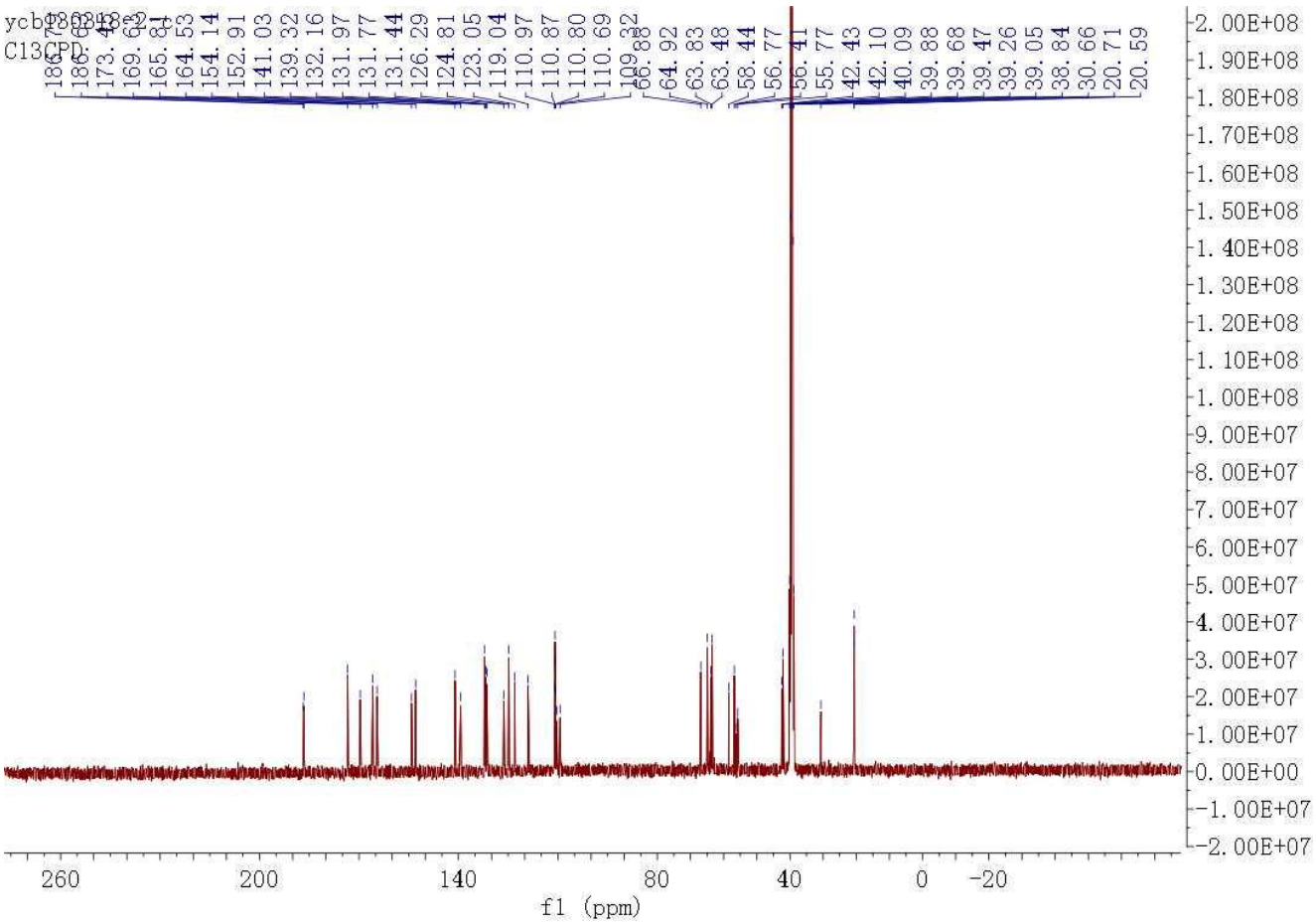
5-Methyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



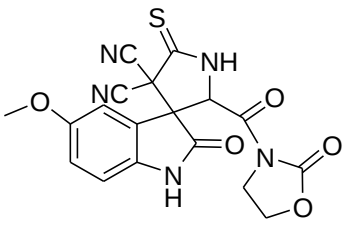
Major diastereoisomer **4h**: white solid; mp 175-178 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.26 (br, 1H), 11.41 (s, 1H), 6.98-7.38 (m, 3H), 5.81 (s, 1H), 4.17-4.59 (dt, J = 8.0 Hz, J = 4.2 Hz, 4H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.63, 173.45, 165.81, 152.91, 141.03, 132.16, 131.77, 124.81, 123.05, 110.83, 109.32, 64.92, 63.48, 56.77, 55.77, 42.10, 20.59. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{13}N_5O_4SNa$: 418.0580, found: 418.0582.

Minor diastereoisomer **4h'**: ^{1}H NMR (400 MHz, DMSO): δ 12.26 (s, 1H), 11.21 (s, 1H), 6.85-6.98 (m, 3H), 5.66 (s, 1H), 3.68-4.17 (dt, J = 8.0 Hz, J = 4.2 Hz, 4H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.79, 169.63, 164.53, 154.14, 139.32, 131.97, 131.77, 126.29, 119.04, 110.83, 110.39, 66.88, 63.83, 58.44, 56.41, 42.43, 20.71.



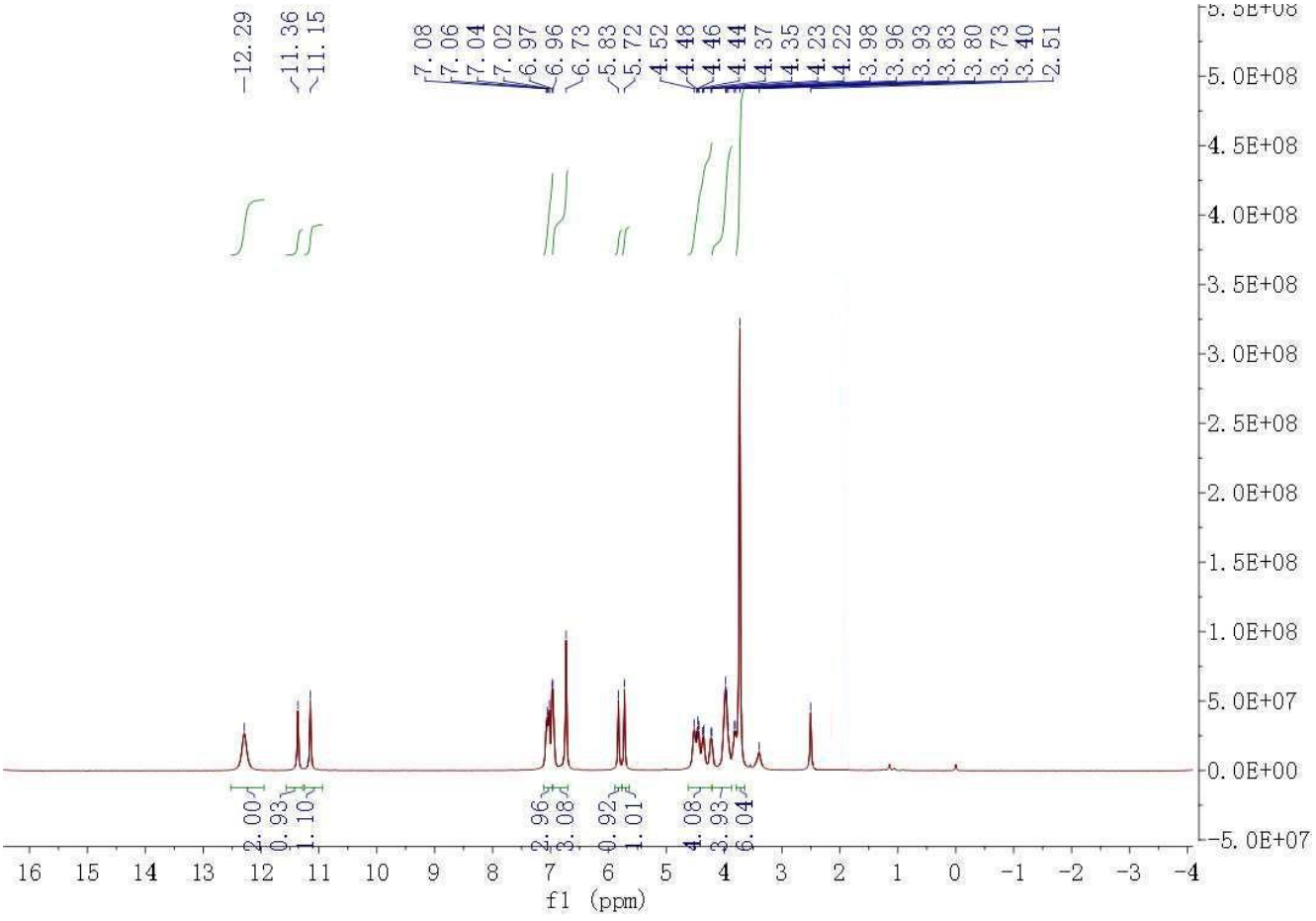


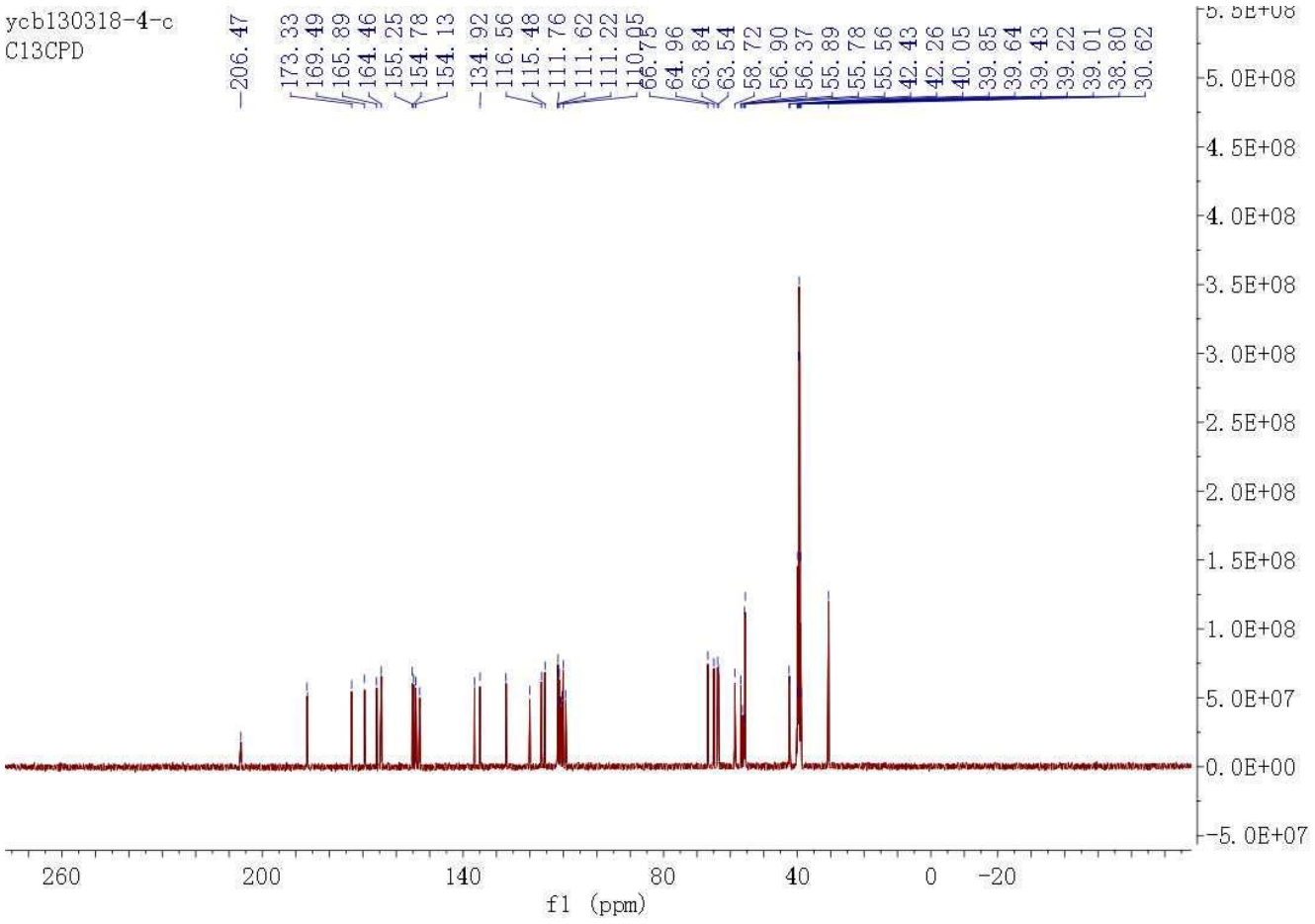
5-Methoxy-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



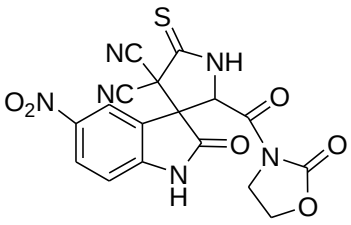
Major diastereoisomer **4i**: white solid; mp 173-175 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.29 (s, 1H), 11.15 (s, 1H), 7.01-7.16 (m, 3H), 5.72 (s, 1H), 4.23-4.57 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.70, 169.49, 164.46, 155.25, 154.13, 134.92, 127.14, 115.48, 111.62, 110.90, 110.37, 110.05, 66.75, 63.84, 58.72, 55.56, 42.43, 30.62. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{13}N_5O_5S$: 434.0530, found: 434.0532.

Minor diastereoisomer **4i'**: ^{1}H NMR (400 MHz, DMSO): δ 12.29 (s, 1H), 11.36 (s, 1H), 6.65-7.01 (m, 3H), 5.83 (s, 1H), 3.86-4.23 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.57, 173.33, 165.89, 154.78, 152.95, 136.57, 120.02, 116.02, 111.76, 111.22, 110.74, 109.28, 64.96, 63.54, 56.90, 55.78, 42.26, 30.62.



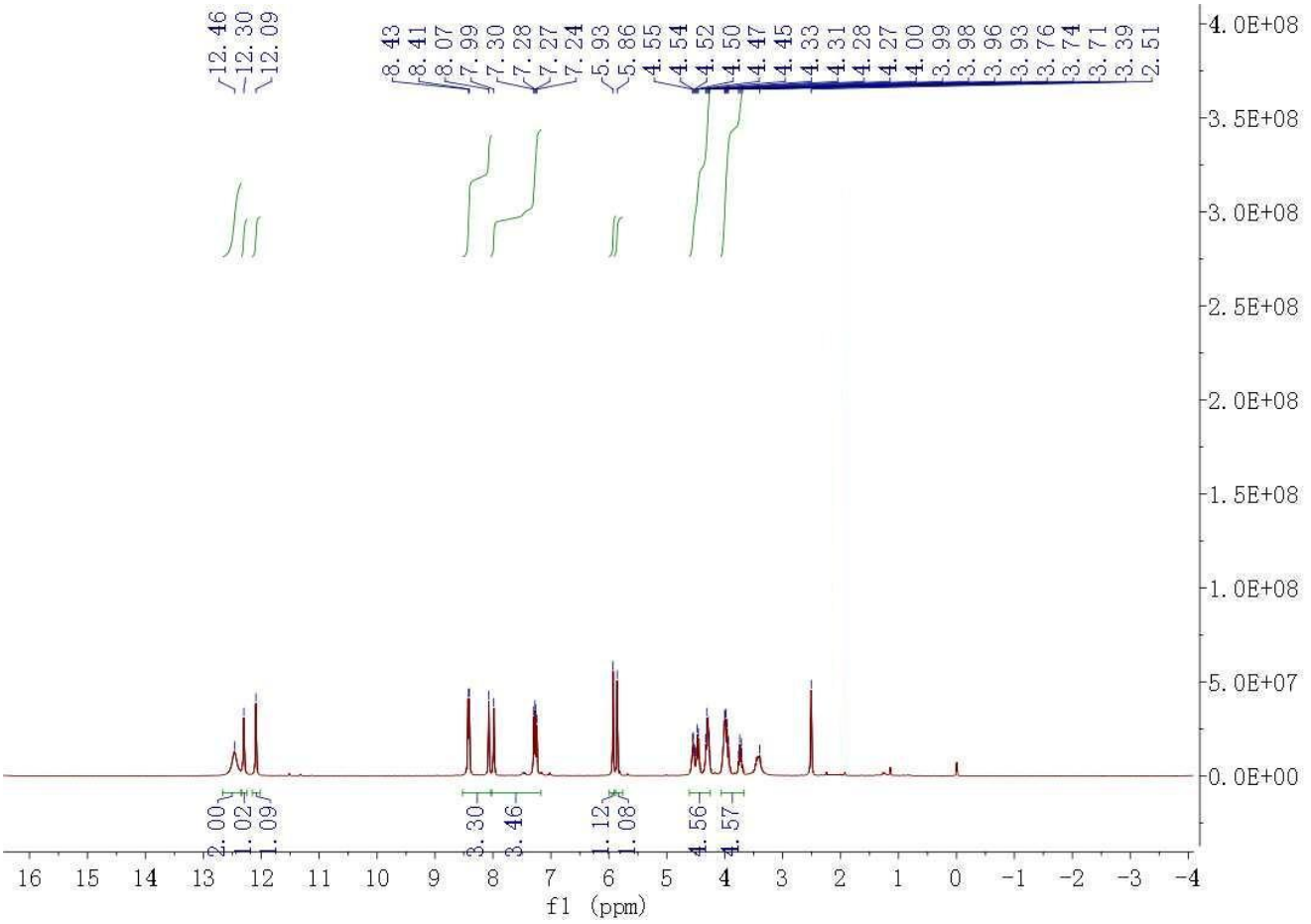


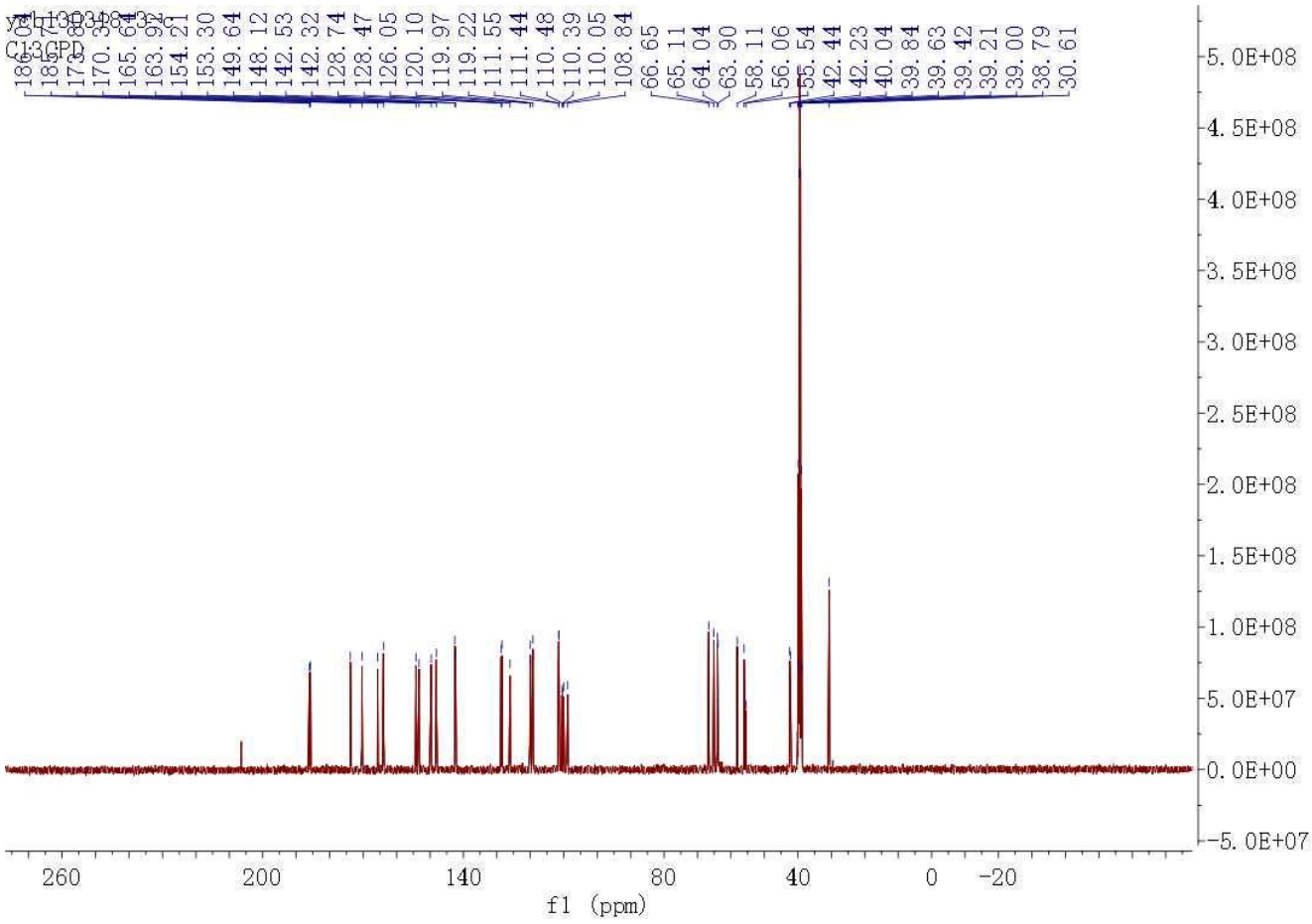
5-Nitro-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



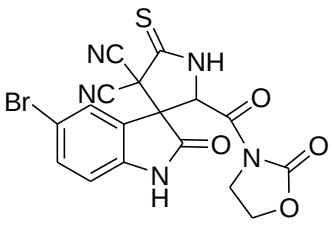
Major diastereoisomer **4j**: white solid; mp 193-195 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.46 (br, 1H), 12.09 (s, 1H), 8.49-8.03 (m, 3H), 5.93 (s, 1H), 4.17-4.62 (dt, J = 7.6 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 185.71, 173.80, 163.92, 154.21, 148.12, 142.53, 128.47, 119.97, 119.22, 111.44, 110.48, 108.84, 66.65, 64.04, 58.11, 42.44, 30.61. HRMS calculated $[M-H]^-$ for $C_{17}H_{10}N_6O_6S$: 425.0305, found: 425.0305.

Minor diastereoisomer **4j'**: ^{1}H NMR (400 MHz, DMSO): δ 12.46 (br, 1H), 12.30 (s, 1H), 7.11-8.03 (m, 3H), 5.86 (s, 1H), 3.65-4.17 (dt, J = 7.6 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.04, 170.35, 165.64, 153.30, 149.64, 142.32, 128.74, 126.05, 120.10, 111.44, 110.39, 110.05, 65.11, 63.90, 56.06, 42.23, 30.61.



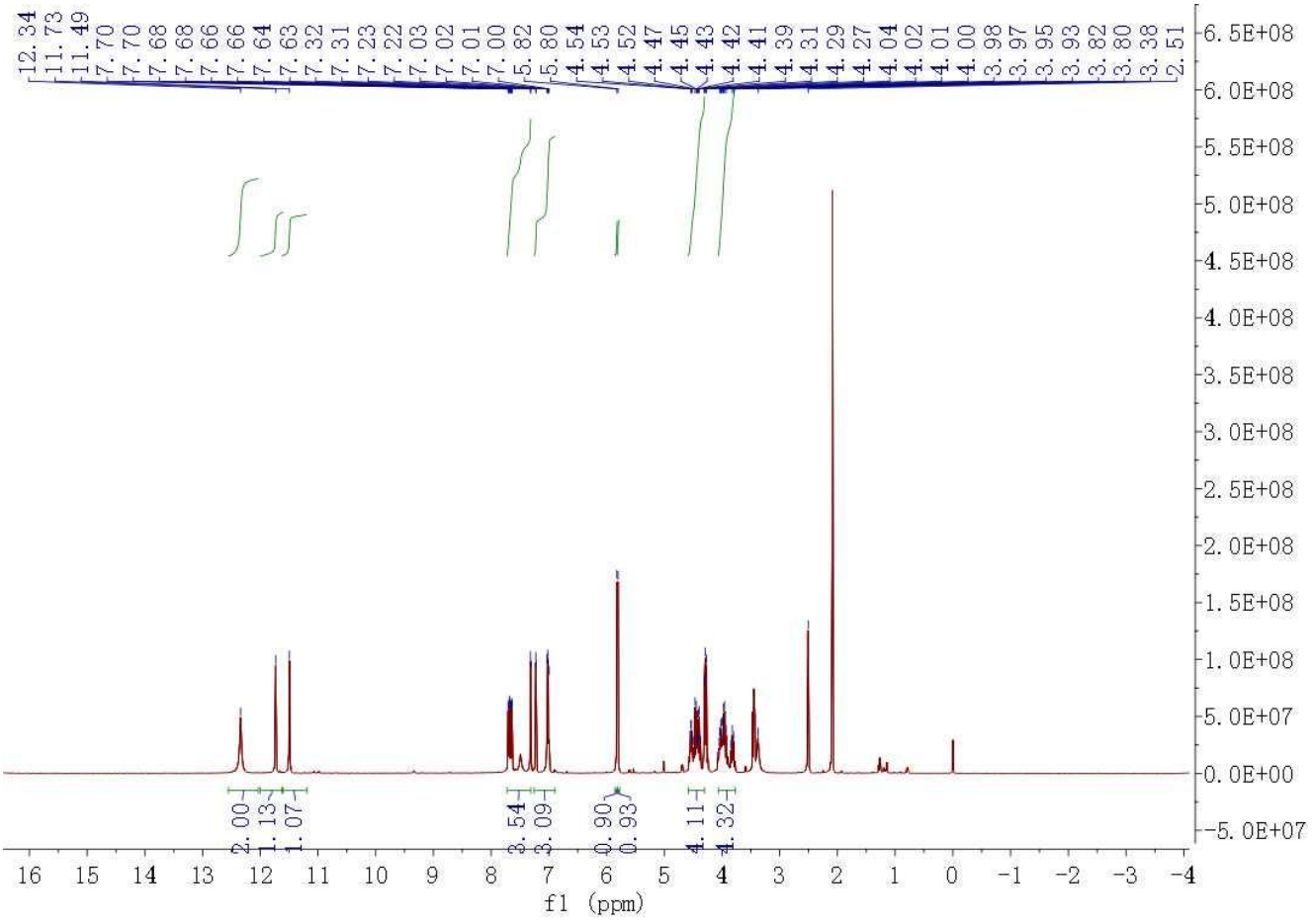


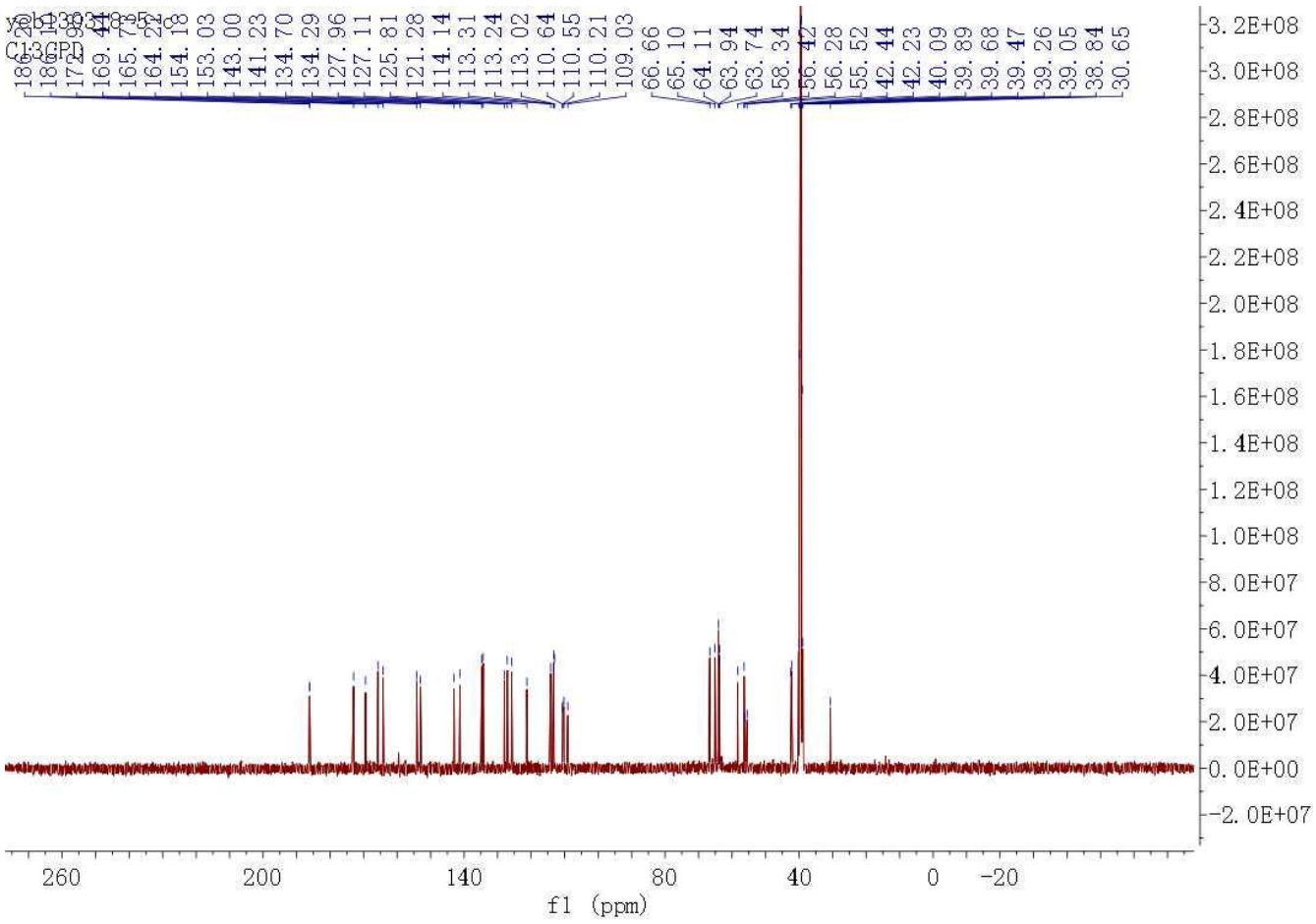
5-Bromo-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



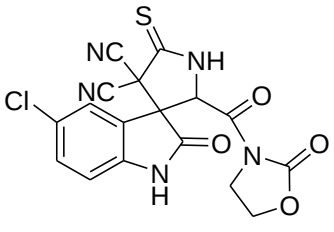
Major diastereoisomer **4k**: white solid; mp 158-160 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.34 (s, 1H), 11.49 (s, 1H), 7.31-7.77 (m, 3H), 5.80 (s, 1H), 4.28-4.59 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.10, 172.98, 165.73, 154.18, 141.23, 134.29, 127.11, 125.81, 113.24, 113.02, 110.55, 110.21, 66.66, 64.11, 56.42, 42.23, 30.65. HRMS calculated $[M+Na]^{+}$ for $C_{17}H_{10}BrN_5O_4S$: 481.9529, found: 481.9535.

Minor diastereoisomer **4k'**: ^{1}H NMR (400 MHz, DMSO): δ 12.34 (s, 1H), 11.73 (s, 1H), 6.95-7.27 (m, 3H), 5.82 (s, 1H), 3.75-4.09 (dt, J = 7.8 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.20, 169.44, 164.22, 153.03, 143.00, 134.70, 127.96, 121.28, 114.14, 113.31, 110.64, 109.03, 65.10, 63.74, 58.34, 42.44, 30.65.



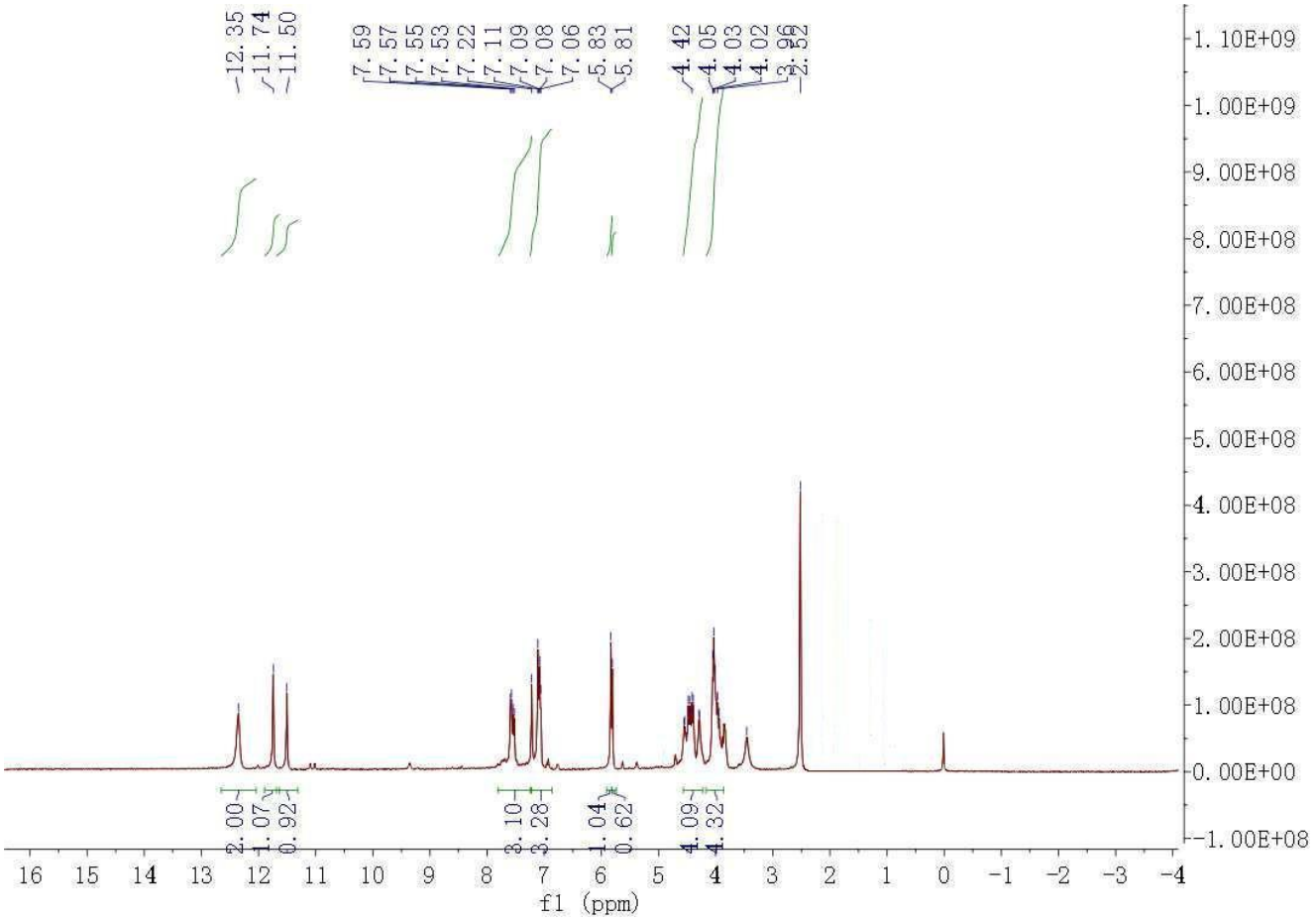


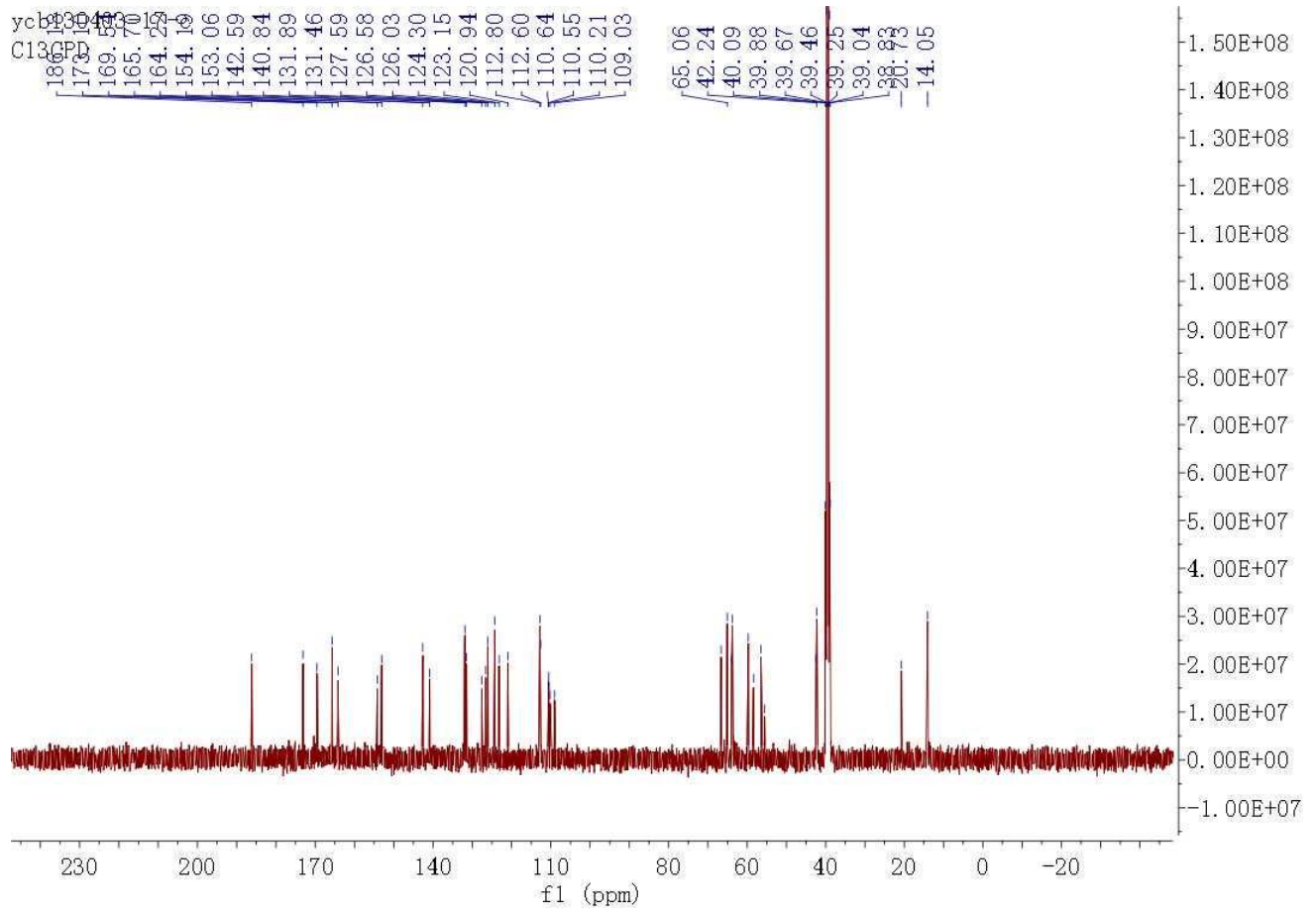
5-Chloro-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



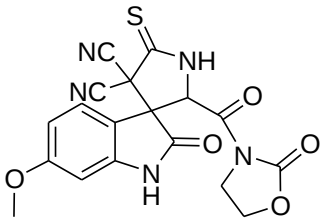
Major diastereoisomer **4l**: white solid; mp 163-165 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.35 (s, 1H), 11.74 (s, 1H), 7.20-7.63 (m, 3H), 5.83 (s, 1H), 4.19-4.59 (dt, J = 8.0 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.18, 173.10, 165.70, 153.06, 142.59, 131.89, 126.58, 124.30, 120.94, 112.80, 110.55, 109.03, 65.06, 63.74, 59.73, 42.24, 14.05. HRMS calculated $[M+Na]^{+}$ for $C_{17}H_{10}ClN_5O_4SNa$: 438.0034, found: 438.0039.

Minor diastereoisomer **4l'**: ^{1}H NMR (400 MHz, DMSO): δ 12.35 (s, 1H), 11.50 (s, 1H), 7.01-7.24 (m, 3H), 5.81 (s, 1H), 3.81-4.15 (dt, J = 8.0 Hz, J = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.10, 169.54, 164.22, 154.19, 140.84, 131.46, 127.59, 126.03, 123.15, 112.60, 110.64, 110.21, 66.63, 63.95, 56.49, 42.44, 20.73.



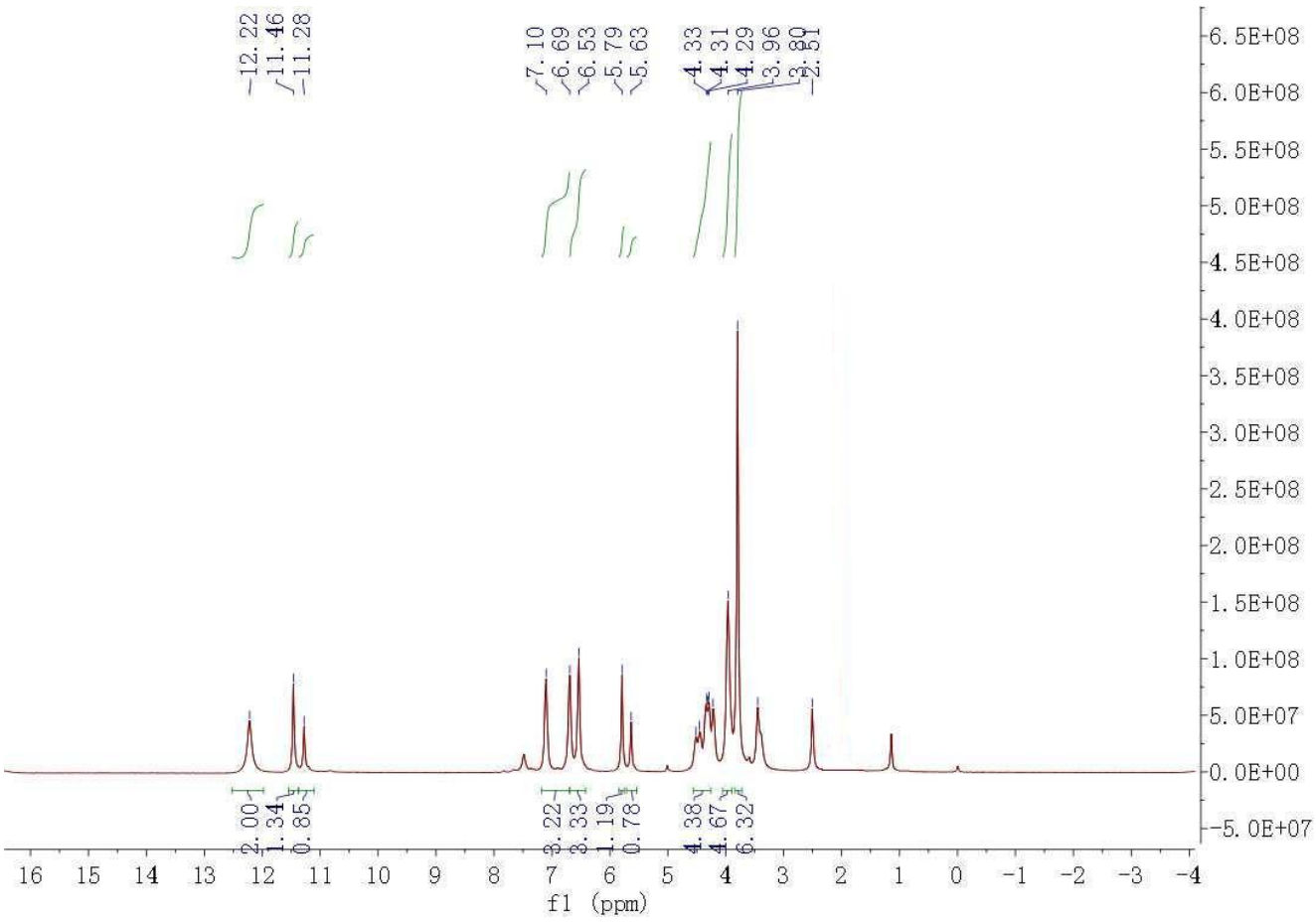


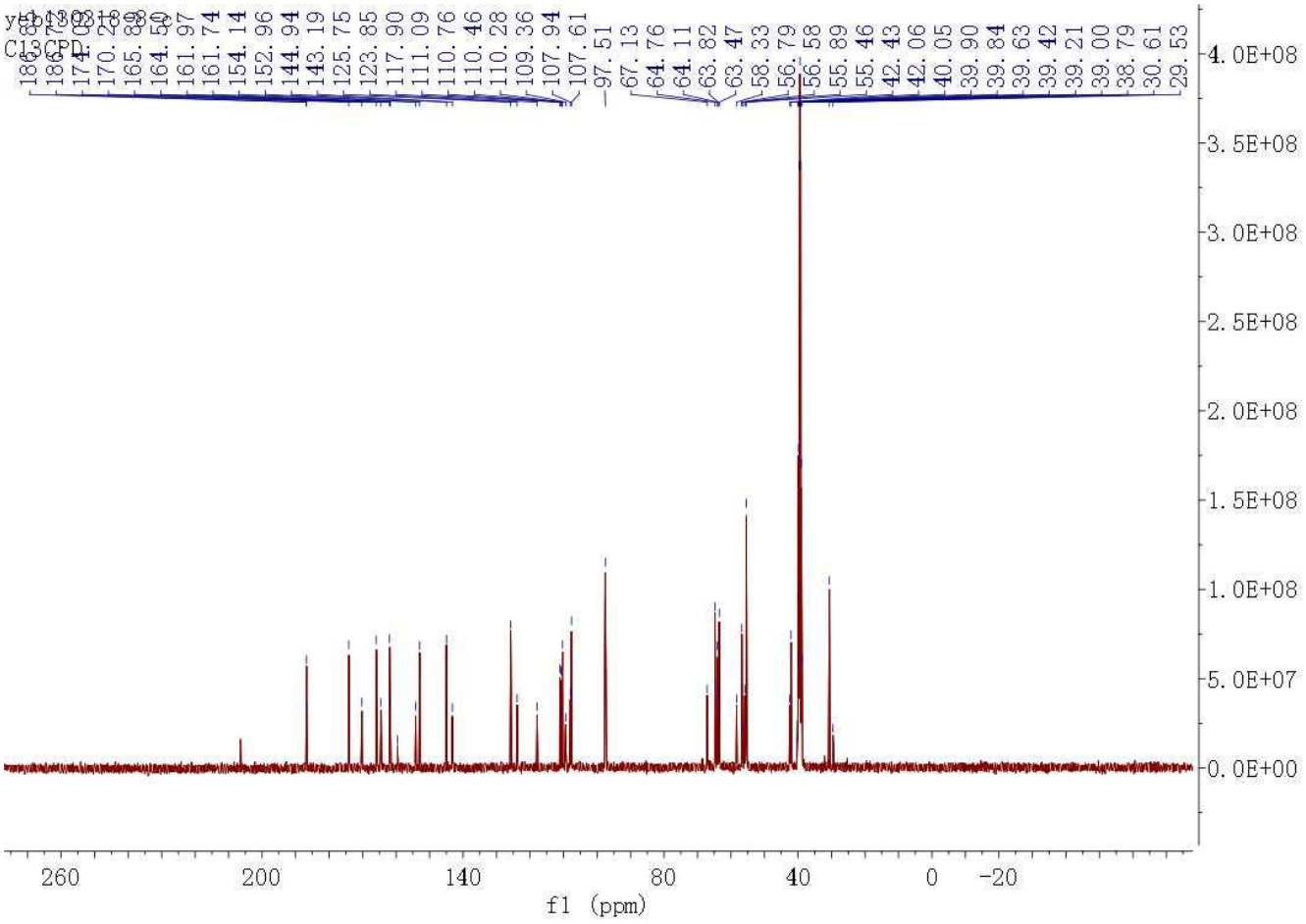
6-Methoxy-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



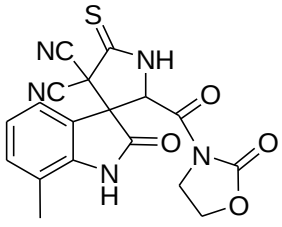
Major diastereoisomer **4m**: white solid; mp 143-145 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.22 (s, 1H), 11.46 (s, 1H), 6.70-7.20 (m, 3H), 5.79 (s, 1H), 4.23-4.58 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.72, 174.09, 165.89, 161.97, 152.96, 144.94, 125.75, 111.09, 110.28, 107.61, 97.51, 67.13, 64.76, 64.11, 55.46, 42.06, 30.61. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{13}N_5O_5SNa$: 434.0530, found: 434.0532.

Minor diastereoisomer **4m'**: ^{1}H NMR (400 MHz, DMSO): δ 12.22 (s, 1H), 11.46 (s, 1H), 6.35-6.68 (m, 3H), 5.63 (s, 1H), 3.86-4.21(dt, J = 7.8 Hz, J = 4.2 Hz, 4H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.85, 170.21, 164.50, 161.74, 154.14, 143.19, 123.85, 111.09, 110.46, 107.94, 97.51, 64.11, 63.82, 58.33, 56.79, 42.43, 29.53.



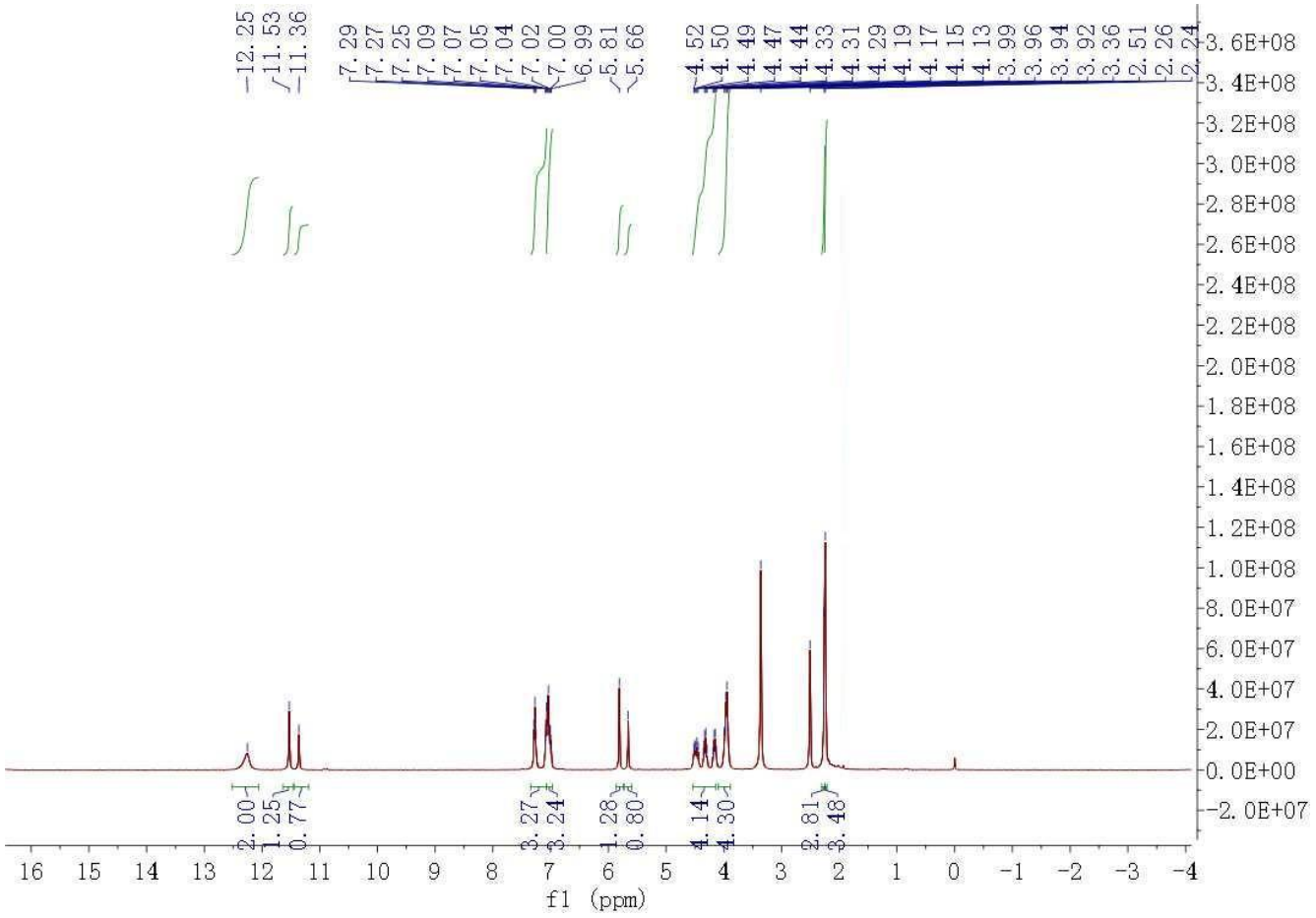


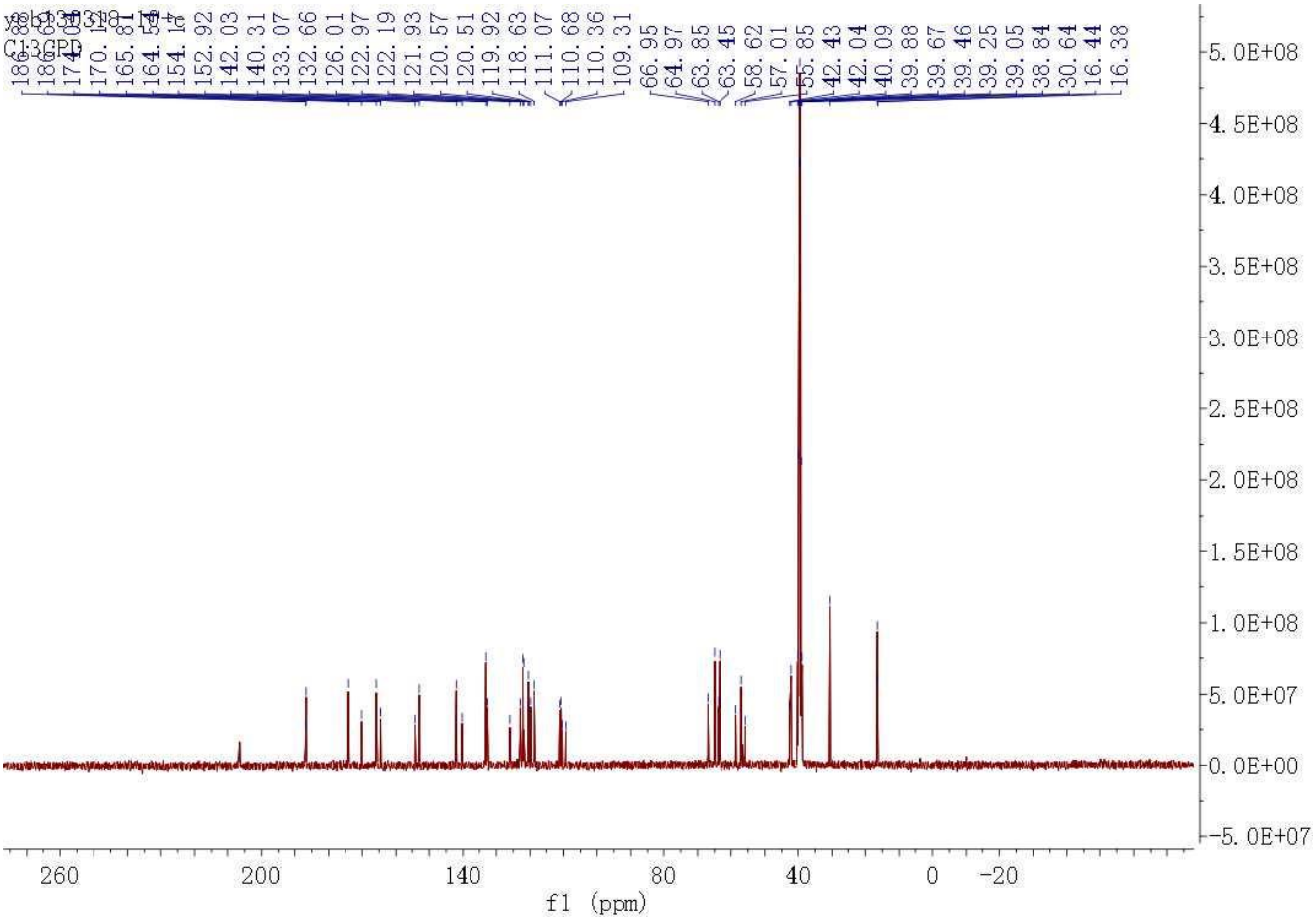
7-Methyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



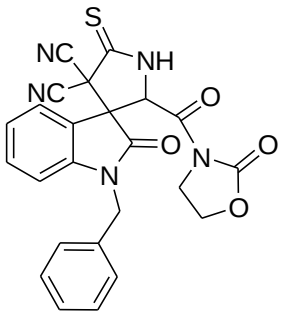
Major diastereoisomer **4n**: white solid; mp 148-151 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.25 (s, 1H), 11.53 (s, 1H), 7.07-7.34 (m, 3H), 5.81 (s, 1H), 4.15-4.56 (dt, J = 7.6 Hz, J = 4.2 Hz, 4H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.69, 174.04, 165.81, 152.92, 142.03, 133.07, 122.19, 121.93, 120.57, 118.63, 111.07, 110.68, 64.97, 63.45, 57.01, 42.04, 30.64, 16.44. HRMS calculated $[M+Na]^{+}$ for $C_{18}H_{13}N_5O_4SNa$: 418.0580, found: 418.0579.

Minor diastereoisomer **4n'**: ^{1}H NMR (400 MHz, DMSO): δ 12.25 (s, 1H), 11.36 (s, 1H), 6.98-7.05 (m, 3H), 5.66 (s, 1H), 3.88-4.11 (dt, J = 7.6 Hz, J = 4.2 Hz, 4H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 186.88, 170.12, 164.54, 154.17, 140.31, 132.66, 126.01, 122.97, 120.52, 119.92, 110.36, 109.31, 66.95, 63.85, 58.62, 42.43, 30.64, 16.38.


12.25
11.53
11.36
7.29
7.27
7.25
7.09
7.07
7.05
7.04
7.02
7.00
6.99
5.81
5.66
4.52
4.50
4.49
4.47
4.44
4.33
4.31
4.29
4.19
4.17
4.15
4.13
3.99
3.96
3.94
3.92
3.36
2.51
2.26
2.24
2.00
1.25
0.77
3.27
3.24
1.28
0.80
4.14
4.30
2.81
3.48
f1 (ppm)

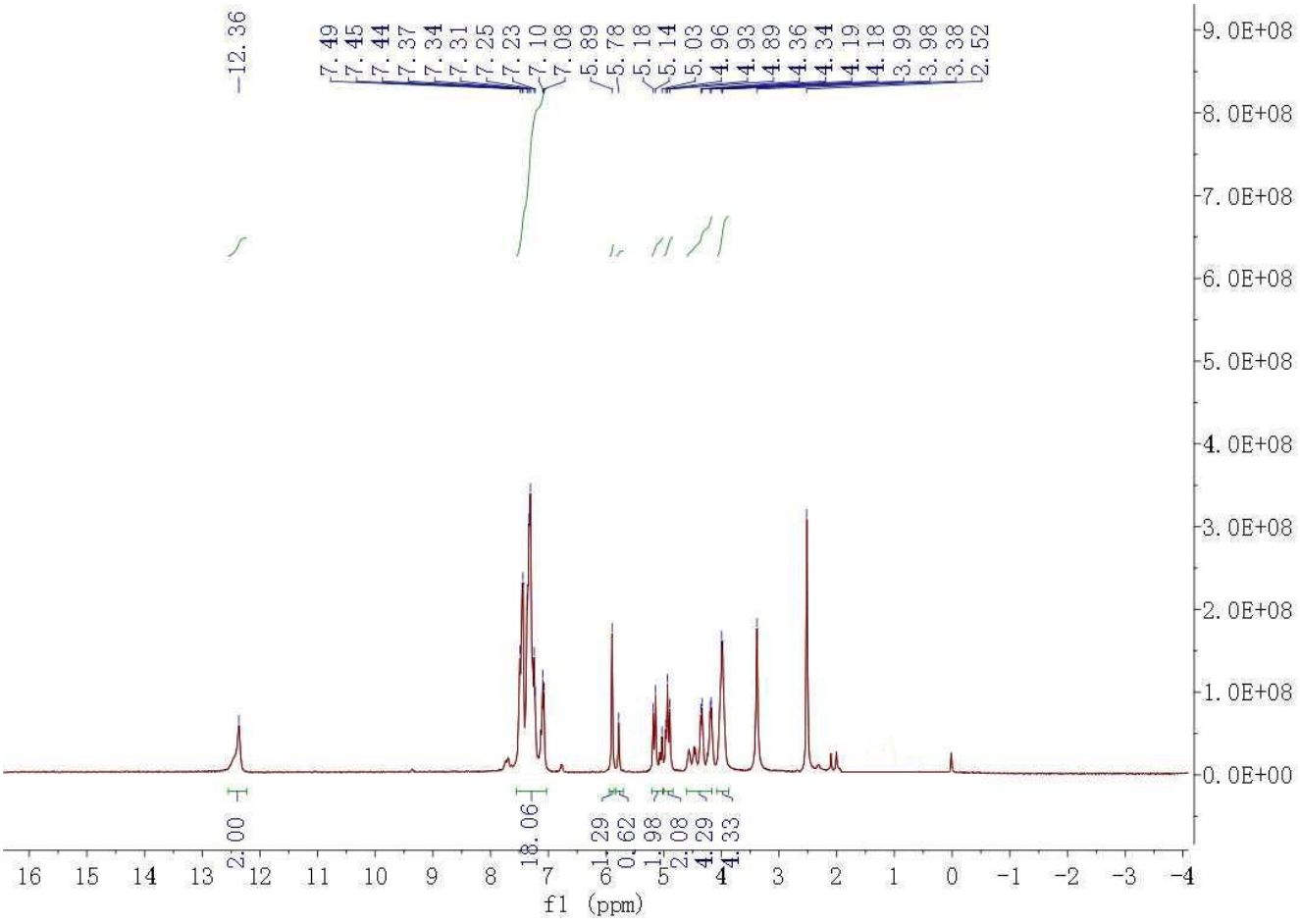

186.38
180.38
174.08
170.14
165.81
164.58
154.14
152.92
142.03
140.31
133.07
132.66
126.01
122.97
122.19
121.93
120.57
120.51
119.92
118.63
111.07
110.68
110.36
109.31
66.95
64.97
63.85
63.45
58.62
57.01
55.85
42.43
42.04
40.09
39.88
39.67
39.46
39.25
39.05
38.84
30.64
16.44
16.38
f1 (ppm)

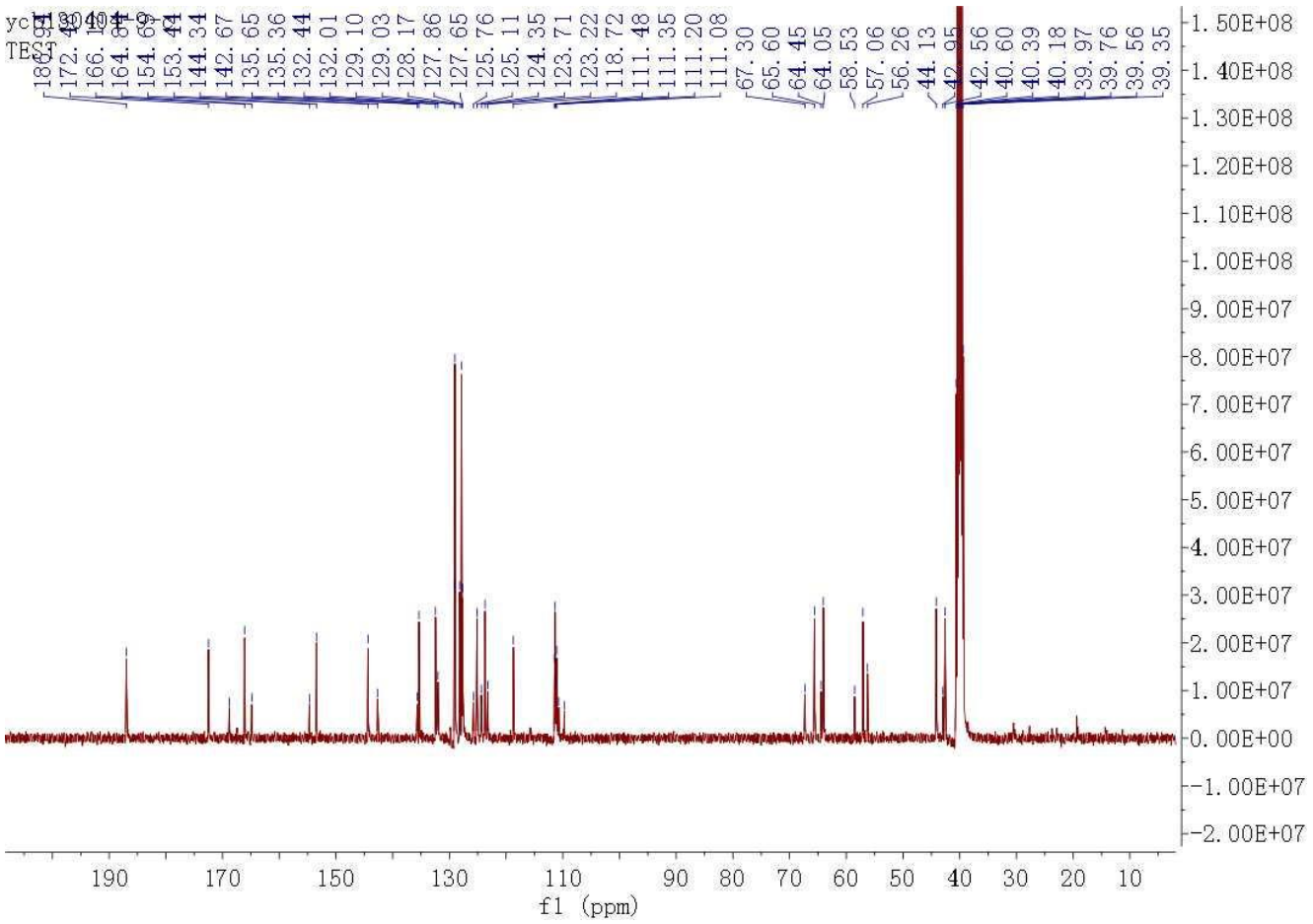
1-Benzyl-2-oxo-2'-(2-oxooxazolidine-3-carbonyl)-5'-thioxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile



Major diastereoisomer **4o**: white solid; mp 218-221 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.36 (br, 1H), 7.55-7.03 (m, 9H), 5.89 (s, 1H), 5.16 (d, J = 16 Hz, 2H), 4.15-4.66 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.94, 172.48, 166.12, 153.44, 144.34, 135.36, 132.44, 129.03, 128.17, 127.86, 125.11, 123.71, 118.72, 111.35, 111.08, 65.60, 64.05, 57.06, 56.26, 44.13, 42.56. HRMS calculated $[M+Na]^{+}$ for $C_{24}H_{17}N_5O_4SNa$: 494.0893, found: 494.0897.

Minor diastereoisomer **4o'**: ^{1}H NMR (400 MHz, DMSO): δ 12.36 (br, 1H), 7.55-7.03 (m, 9H), 5.78 (s, 1H), 4.90 (d, J = 16 Hz, 2H), 3.81-4.08 (dt, J = 7.8 Hz, J = 4.2 Hz, 4H). ^{13}C NMR (101 MHz, DMSO): δ 186.94, 168.81, 164.84, 154.69, 142.67, 135.65, 132.01, 129.10, 127.65, 125.76, 124.35, 123.22, 118.72, 111.48, 111.20, 67.30, 64.45, 58.53, 57.00, 44.13, 42.95.





Single Crystal X-Ray Analysis **4b** (CCDC 939641 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.)

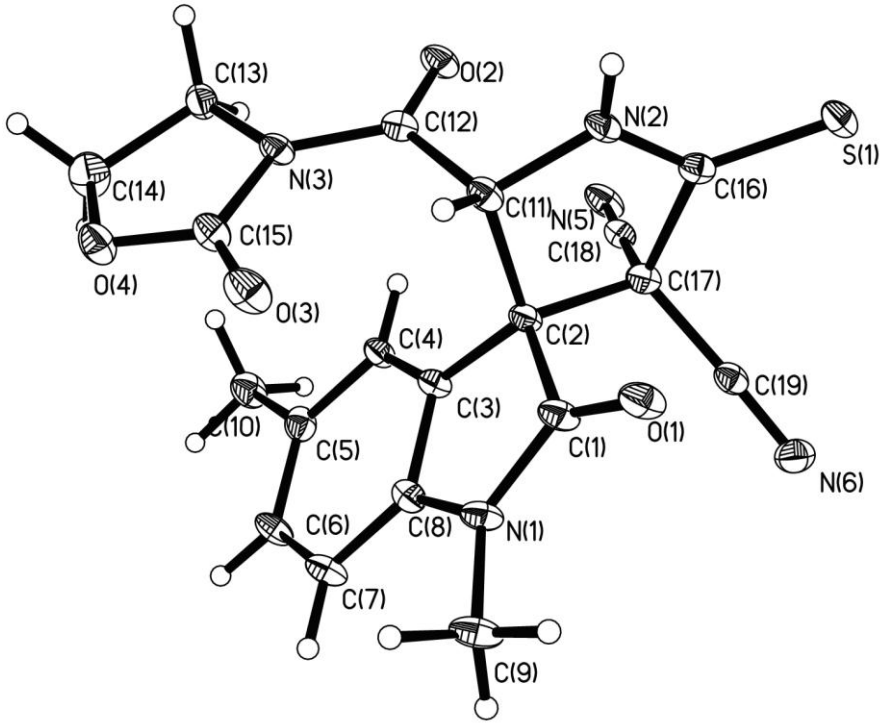


Table 1. Crystal data and structure refinement for shelx.

Identification code	shelx
Empirical formula	C20 H19 N5 O5 S
Formula weight	441.46
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.415(7) A alpha = 90 deg.
	b = 14.394(10) A beta = 97.725(13) deg.
	c = 15.100(10) A gamma = 90 deg.
Volume	2028(2) A^3

Z, Calculated density	4, 1.446 Mg/m^3
Absorption coefficient	0.204 mm^-1
F(000)	920
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	1.96 to 25.01 deg.
Limiting indices	-11<=h<=11, -17<=k<=17, -14<=l<=17
Reflections collected / unique	16563 / 3563 [R(int) = 0.1316]
Completeness to theta = 25.01	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9759 and 0.9603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3563 / 1 / 285
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0615, wR2 = 0.1126
R indices (all data)	R1 = 0.0944, wR2 = 0.1233
Largest diff. peak and hole	0.327 and -0.340 e.A^-3