Supporting Information

Concise synthesis of Didebromohamacanthin B and Demethylaplysinopsine : Addition of Ethylenediamine and Guanidine Derivatives to the Pyrrole - Amino Acid Diketopiperazines in Oxidative Conditions

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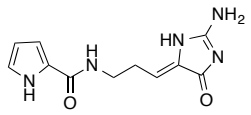
General considerations

Unless otherwise noted, reagents were purchased from Aldrich and used without further purification. *tert*-Butyl 3-(1,2-diaminoethyl)-1*H*-indole-1-carboxylate **5d** was purchased from Amra Scientific. **5b.**2HCl salt was given by Dr. Karchava A. (Moscow State University). Chromatographic purifications were performed by flash chromatography using silica gel P60 (230-400 mesh). THF was distilled from sodium/benzophenone. Anhydrous DMF and CH_2Cl_2 were purchased from Aldrich. NMR spectra were recorded on Spectrometers Avance 300 MHz and 500 MHz Brucker. Chemical shifts (expressed in ppm) were referenced to the solvent peaks δ_H 2.05 and δ_C 29.9, 206.7 for acetone-*d6*, δ_H 2.50 and δ_C 39.5 for DMSO-*d6*, δ_H 7.26 and δ_C 77.2 for $CDCl_3$, δ_H 3.58, 1.73 and δ_C 64.7, 25.2 for THF-*d8*, δ_H 8.04, 2.93, 2.72 and δ_C 162.4, 34.9, 29.8 for DMF-*d*7. HRMS mass spectra were obtained using electrospray source (Lockspray) coupled with a time of flight analyser (LCT, Micromass). Samples were prepared in acetonitrile and injected in the MS system using a Waters 2795 system. IR spectra were acquired (neat) using a Perkin Elmer Spectrometer BX FT-IR system.

Experimental Procedures

(*Z*)-*N*-(3-(2-amino-4-oxo-1*H*-imidazol-5(4*H*)-ylidene)propyl)-1*H*-pyrrole-2-carboxamide (3aa)

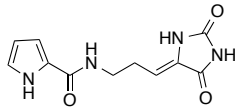


Diketopiperazine pyrrole-proline (**1a**) (190 mg, 1.0 mmol, 1 eq.) was added to a solution of Bu_2S (0.62 mL, 4.0 mmol, 4 eq.) in dry DMF (25 mL) and stirred in the presence of O_2 flow for 1 h. Guanidine carbonate (360 mg, 2.0 mmol, 2 eq.) was added and the stirring was continued for 1 h at 60°C. The solvent was evaporated under vacuo and the residue was treated by column chromatography using CH_2Cl_2 (sat. with NH_3)/MeOH : 4/1 to afford **3aa** (230 mg, 95% yield). Analytical and spectroscopic data are in agreement with the literature data.[1c]

^{1}H NMR (CD_3OD, 300 MHz): δ 6.93 (m, 1H), 6.79 (m, 1H), 6.18 (m, 1H), 5.79 (m, 1H), 3.48 (m, 2H), 2.54 (m, 2H).

^{13}C NMR (CD_3OD, 75 MHz): δ 169.2, 163.7, 136.9, 126.9, 122.9, 111.7, 110.2, 106.1, 39.7, 28.6.

(*Z*)-*N*-(3-(2,5-Dioxoimidazolidin-4-ylidene)propyl)-1*H*-pyrrole-2-carboxamide (3ab)



Diketopiperazine pyrrole-proline (**1a**) (50 mg, 0.26 mmol) was added to a solution of Bu_2S (0.23 mL, 1.3 mmol, 5 eq.) in dry DMF (2.0 mL) and stirred in the presence of O_2 flow for 1 h. Urea (79 mg, 1.3 mmol, 5 eq.) and DBU (78 μL, 0.53 mmol, 2 eq.) were added and the stirring was continued for 1 h. The solvent was evaporated in vacuo and the residue was purified by preparative TLC chromatography using CH_2Cl_2 (sat. with NH_3)/MeOH : 7/3 to afford **3ab** (30 mg, 40 % yield).

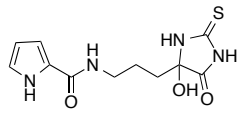
^{1}H NMR (CD_3OD, 300 MHz): δ 6.94 (m, 1H), 6.78 (dd, J = 1.7, 3.7 Hz, 1H), 6.19 (m, 1H), 5.70 (t, J = 8.0 Hz, 1H), 3.45 (t, J = 7.0 Hz, 2H), 2.49 (m, 2H).

^{13}C NMR (CD_3OD, 75 MHz): δ 176.5, 164.0, 163.6, 146.7, 126.9, 122.9, 111.7, 110.2, 106.1, 39.5, 28.6.

HRMS ESI$^+$: $[M+Na]^+$ *m/z* calcd. for $C_{11}H_{12}N_4O_3Na$: 271.0807, found: 271.0807.

IR (ν_{max} cm^{-1}): 3340-3150, 1737, 1693, 1603, 1523, 1431.

***N*-(3-(4-Hydroxy-5-oxo-2-thioxoimidazolidin-4-yl)propyl)-1*H*-pyrrole-2-carboxamide (4ac)**



Diketopiperazine pyrrole-proline (**1a**) (76 mg, 0.4 mmol) was added to a solution of Bu_2S (0.35 mL, 2.0 mmol, 5 eq.) in dry DMF (2.7 mL) and stirred in the presence of O_2 flow for 1 h. Thiourea (45.6 mg, 0.6 mmol, 1.5 eq.) and DBU (80 μL, 0.6 mmol, 1.5 eq.) was added and the stirring was continued for 1 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography using CH_2Cl_2/MeOH : 9/1 to afford **3ac** (62 mg, 55 % yield).

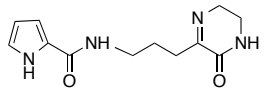
^{1}H NMR (CD_3OD, 300 MHz): δ 6.91 (dd, J = 1.5, 2.6 Hz, 1H), 6.78 (dd, J = 1.3, 3.8 Hz, 1H), 6.17 (dd, J = 2.6, 3.8 Hz, 1H), 3.36 (m, 2H), 1.92 (m, 2H), 1.68, 1.55 (2m, 2H).

^{13}C NMR (CD_3OD, 75 MHz): δ 182.5, 176.0, 162.5, 125.4, 121.4, 110.2, 108.8, 87.0, 38.4, 33.2, 23.1.

HRMS ESI$^+$: $[M+Na]^+$ *m/z* calcd. for $C_{11}H_{14}N_4O_3NaS$: 305.0684, found: 305.0658.

IR (ν_{max} cm^{-1}): 3600-3100, 1748, 1605, 1514, 1325, 1181.

***N*-(3-(3-Oxo-3,4,5,6-tetrahydropyrazin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6aa)**



Diketopiperazine pyrrole-proline (**1a**) (770 mg, 4.05 mmol) was added to a solution of Bu_2S (3.5 mL, 20.26 mmol, 5 eq.) in dry DMF (27 mL) and stirred in the presence of O_2 flow for 1 h. Ethylene diamine (1.1 mL, 16.2 mmol, 4 eq.) was added and the stirring was continued for 5 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography using CH_2Cl_2/MeOH : 95/5 to afford **6aa** (753 mg, 75% yield).

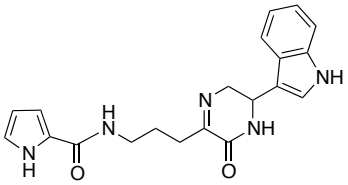
^{1}H NMR (CD_3OD, 300 MHz): δ 6.90 (d, J = 2.6 Hz, 1H), 6.77 (d, J = 3.7 Hz, 1H), 6.16 (dd, J = 3.7, 2.6 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 3.37 (m, 4H), 2.64 (t, J = 7.5 Hz, 2H), 1.88 (m, 2H).

^{13}C NMR (CD_3OD, 75 MHz): δ 167.8, 163.8, 159.2, 126.9, 122.9, 111.6, 110.3, 48.4, 39.7, 39.4, 32.0, 27.4.

HRMS ESI$^+$: $[M+Na]^+$ *m/z* calcd. for $C_{12}H_{16}N_4O_2Na$: 271.1171, found: 271.1165.

IR (ν_{max} cm^{-1}): 3226, 2365, 1678, 1620, 1523, 1321, 1200, 734.

***N*-(3-(6-(1*H*-Indol-3-yl)-3-oxo-3,4,5,6-tetrahydropyrazin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6ab)**



Diketopiperazine pyrrole-proline (**1a**) (200 mg, 1.05 mmol, 1 eq.) was added to a solution of Bu_2S (0.9 mL, 5.26 mmol, 5 eq.) in dry DMF (27 mL) and stirred in the presence of O_2 flow for 1 h. (3-Indolyl)-ethylene diamine dihydrochloride (324 mg, 1.31 mmol, 1.3 eq.) was dissolved in MeOH (10 mL) and stirred for 15 min in the presence of Amberlyst A-21 (1 g). Methanolic solution was filtered, evaporated in vacuo, the residue was dissolved in DMF (3 mL), added to reaction mixture and the stirring was continued for 15 h. The solvent was evaporated in vacuo and the residue was purified by silica gel chromatography using CH_2Cl_2 /MeOH : 97/3 to afford **6ab** (125 mg, 33% yield).

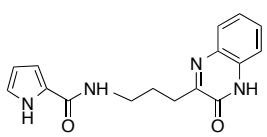
^{1}H NMR (CD_3OD, 500 MHz): δ 7.61 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.14 (dd, J = 8.0 et 7.1 Hz, 1H), 7.14 (s, 1H), 7.06 (dd, J = 8.0 et 7.1 Hz, 1H), 6.91 (d, J = 2.6 Hz, 1H), 6.77 (d, J = 3.9 Hz, 1H), 6.17 (dd, J = 3.9, 2.6 Hz, 1H), 5.17 (dd, J = 8.4, 5.6 Hz, 1H), 3.65 (m, 2H), 3.44 (m, 1H), 2.74 (m, 1H), 1.97 (m, 1H).

^{13}C NMR (CD_3OD, 75 MHz): δ 167.2, 163.9, 159.5, 138.5, 127.3, 127.0, 123.9, 122.8, 122.7, 120.3, 119.7, 114.2, 112.6, 111.7, 110.2, 55.7, 45.0, 39.7, 31.9, 27.6.

HRMS ESI$^+$: $[M+Na]^+$ *m/z* calcd. for $C_{20}H_{21}N_5O_2Na$: 386.1593, found: 386.1593.

IR (ν_{max} cm^{-1}): 3259, 1676, 1623, 1327, 743.

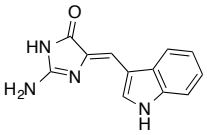
***N*-(3-(3-Oxo-3,4-dihydroquinoxalin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6ac)**



Diketopiperazine pyrrole-proline (**1a**) (50 mg, 0.26 mmol) was added to a solution of Bu_2S (0.23 mL, 1.3 mmol, 5 eq.) in dry DMF (2 mL) and stirred in the presence of O_2 flow for 1 h. *o*-Phenylendiamine (57 mg, 0.53 mmol, 2 eq.) was added and the stirring was continued for 2 h at 80°C. The solvent was evaporated in vacuo and the residue was purified by preparative TLC using CH_2Cl_2 (sat. with NH_3)/MeOH : 95/5 to afford **6ac** (42 mg, 55% yield).

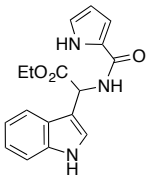
^{1}H NMR (CD_3OD, 500 MHz): δ 8.57 (s, 1H), 7.78 (dd, J = 7.9, 1.3 Hz, 1H), 7.50 (m, 1H), 7.32 (m, 2H), 7.04 (s, 1H), 6.92 (d, J = 2.6 Hz, 1H), 6.78 (d, J = 3.7 Hz, 1H), 6.15 (dd, J = 3.7, 2.6 Hz, 1H), 3.48 (t, J = 6.9 Hz, 2H), 2.98 (t, J = 7.4 Hz, 2H), 2.11 (m, 2H).
^{13}C NMR (CD_3OD, 75 MHz): δ 163.8, 162.5, 157.0, 133.9, 132.9, 130.9, 129.4, 127.1, 124.9, 122.7, 116.5, 111.6, 110.1, 39.9, 31.7, 27.6.
HRMS ESI$^+$: $[M+Na]^+$ *m/z* calcd. for $C_{16}H_{16}N_4O_2Na$: 319.1171, found: 319.1167.
IR (ν_{max} cm^{-1}): 1639, 1590, 1533.

(*Z*)-4-((1*H*-Indol-3-yl)methylene)-2-amino-1*H*-imidazol-5(4*H*)-one (7ca)



Diketopiperazine pyrrole-tryptophan (**1c**) (140 mg, 0.5 mmol, 1 eq.) was added to a solution of Ph_3P (395 mg, 1.5 mmol, 3 eq.) in dry DMF (14 mL) and stirred in the presence of O_2 flow for 3 h. Guanidine carbonate (180 mg, 1.0 mmol, 2 eq.) was added and the stirring was continued for 1h at 80°C. The solvent was evaporated in vacuo and the residue was purified by column chromatography using CH_2Cl_2/MeOH : 85/15 to afford **7ca** (24 mg, 20% yield).
^{1}H NMR (DMSO-*d6*, 300 MHz): δ 11.54 (s, 1H), 10.23 (br s, 1H), 8.05 (br s, 1H), 7.85 (d, J = 6.7 Hz, 1H), 7.42 (d, J = 6.7 Hz, 1H), 7.12 (m, 2H), 6.93 (br s, 2H), 6.65 (s, 1H).
^{13}C NMR (DMSO-*d6*, 75 MHz): δ 181.5 (HMBC), 174.1 (HMBC), 135.8, 128.6 (HMQC), 126.8, 121.8, 121.7, 119.7, 118.5, 111.8, 110.7, 105.4 (HMQC).
^{15}N (DMSO-*d6*, 60.8 MHz): δ 69.3 (NH_2-6), 139.4 (NH-10), 141.5 (NH-1).
HRMS ESI$^+$: $[M+H]^+$ *m/z* calcd. for $C_{12}H_{11}N_4O$ 227.0933, found: 227.0920.
IR (ν_{max} cm^{-1}): 3393, 3237, 3036, 1659, 1623, 1491.

Ethyl 2-(1*H*-indol-3-yl)-2-(1*H*-pyrrole-2-carboxamido)acetate (Ab)



To a mixture of 1H-pyrrole-2-carboxylic acid (3.47 g, 31.2 mmol, 1 eq.) and indolylglycine (6.94 g, 31.2 mmol, 1 eq.) in dry DCM (90 mL) was added EDCI (6.53 g, 34.4 mmol, 1.1 eq.) and DMAP (191 mg, 1.56 mmol, 5% mol) at 0°C. The reaction mixture was stirred at room temperature during 12 h and then concentrated in dry. The residue was dissolved in EtOAc

(300 mL) and washed successively with H_2O, 1N HCl, saturated aq. $NaHCO_3$ and brine. The organic layer was dried on $MgSO_4$, the solvent was evaporated and the residue was purified by flash chromatography using heptane/EtOAc : 7/3 to give **Ab (**8.73g, 90% yield).

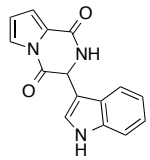
^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.77 (s, 1H), 8.36 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 2.4 et 7.8 Hz, 1H), 7.17 (dd, J = 2.4, 7.8 Hz, 1H), 7.15 (s, 1H), 6.85 (d, J = 3.5 Hz, 1H), 6.83 (s, 1H), 6.62 (d, J = 3.9 Hz, 1H), 6.19 (dd, J = 3.5, 3.9 Hz, 1H), 6.00 (d, J = 6.9 Hz, 1H), 4.22 (m, 2H), 1.22 (t, J = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.6, 160.9, 136.5, 125.7, 125.3, 123.9, 122.8, 122.1, 120.4, 119.3, 111.7, 111.3, 110.1, 110.0, 61.9, 50.0, 14.2.

HRMS ESI$^+$ $[M+Na]^+$ *m/z* calcd. for $C_{17}H_{17}N_3O_3Na$ 334.1168, found: 334.1155.

IR (ν_{max} cm^{-1}): 3270, 2359, 1724, 1620, 1503, 1337, 1232, 1182, 1111, 737.

3-(1*H*-Indol-3-yl)-2,3-dihydropyrrolo[1,2-*a*]pyrazine-1,4-dione (1b)



Ethyl ester **Ab** (500 mg, 1.6 mmol, 1 eq.) was dissolved in degassed anhydrous THF (45 mL) and cooled to 0°C. Sodium hydride (57 mg, 2.4 mmol, 1.5 eq.) was added and the mixture was stirred at 0°C for 10 minutes and then at room temperature for 3 h. After the completion of the reaction, the mixture was poured into phosphate buffer pH 3.8 (90 mL) and quickly extracted with EtOAc. The organic layer was dried on $MgSO_4$, the solvent was evaporated and the residue was purified by flash chromatography using heptane/EtOAc : 45/55 to give diketopiperazine **1b (**275.6 mg, 65% yield).

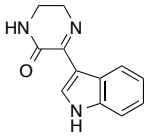
^{1}H NMR (acetone *d6*, 300 Hz): δ 10.43 (s, 1H), 7.59 (s, 1H), 7.54 (d, J = 3.3 Hz, 1H), 7.45 (m, 3H), 7.16 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 3.3 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.63 (t, J = 3.3 Hz, 1H), 5.94 (s, 1H).

^{13}C NMR (acetone *d6*, 125 MHz): δ 164.7, 156.9, 138.1, 126.6, 125.5, 122.9, 122.4, 120.5, 120.1, 119.6, 118.5, 118.1, 115.8, 112.8, 56.3.

HRMS ESI$^-$ $[M-H]^-$ *m/z* calcd. for $C_{15}H_{10}N_3O_2$ 264.0773, found: 264.0765.

IR (ν_{max} cm^{-1}): 3228, 2362, 1718, 1654, 1413, 1334, 740.

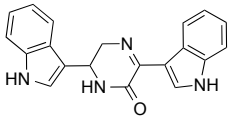
3-(1*H*-Indol-3-yl)-5,6-dihydropyrazin-2(1*H*)-one (8ba)



Diketopiperazine pyrrole-indolylglycine (**1b**) (325 mg, 1.23 mmol, 1 eq.) was added to a solution of Bu_2S (1.1 mL, 6.15 mmol, 5 eq.) in dry DMF (27 mL) and stirred in the presence of O_2 flow for 3 h. Ethylene diamine (0.33 mL, 4.92 mmol, 4 eq.) was added and the stirring was continued for 17 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography using CH_2Cl_2/MeOH : 98/2 to afford **8ba** (57.6 mg, 22% yield).

^{1}H NMR (acetone *d6*, 500 MHz): δ 10.59 (s, 1H), 8.54 (d, J = 7.3 Hz, 1H), 8.52 (s, 1H), 7.47 (d, J = 7.3 Hz, 2H), 7.18 (dd, J = 7.3, 5.9 Hz, 1H), 7.13 (dd, J = 7.3, 5.9 Hz, 1H), 3.90 (t, J = 6.3 Hz, 2H), 3.49 (t, J = 6.3 Hz, 2H).
^{13}C NMR (acetone *d6*, 75 MHz): δ 158.9, 158.7, 137.3, 132.5, 127.4, 123.9, 123.1, 121.4, 113.0, 112.1, 48.6, 39.3.
HRMS ESI$^+$: $[M+H]^+$ *m/z* calcd. for $C_{12}H_{12}N_3O$ 214.0980, found: 214.0974.
IR (ν_{max} cm^{-1}): 3218, 2358, 1659, 1580, 1426, 1339, 1122, 1010, 742.

3,6-Di(1*H*-indol-3-yl)-5,6-dihydropyrazin-2(1*H*)-one (8bb)



Diketopiperazine pyrrole-indolylglycine (**1b**) (318 mg, 1.2 mmol, 1 eq.) was added to a solution of Bu_2S (1.0 mL, 6.0 mmol, 5 eq.) in dry DMF (27 mL) and stirred in the presence of O_2 flow for 3 h. (3-Indolyl)-ethylene diamine (280 mg, 1.6 mmol, 1.3 eq.) was added and the stirring was continued for 17 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography using heptane/EtOAc : 15/85 to afford **8bb** (60.6 mg, 15% yield).

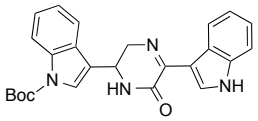
^{1}H NMR (DMSO *d6*, 300 MHz): δ 11.51 (s, 1H), 11.04 (s, 1H), 8.76 (s, 1H), 8.42 (s, 1H), 8.39 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 4.99 (dd, J = 8.3, 5.1 Hz, 1H), 4.12 (m, 2H).

^{13}C NMR (DMSO *d6*, 75 MHz): δ 158.4, 158.2, 136.9, 136.6, 132.4, 126.5, 126.1, 124.0, 123.1, 122.5, 121.9, 120.9, 119.5, 119.3, 113.3, 112.2, 112.1, 111.5, 54.0, 46.9.

HRMS ESI$^+$: $[M+H]^+$ *m/z* calcd. for $C_{20}H_{17}N_4O$: 329.1402, found: 329.1406.

IR (ν_{max} cm^{-1}): 3228, 2360, 1660, 1581, 1417, 1333, 1244, 741.

***tert*-Butyl 3-(5-(1*H*-indol-3-yl)-6-oxo-1,2,3,6-tetrahydropyrazin-2-yl)-1*H*-indole-1-carboxylate (8bd)**



Diketopiperazine pyrrole-indolylglycine (**1b**) (318 mg, 1.2 mmol, 1 eq.) was added to a solution of Bu_2S (1.0 mL, 6.0 mmol, 5 eq.) in dry DMF (27 mL) and stirred in the presence of O_2 flow for 3 h. *tert*-Butyl 3-(1,2-diaminoethyl)-1H-indole-1-carboxylate (440 mg, 1.6 mmol, 1.3 eq.) was added and the stirring was continued for 17 h. The solvent was evaporated in vacuo and the residue was purified by silica gel chromatography using CH_2Cl_2/MeOH : 97/3 to afford **8bd** (100 mg, 21% yield).

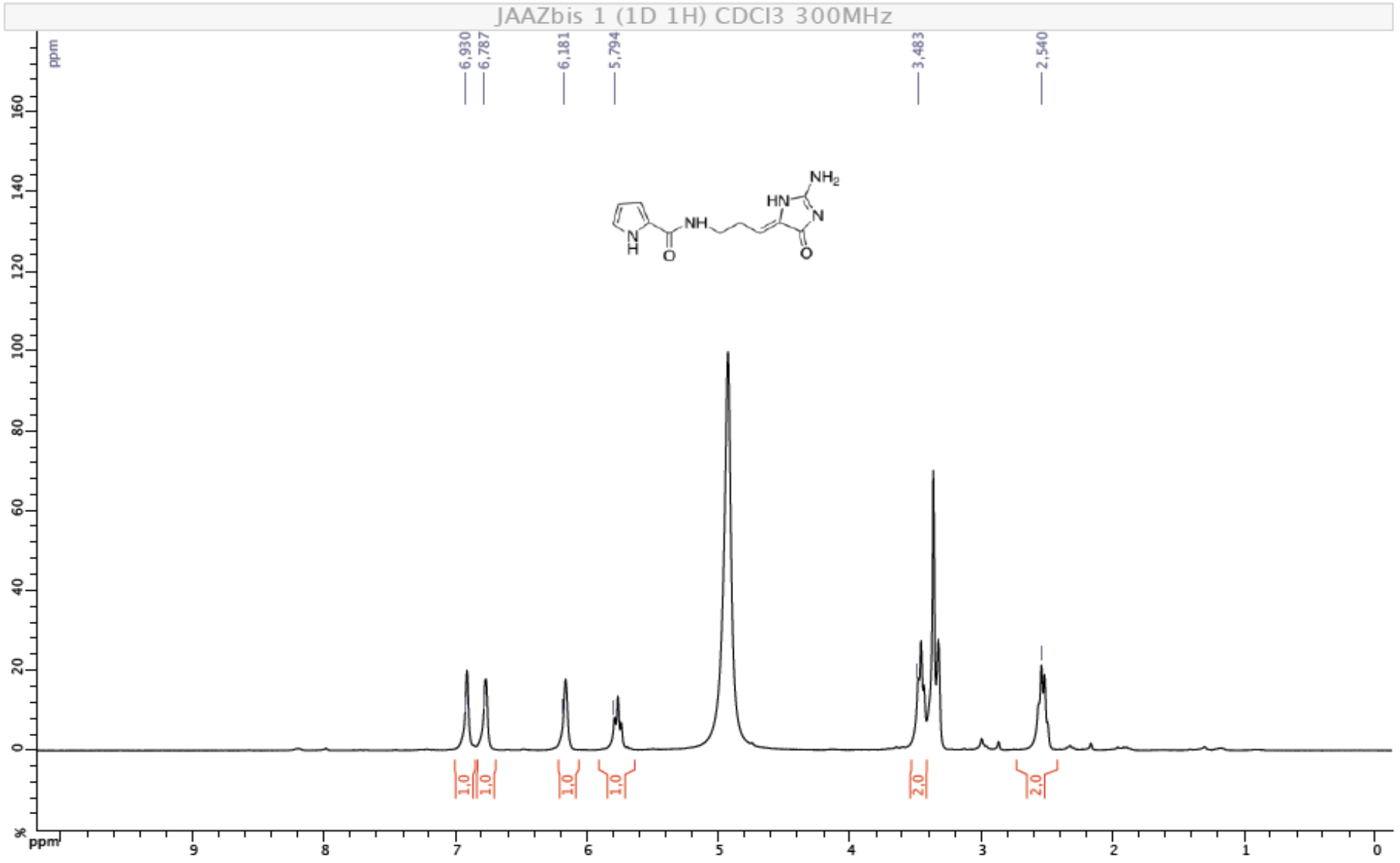
^{1}H NMR (acetone *d6*, 500 MHz): δ 10.74 (s, 1H), 8.66 (m, 2H), 8.24 (d, J = 7.5 Hz, 1H), 7.86 (m, 2H), 7.68 (s, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 5.30 (dd, J = 10.9, 4.9 Hz, 1H), 3.94 (ddd, J = 12.8, 10.9, 2.1 Hz, 1H), 3.63 (dd, J = 12.8, 4.9 Hz, 1H), 1.74 (s, 9H).

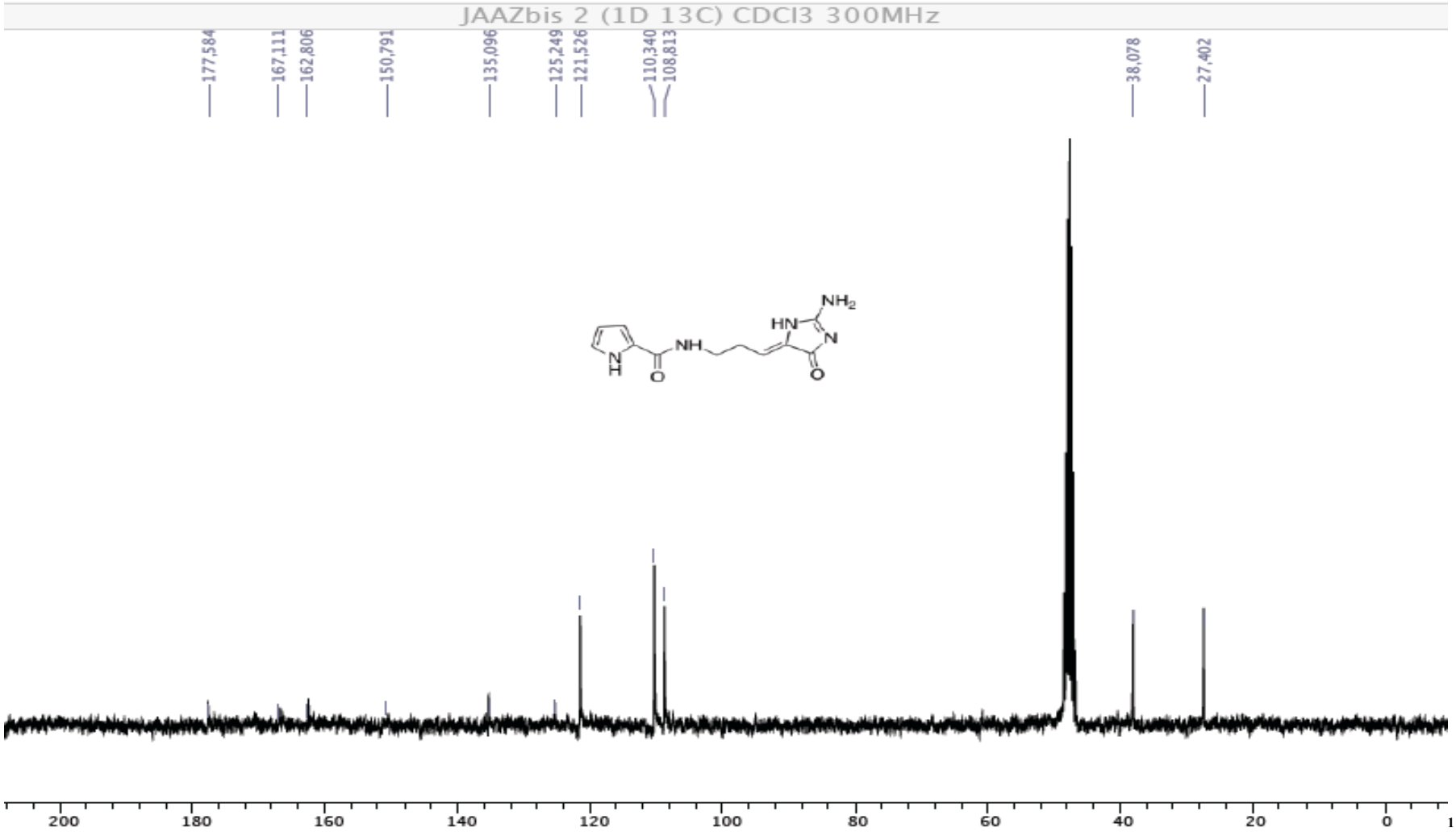
^{13}C NMR (acetone *d6*, 75 MHz): δ 159.0, 158.7, 150.5, 137.5, 136.9, 133.4, 127.5, 125.3, 124.5, 124.0, 123.4, 123.3, 122.1, 121.6, 120.8, 116.1, 112.9, 112.4, 112.3, 84.4, 55.1, 44.6, 28.3.

HRMS ESI$^+$: $[M+H]^+$ *m/z* calcd. for $C_{25}H_{25}N_4O_3$: 429.1927, found: 429.1928.

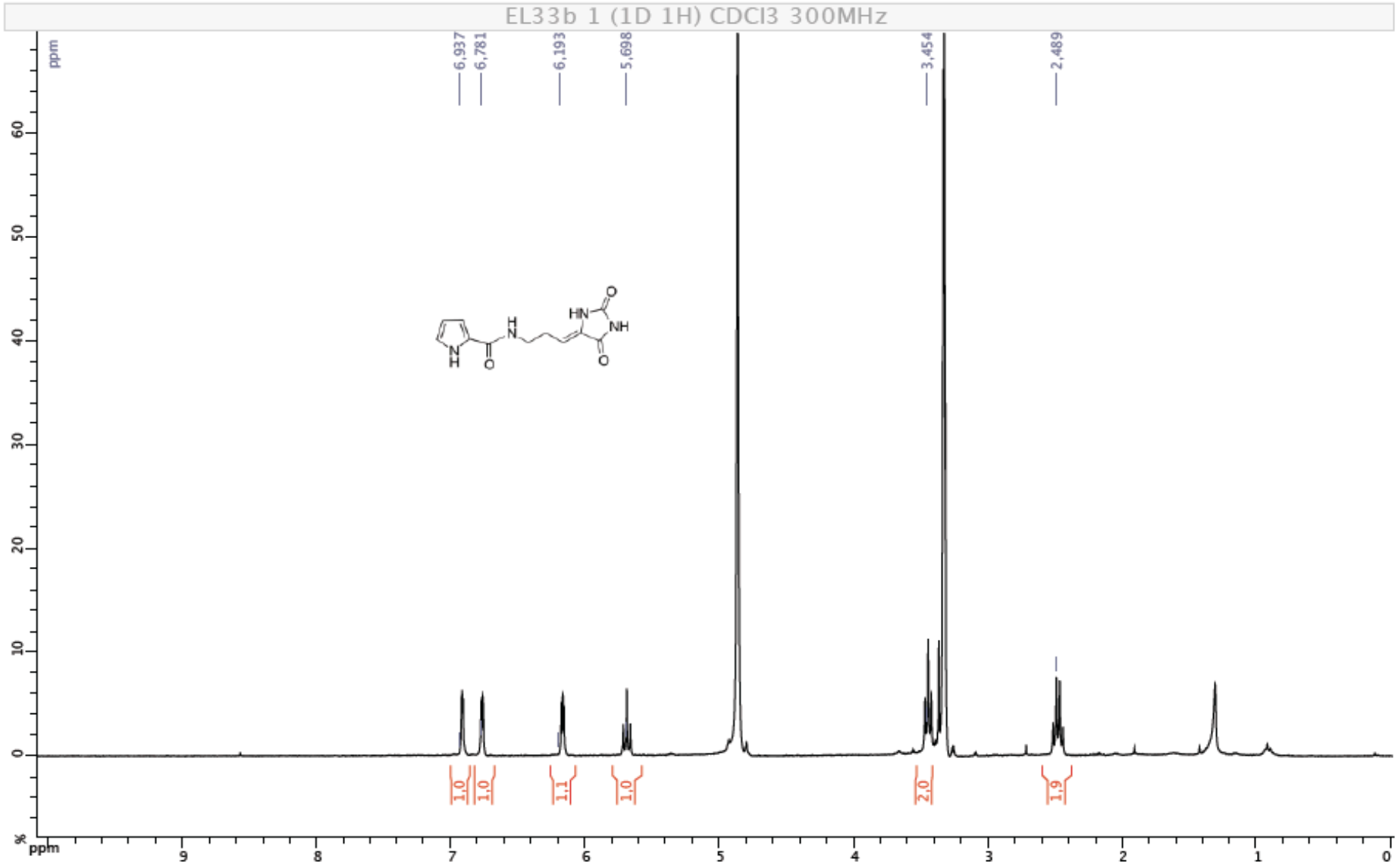
IR (ν_{max} cm^{-1}): 3244, 2340, 1670, 1568, 1368, 1153.

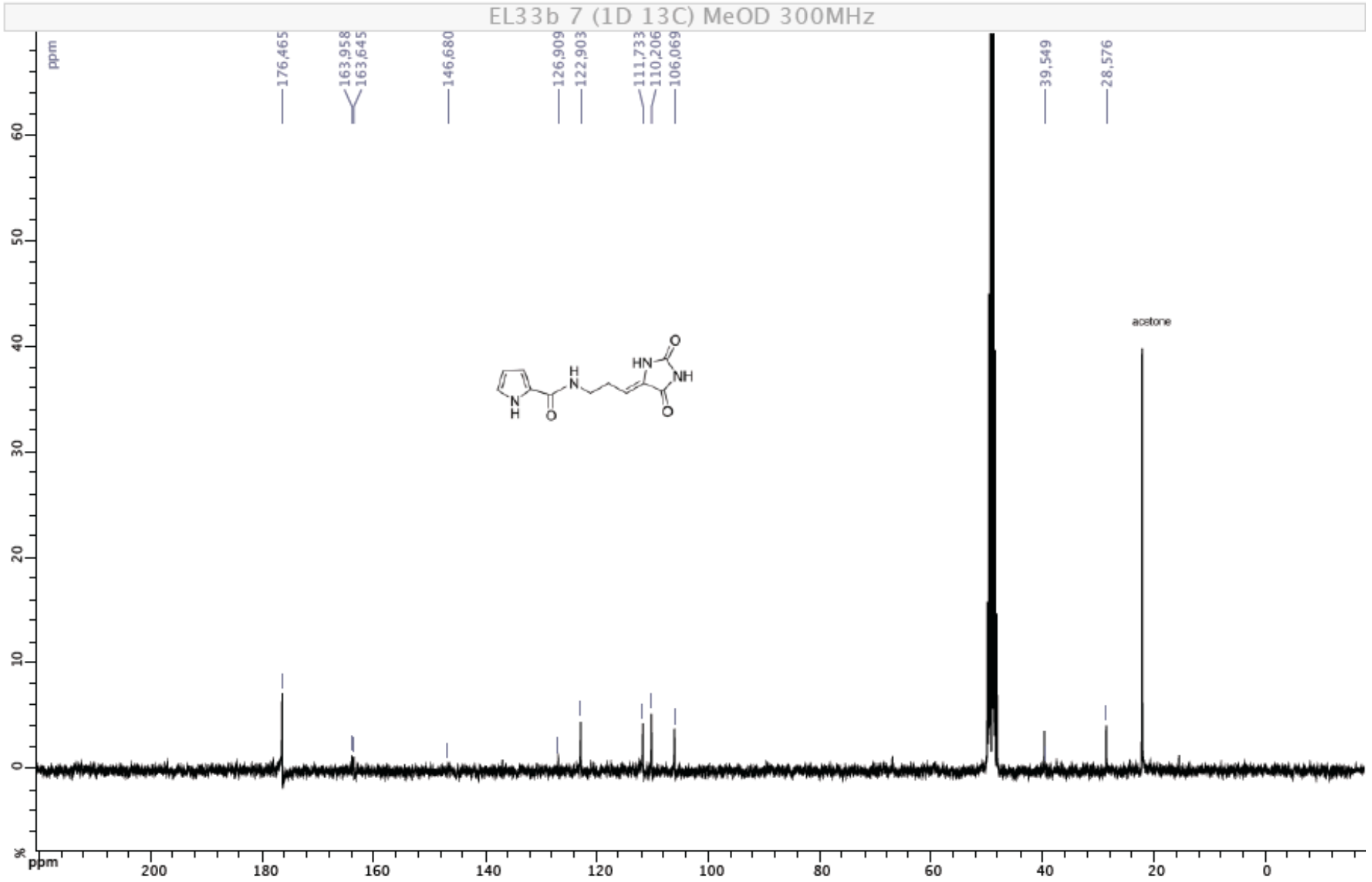
(*Z*)-*N*-(3-(2-amino-4-oxo-1*H*-imidazol-5(4*H*)-ylidene)propyl)-1*H*-pyrrole-2-carboxamide (3aa)



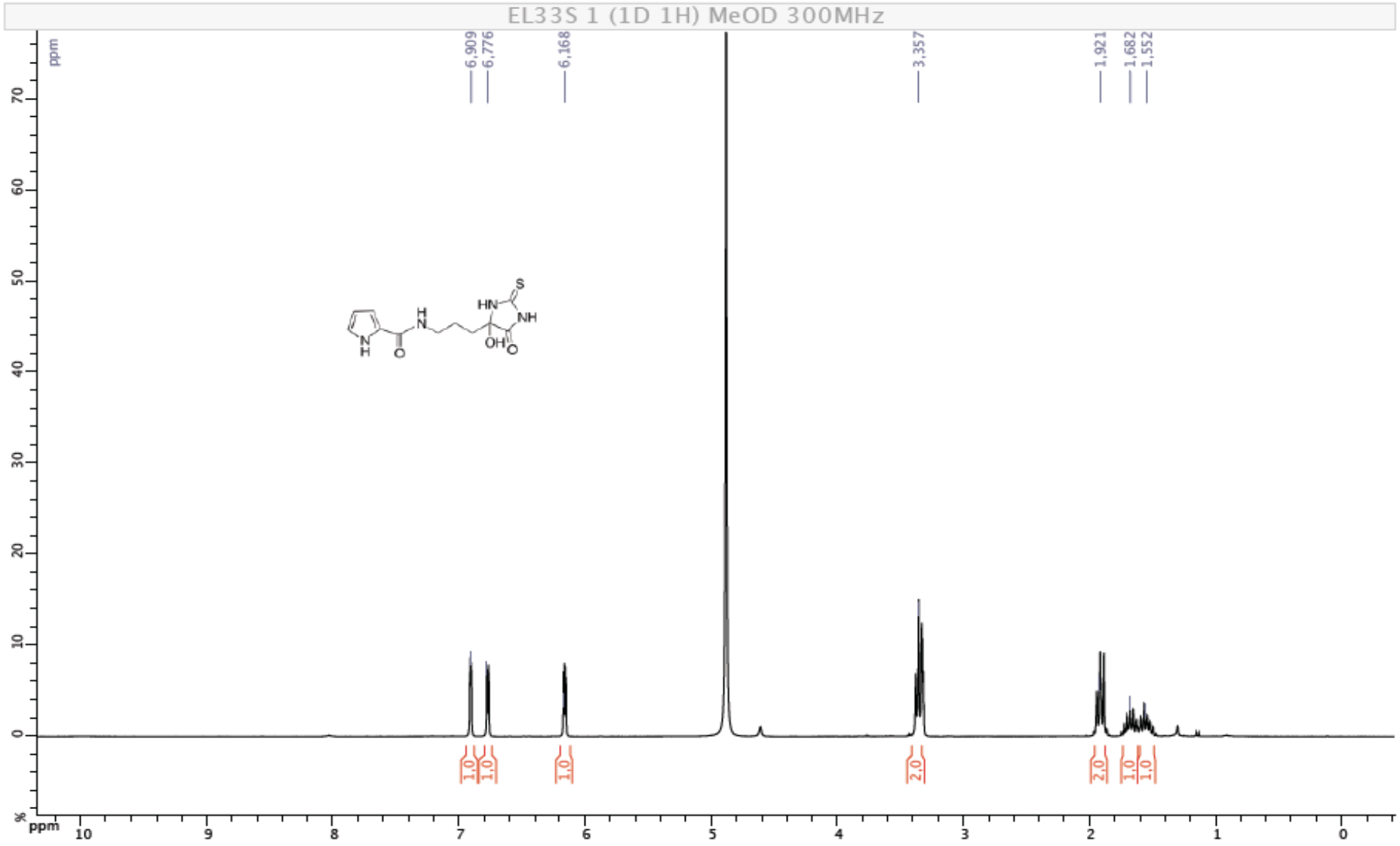

JAAZbis 2 (1D 13C) CDCl3 300MHz
177,584
167,111
162,806
150,791
135,096
125,249
121,526
110,340
108,813
38,078
27,402
NH2
HN
N
NH
N
H
O
O
200
180
160
140
120
100
80
60
40
20
0

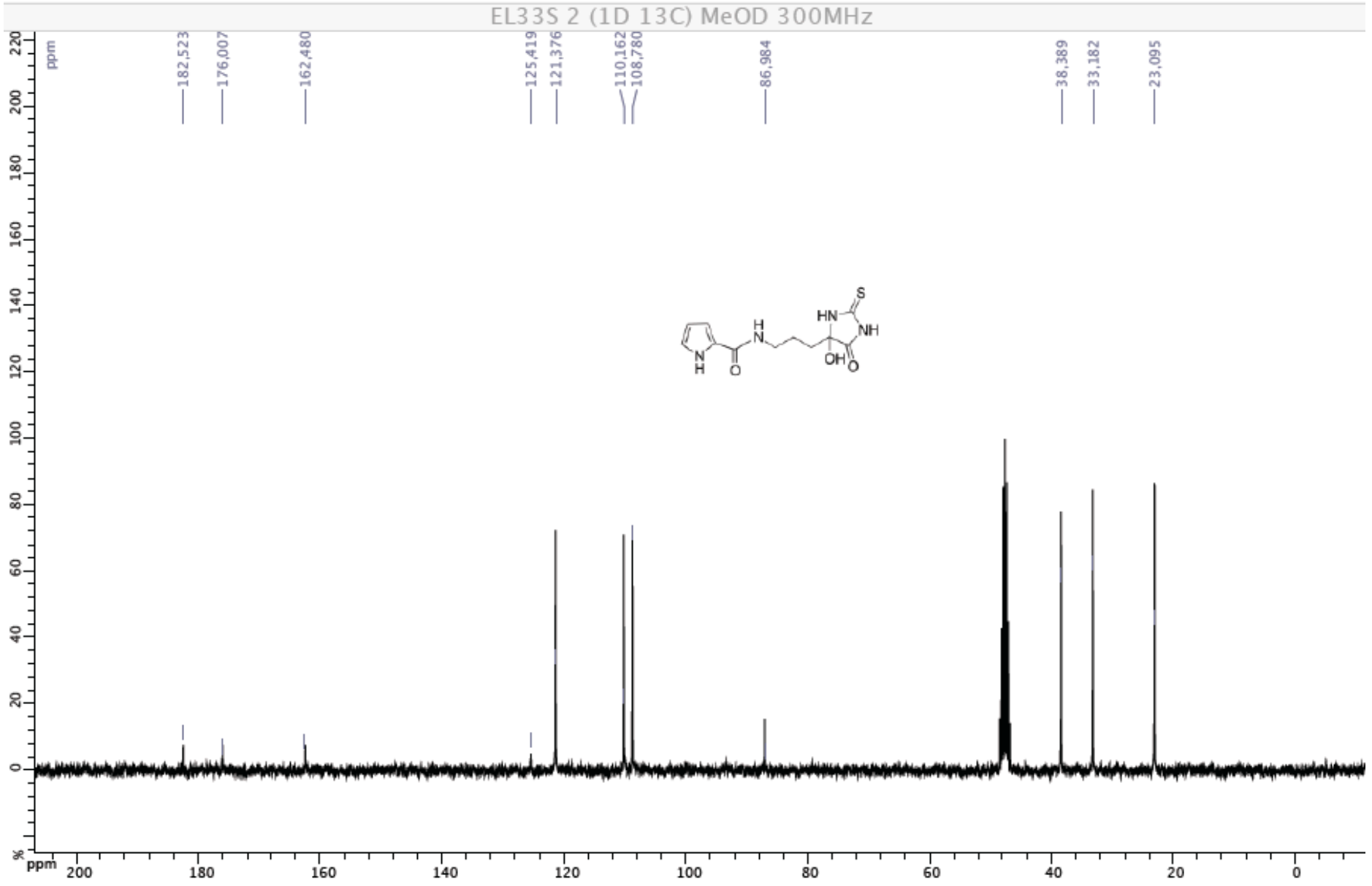
(*Z*)-*N*-(3-(2,5-Dioxoimidazolidin-4-ylidene)propyl)-1*H*-pyrrole-2-carboxamide (3ab)



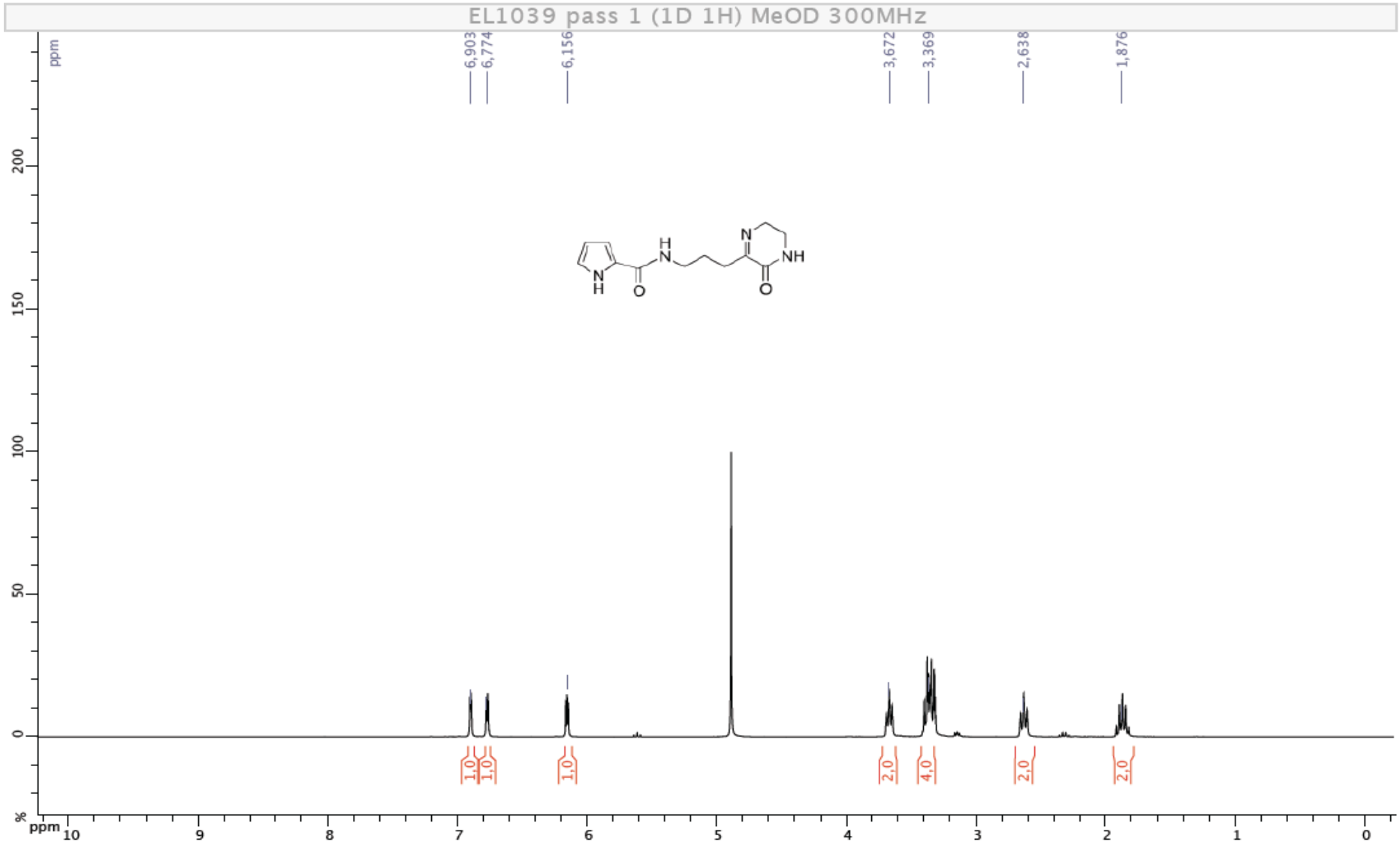

EL33b 7 (1D 13C) MeOD 300MHz
ppm
176,465
163,958
163,645
146,680
126,909
122,903
111,733
110,206
106,069
39,549
28,576
acetone
HN
NH
H
N
N
H
O
O
O
%
ppm
200
180
160
140
120
100
80
60
40
20
0
60
50
40
30
20
10
0

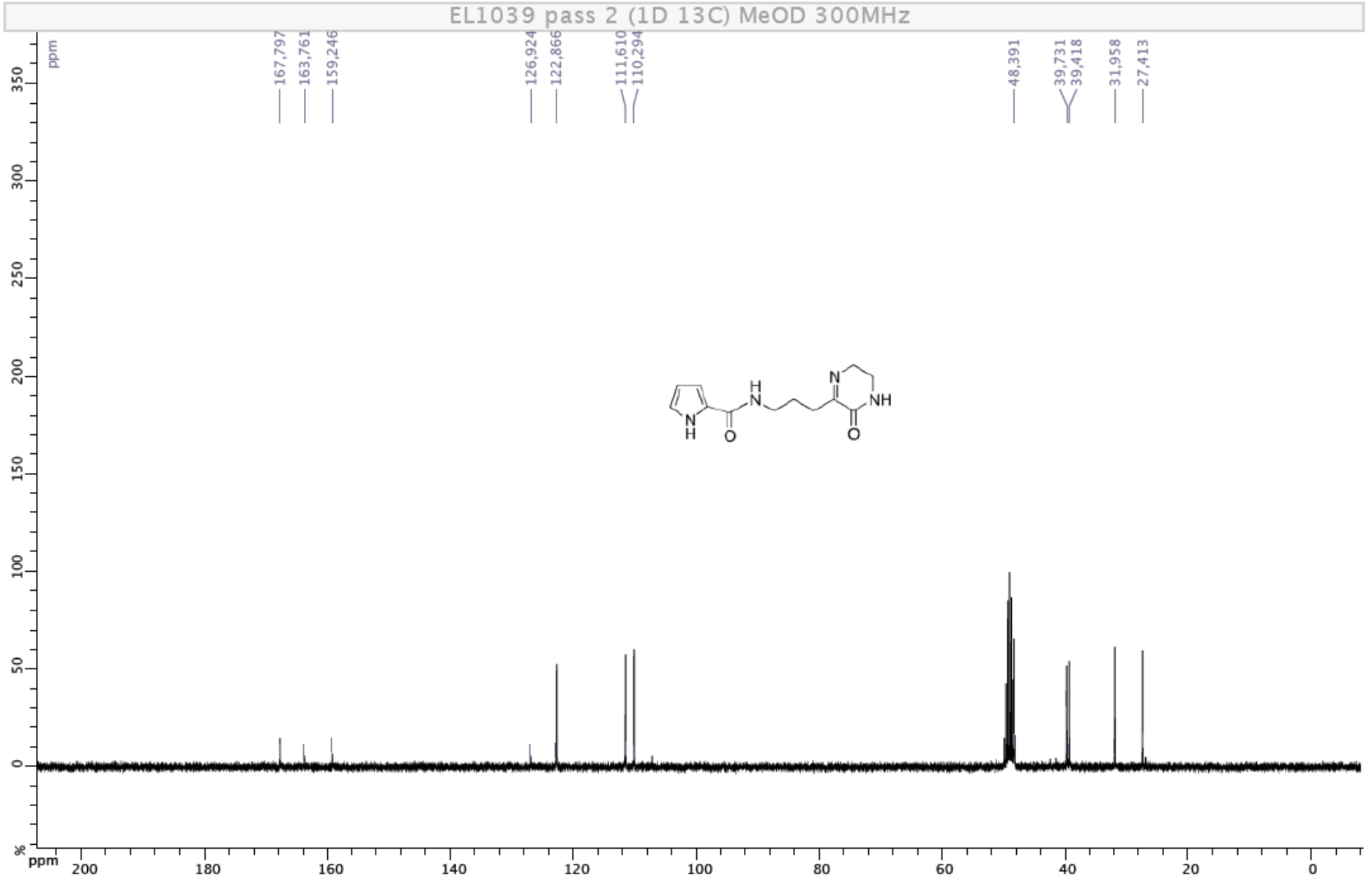
***N*-(3-(4-Hydroxy-5-oxo-2-thioxoimidazolidin-4-yl)propyl)-1*H*-pyrrole-2-carboxamide (4ac)**



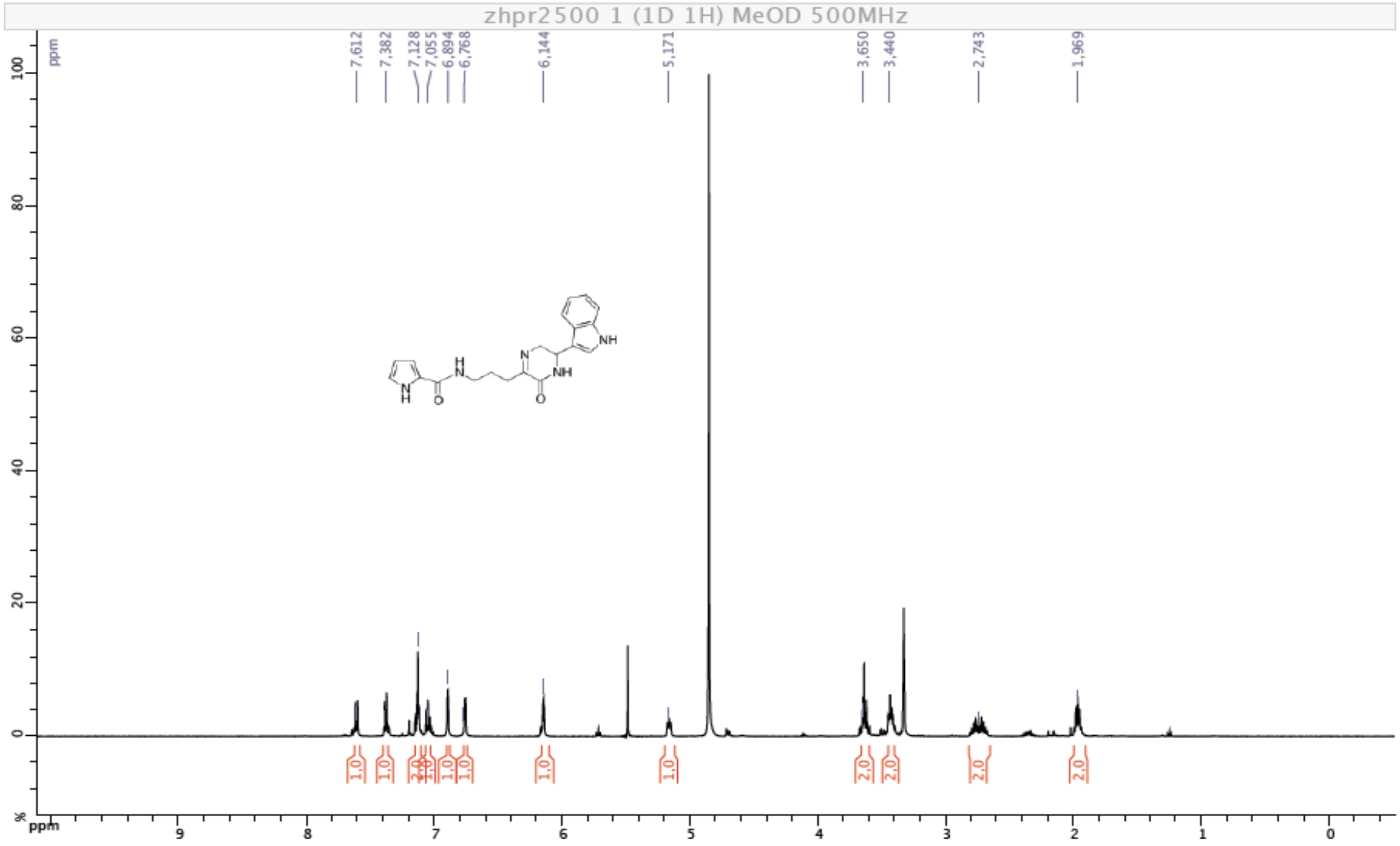

EL33S 2 (1D 13C) MeOD 300MHz
ppm
182,523
176,007
162,480
125,419
121,376
110,162
108,780
86,984
38,389
33,182
23,095
HN
S
NH
H
N
OH
O
N
H
O
%
ppm
200
180
160
140
120
100
80
60
40
20
0

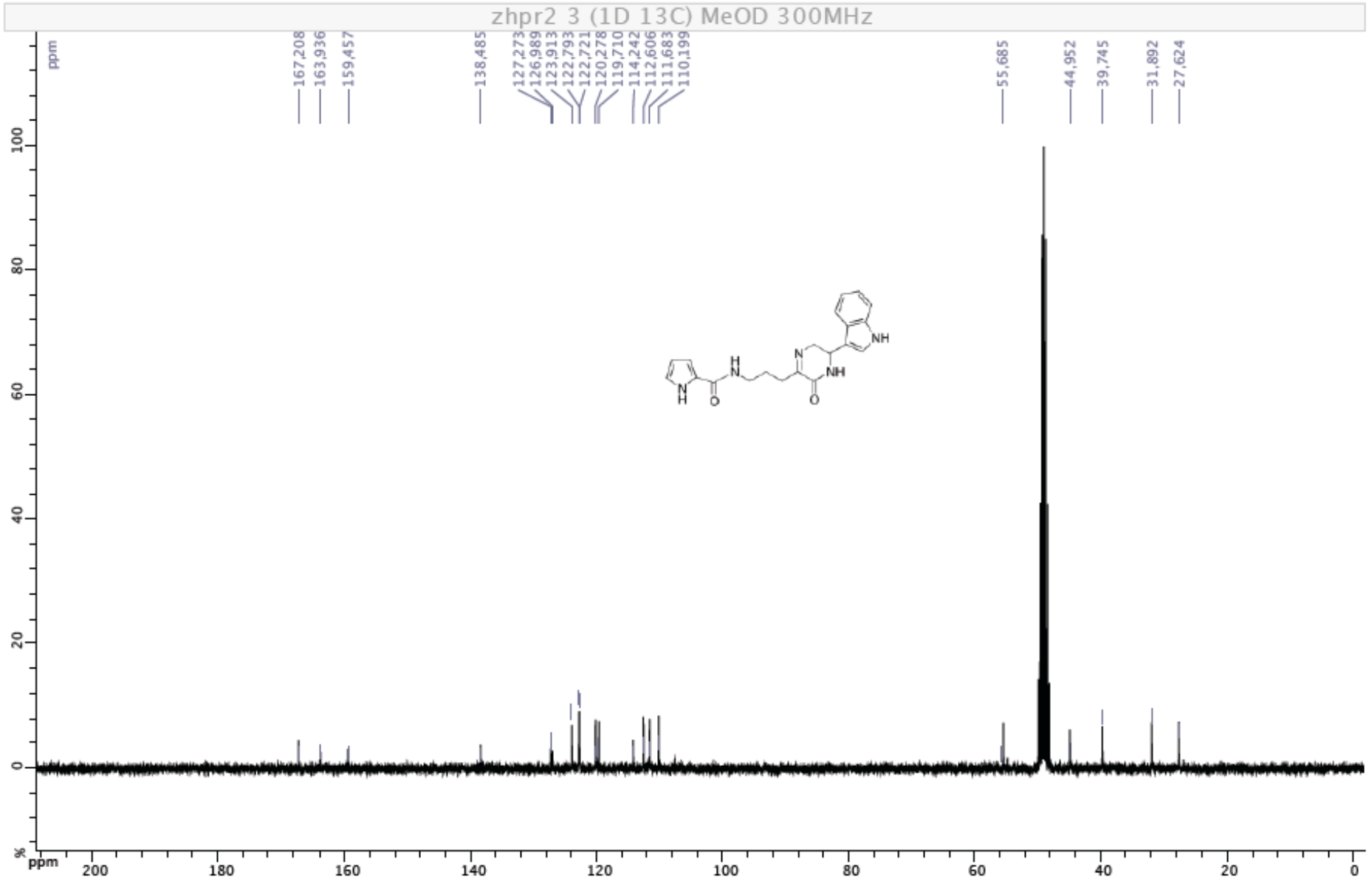
***N*-(3-(3-Oxo-3,4,5,6-tetrahydropyrazin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6aa)**

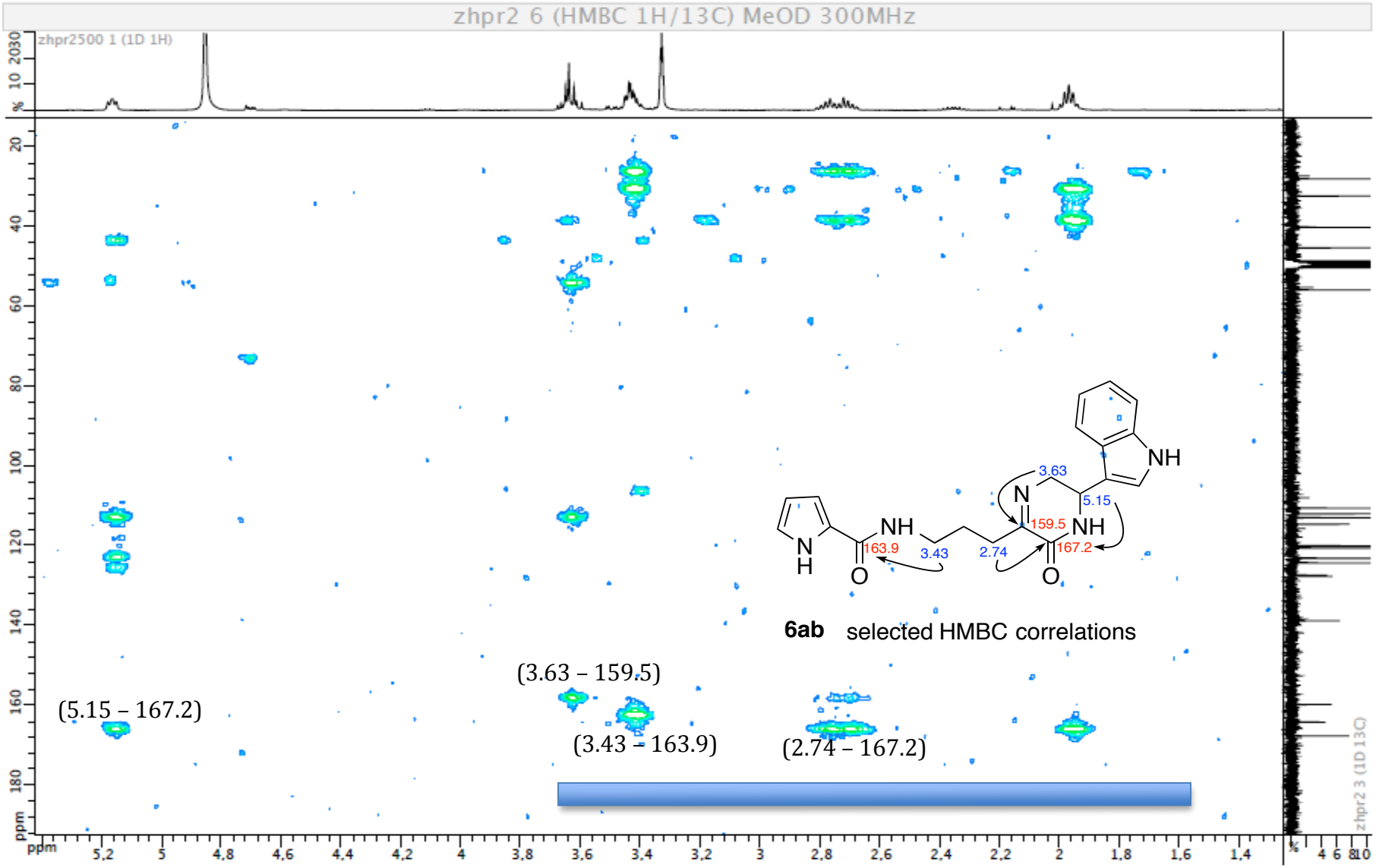



EL1039 pass 2 (1D 13C) MeOD 300MHz
ppm
167,797
163,761
159,246
126,924
122,866
111,610
110,294
48,391
39,731
39,418
31,958
27,413
350
300
250
200
150
100
50
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0
H
N
N
O
N
H
N
NH
O

***N*-(3-(6-(1*H*-Indol-3-yl)-3-oxo-3,4,5,6-tetrahydropyrazin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6ab)**

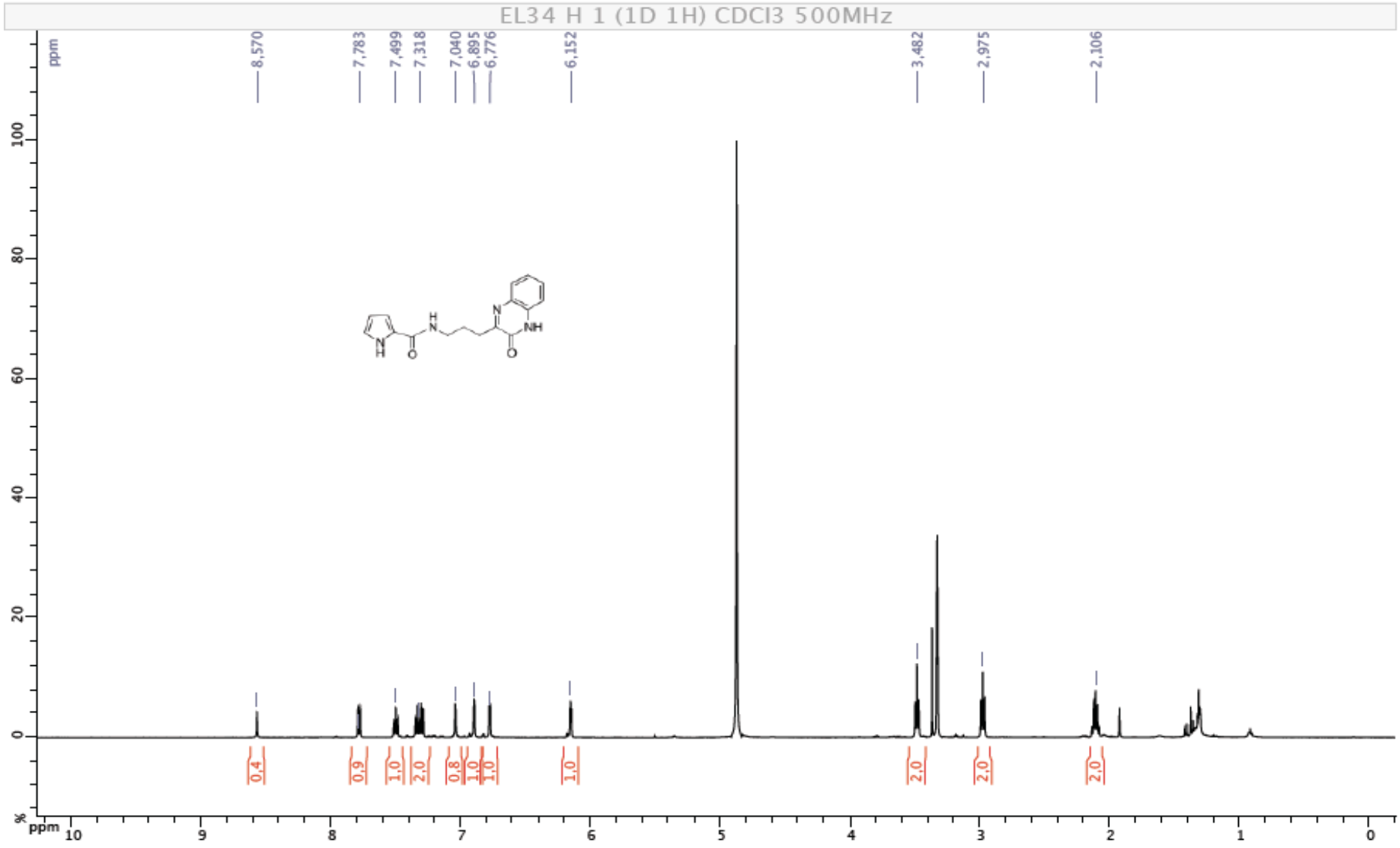


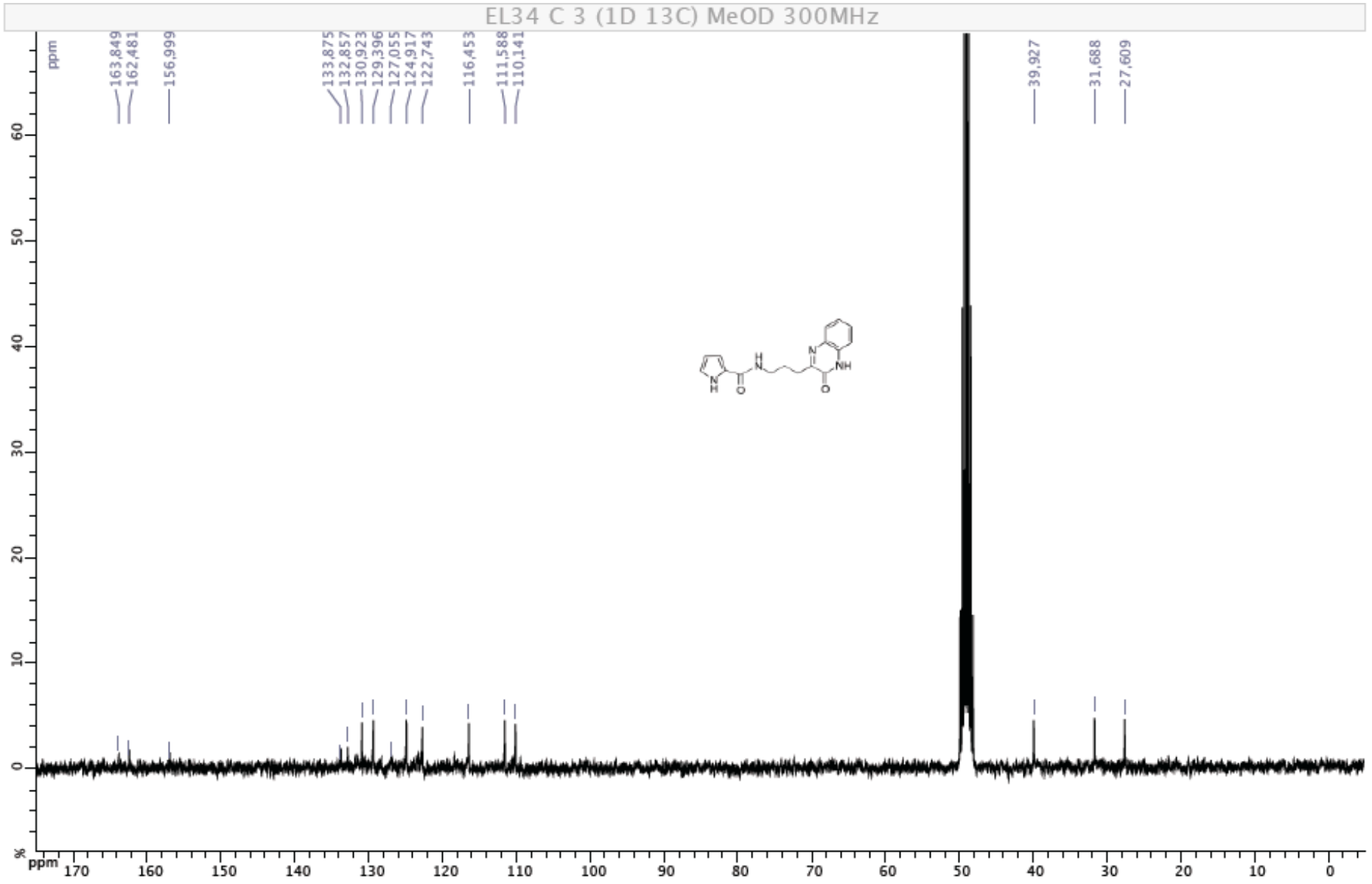

zhpr2 3 (1D 13C) MeOD 300MHz
ppm
167,208
163,936
159,457
138,485
127,273
126,989
123,913
122,793
122,721
120,278
119,710
114,242
112,606
111,683
110,199
55,685
44,952
39,745
31,892
27,624
NH
NH
N
H
N
H
O
O
100
80
60
40
20
0
%
ppm
200
180
160
140
120
100
80
60
40
20
0



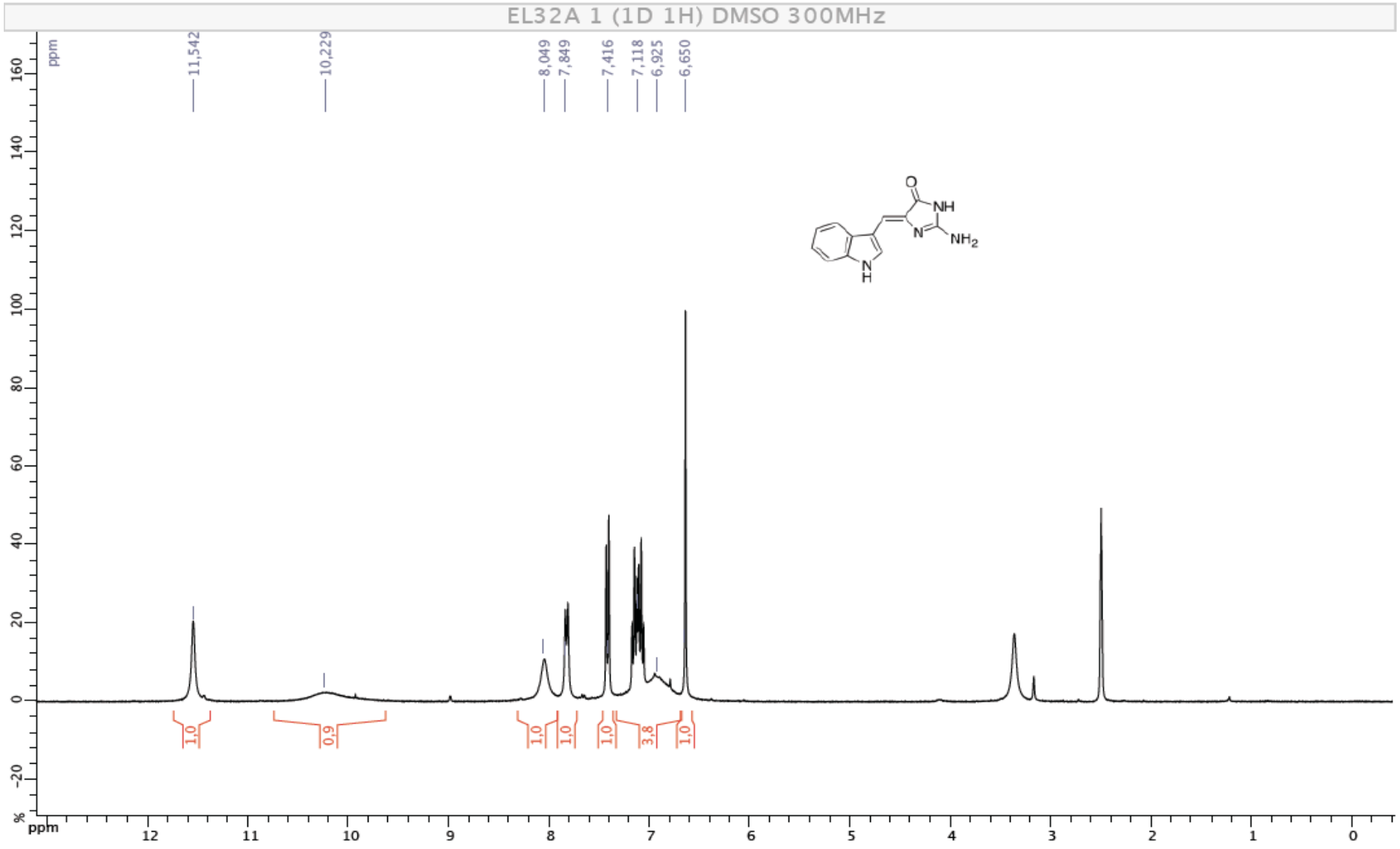
6ab selected HMBC correlations

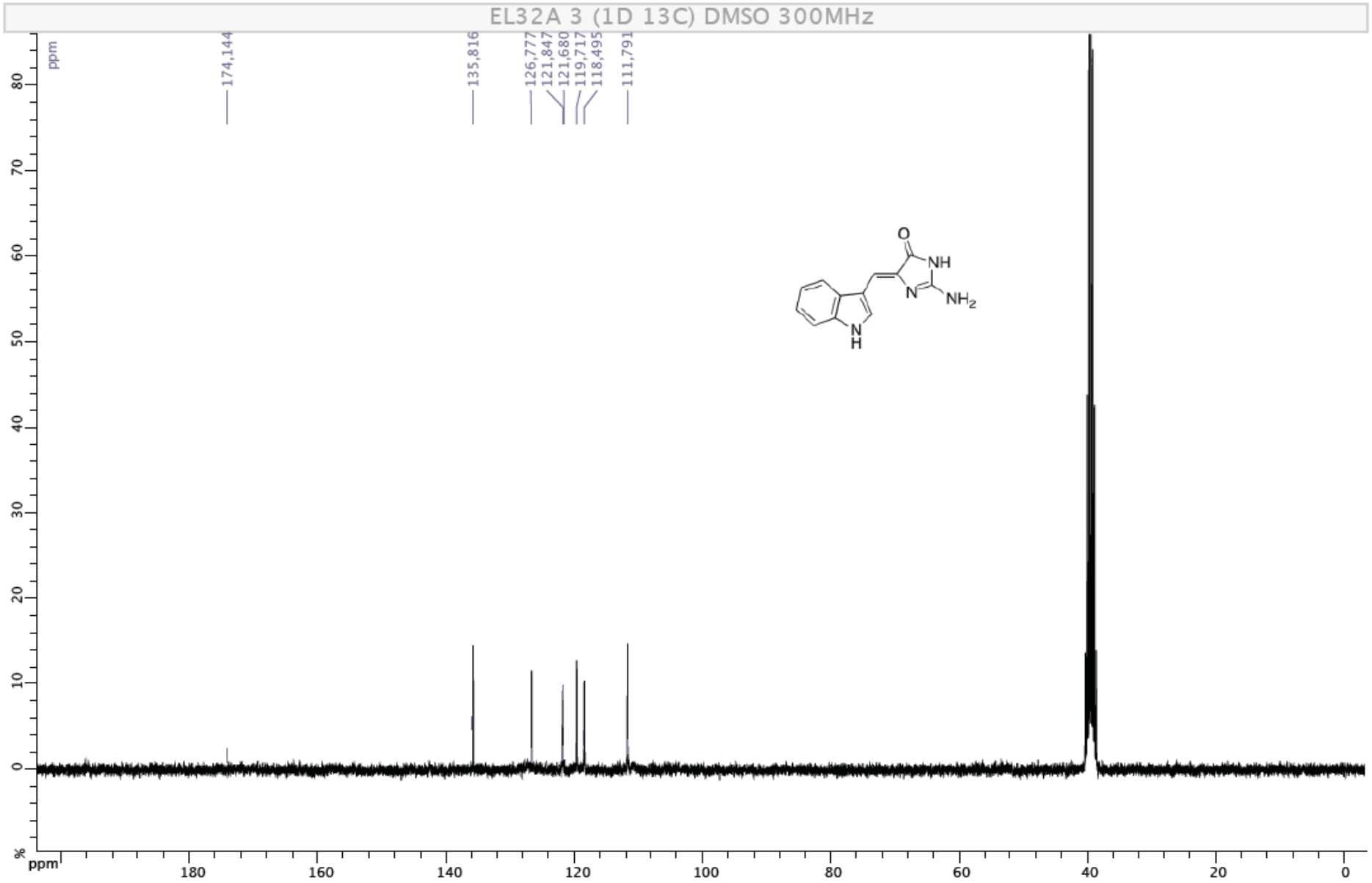
***N*-(3-(3-Oxo-3,4-dihydroquinoxalin-2-yl)propyl)-1*H*-pyrrole-2-carboxamide (6ac)**



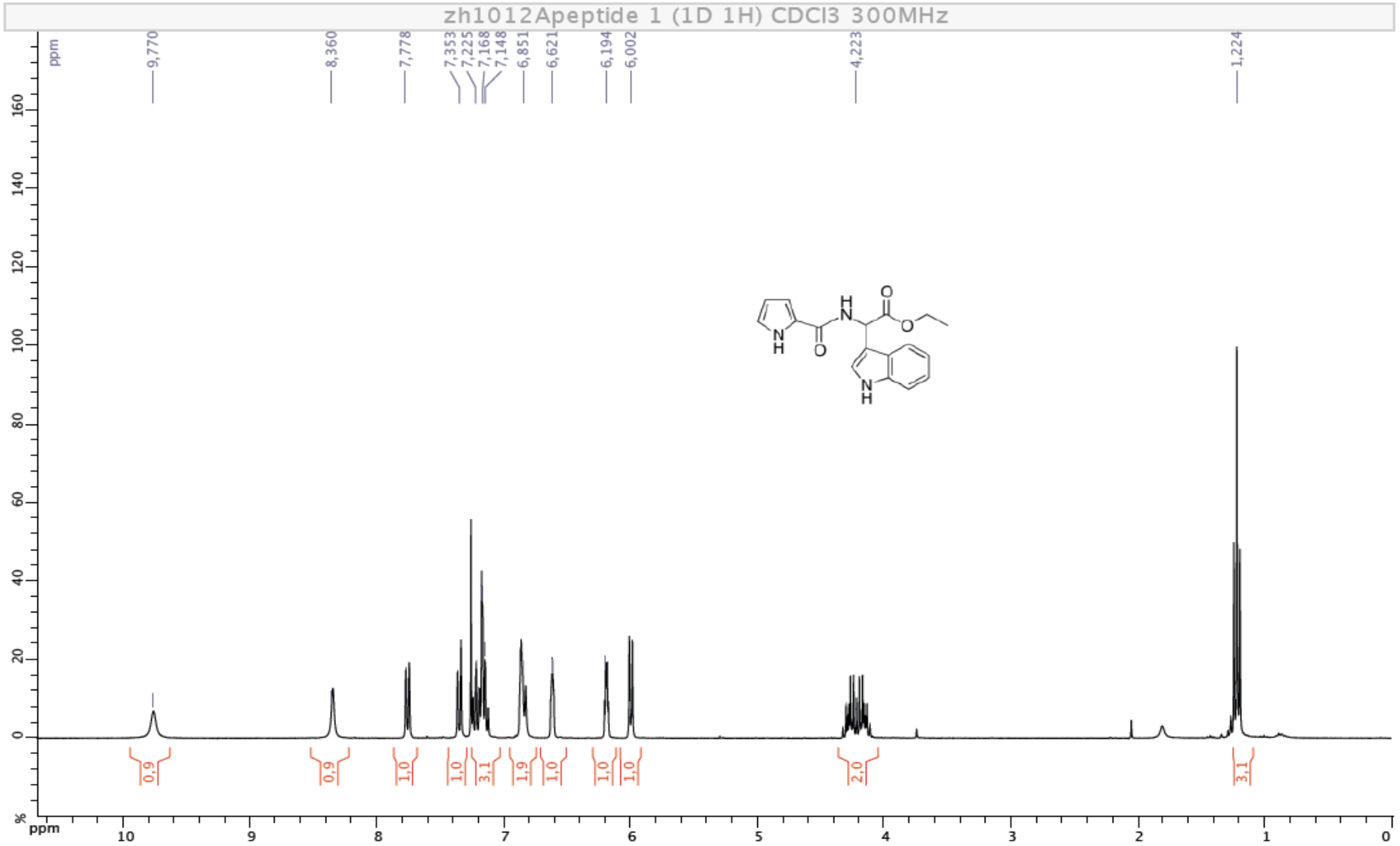

EL34 C 3 (1D 13C) MeOD 300MHz
ppm
163,849
162,481
156,999
133,875
132,857
130,923
129,396
127,055
124,917
122,743
116,453
111,588
110,141
39,927
31,688
27,609
NH
O
O
%
ppm

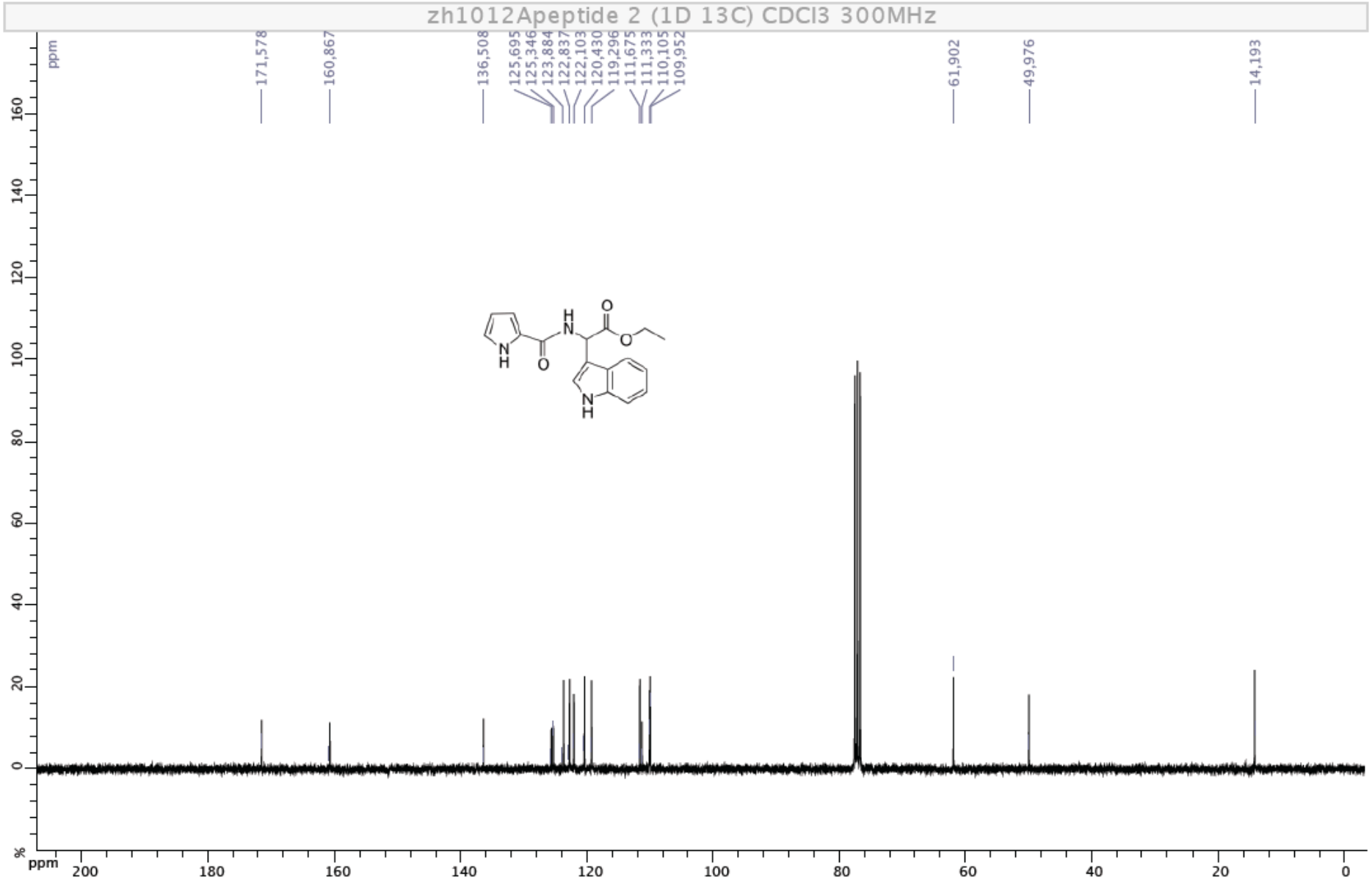
(*Z*)-4-((1*H*-Indol-3-yl)methylene)-2-amino-1*H*-imidazol-5(4*H*)-one (7ca)



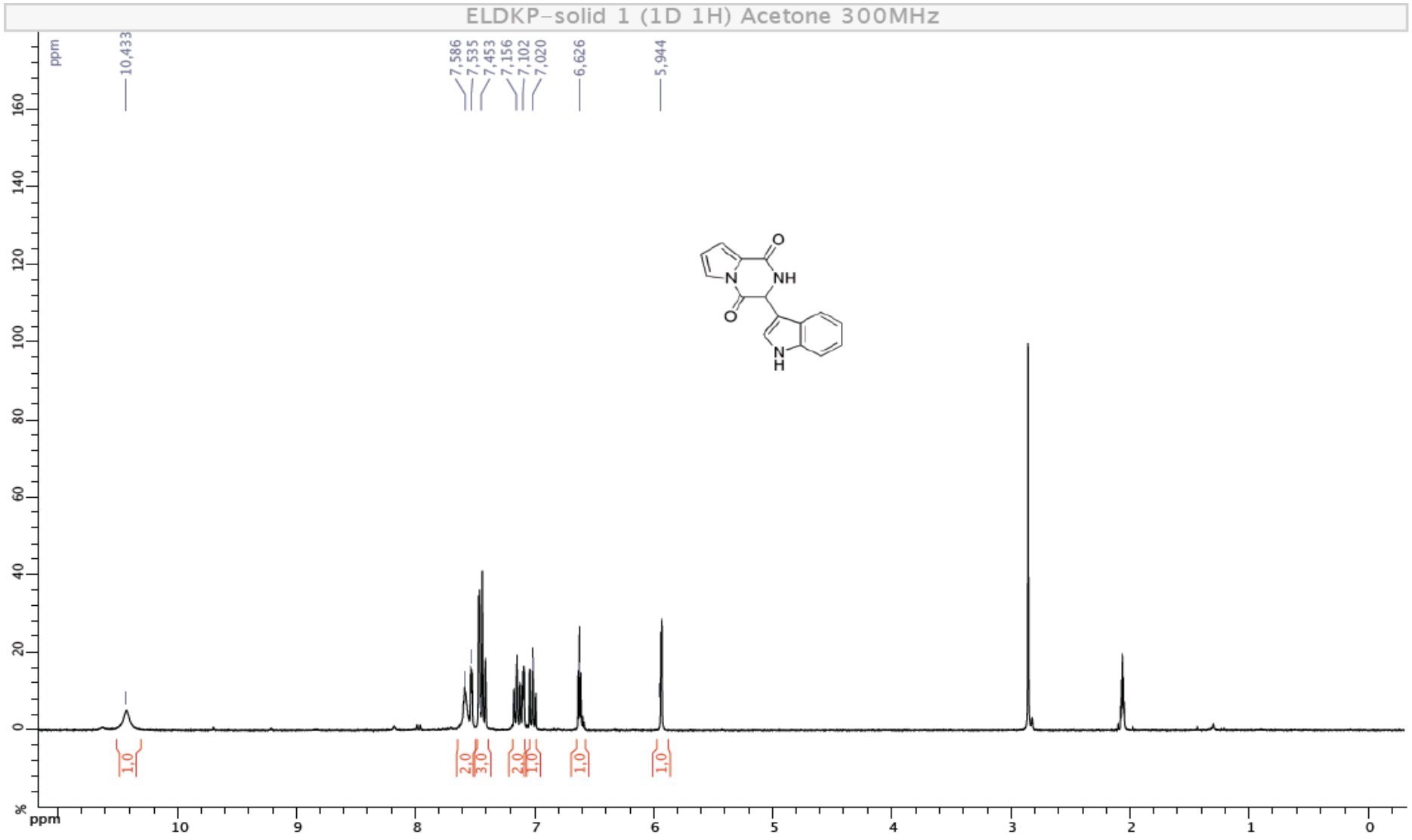

EL32A 3 (1D 13C) DMSO 300MHz
ppm
174,144
135,816
126,777
121,847
121,680
119,717
118,495
111,791
O
NH
N
NH2
N
H
%
ppm
180
160
140
120
100
80
60
40
20
0

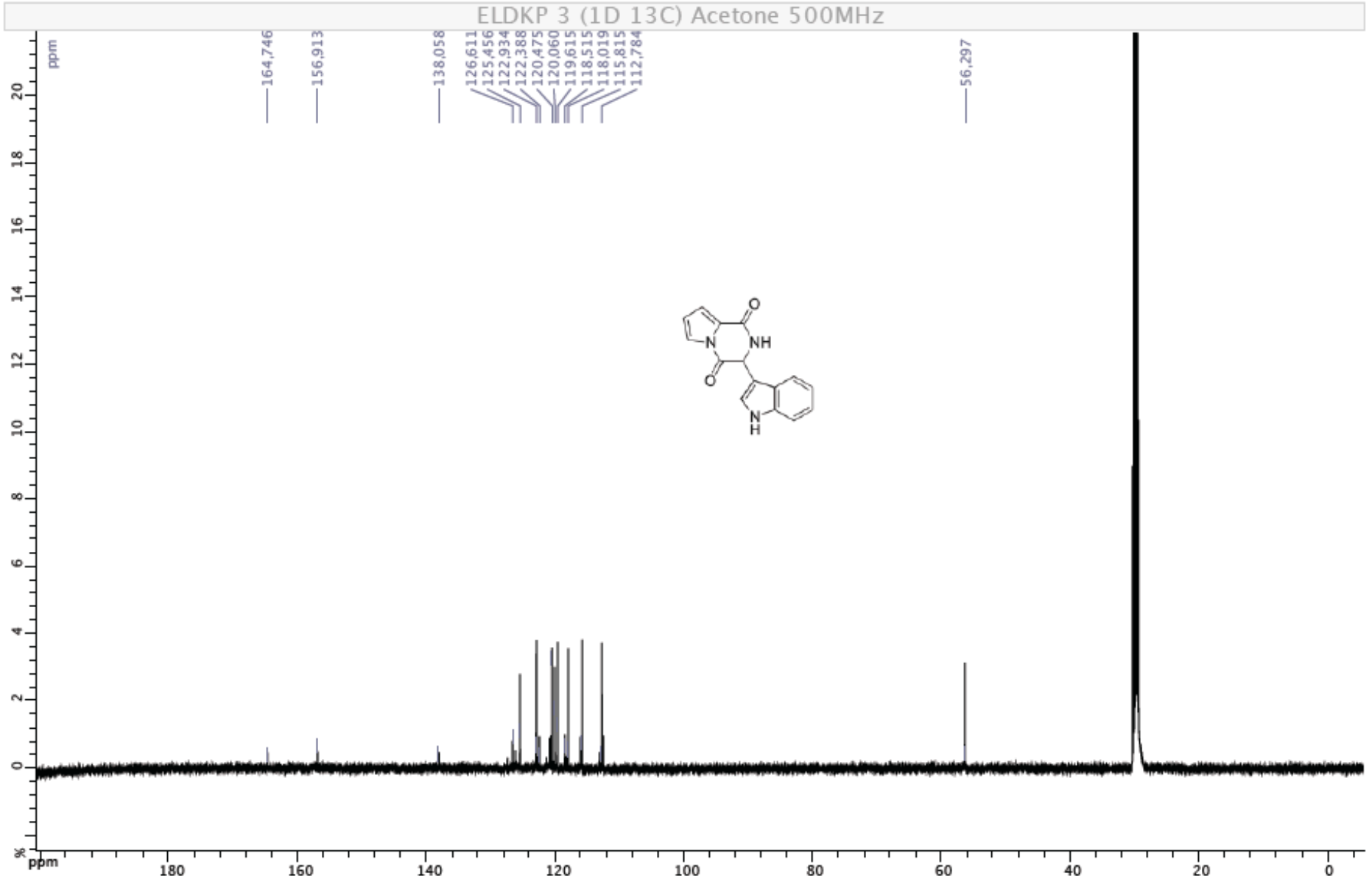
Ethyl 2-(1*H*-indol-3-yl)-2-(1*H*-pyrrole-2-carboxamido)acetate (Ab)



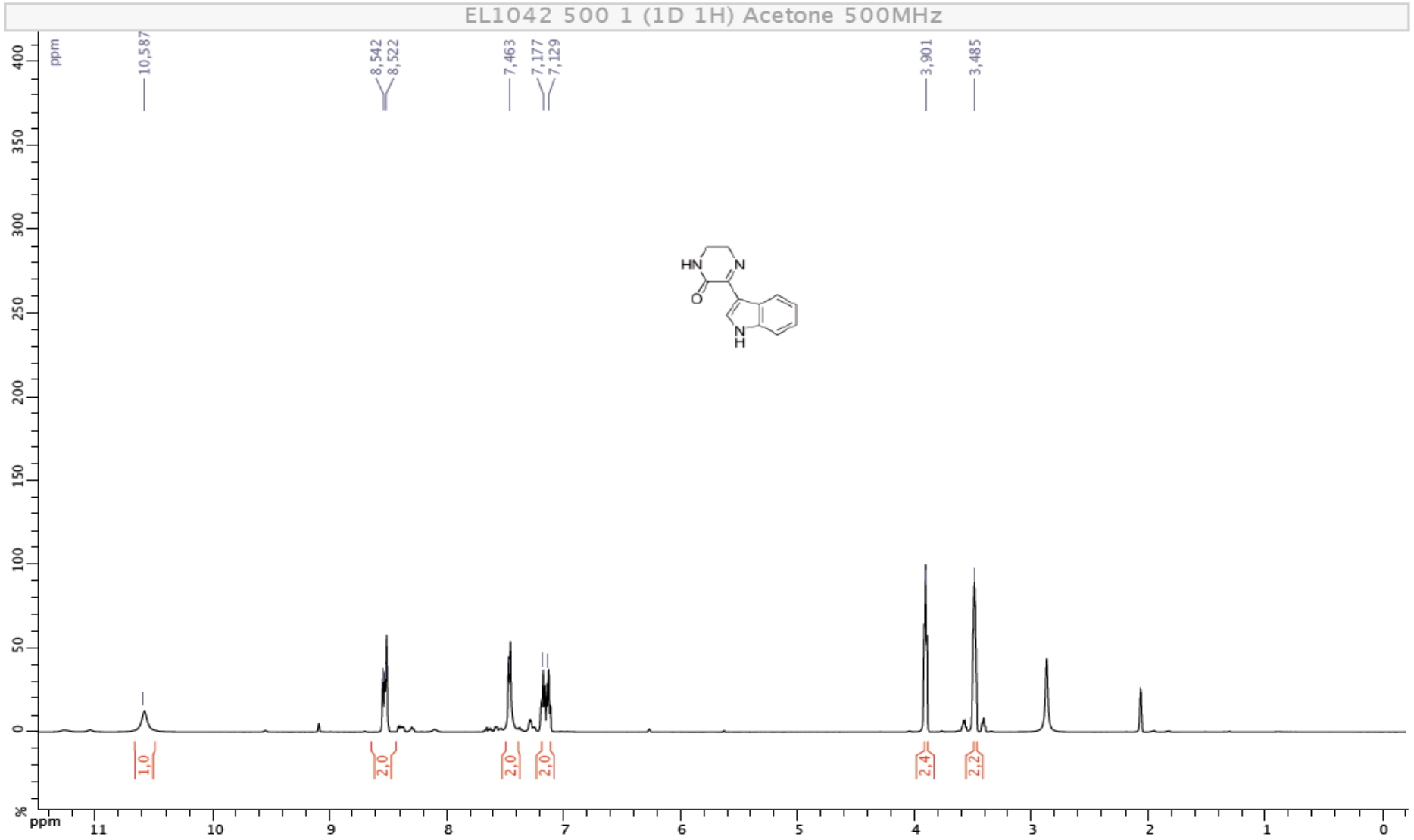

zh1012Apeptide 2 (1D 13C) CDCl3 300MHz
ppm
171,578
160,867
136,508
125,695
125,346
123,884
122,837
122,103
120,430
119,296
111,675
111,333
110,105
109,952
61,902
49,976
14,193
%
ppm
200
180
160
140
120
100
80
60
40
20
0

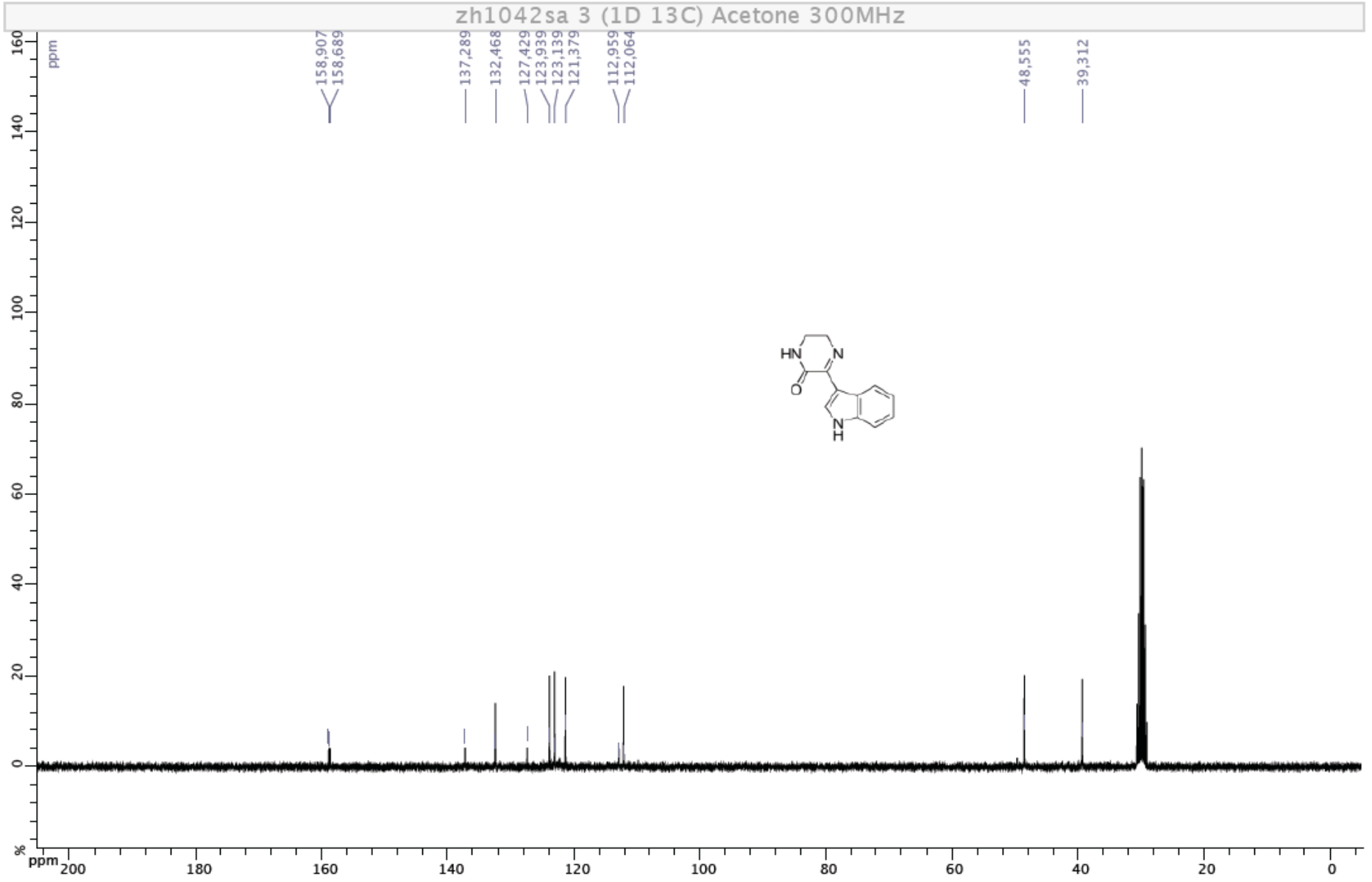
3-(1*H*-Indol-3-yl)-2,3-dihydropyrrolo[1,2-*a*]pyrazine-1,4-dione (1b)



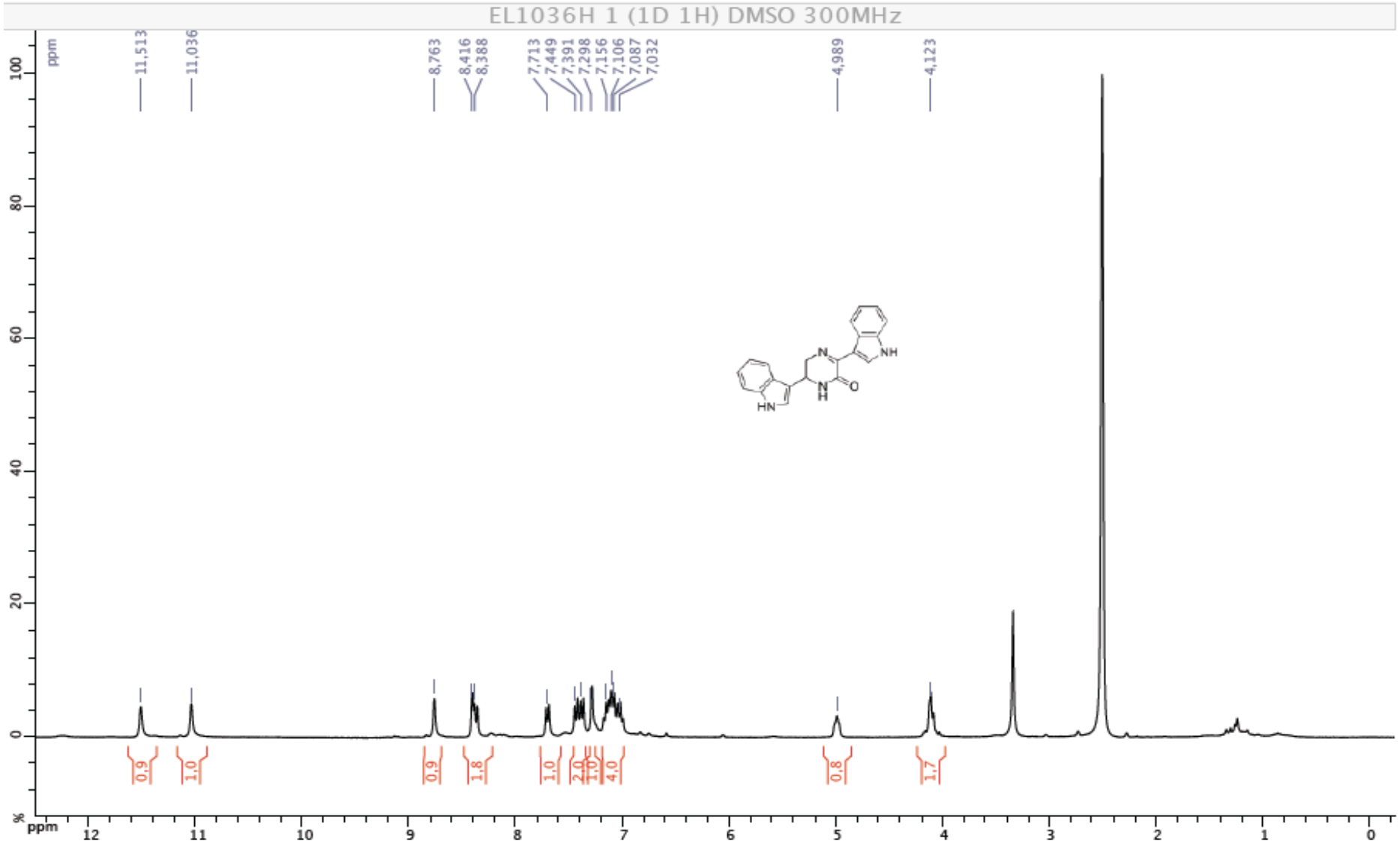

ELDKP 3 (1D 13C) Acetone 500MHz
ppm
164,746
156,913
138,058
126,611
125,456
122,934
122,388
120,475
120,060
119,615
118,515
118,019
115,815
112,784
56,297
O
NH
N
O
NH
%
ppm
180
160
140
120
100
80
60
40
20
0

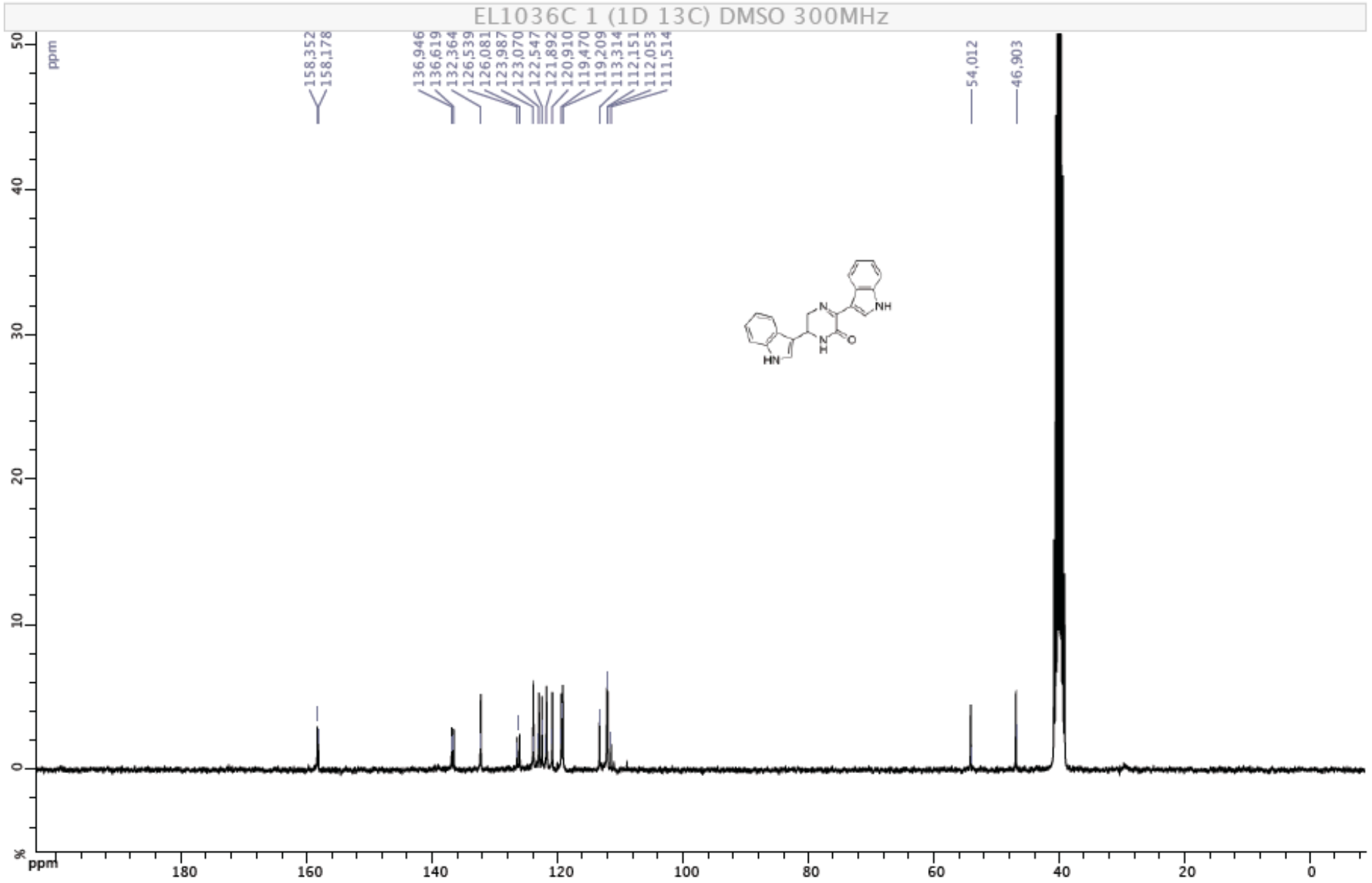
3-(1*H*-Indol-3-yl)-5,6-dihydropyrazin-2(1*H*)-one (8ba)



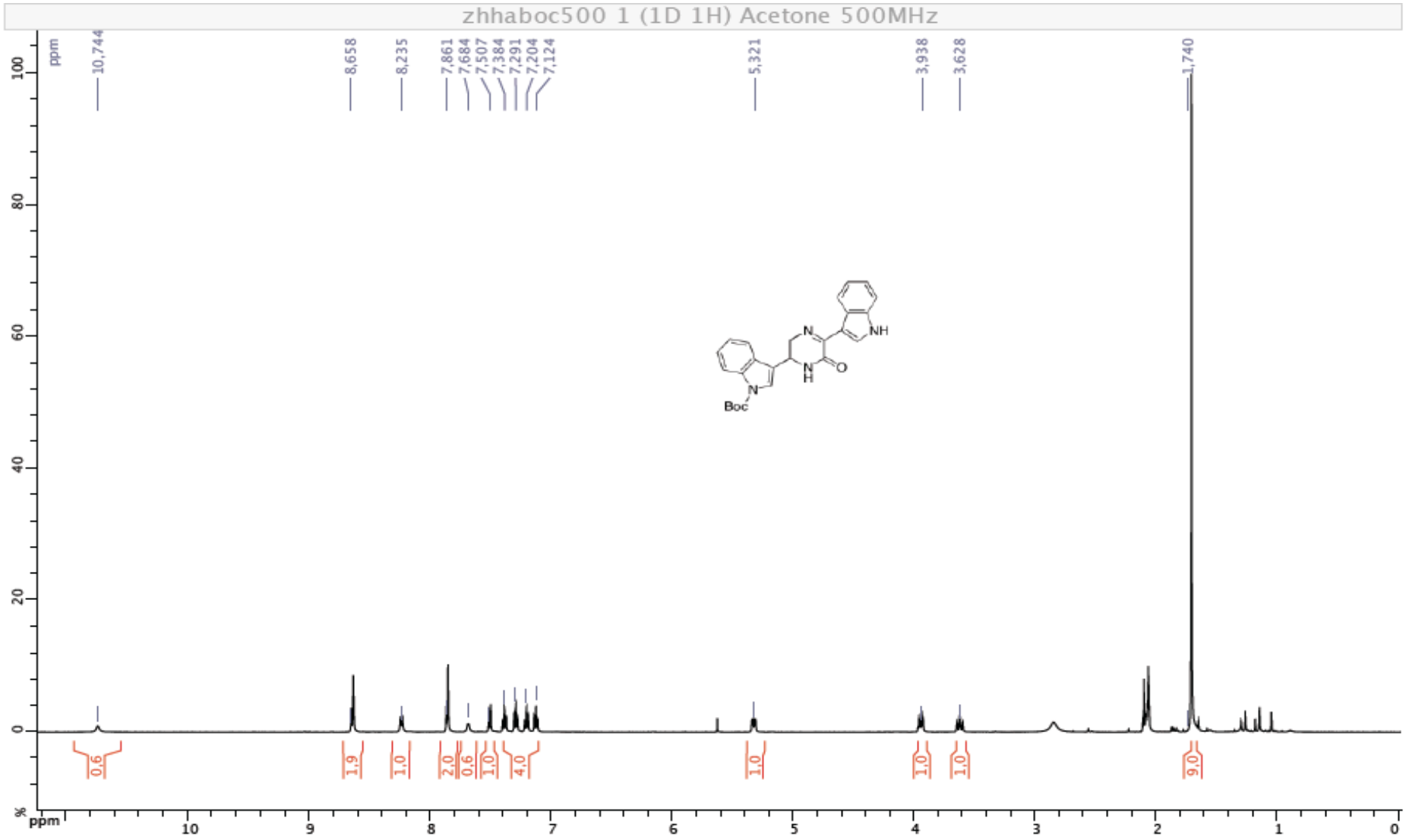

zh1042sa 3 (1D 13C) Acetone 300MHz
ppm
158,907
158,689
137,289
132,468
127,429
123,939
123,139
121,379
112,959
112,064
48,555
39,312
HN
N
O
N
H
%
ppm
200
180
160
140
120
100
80
60
40
20
0

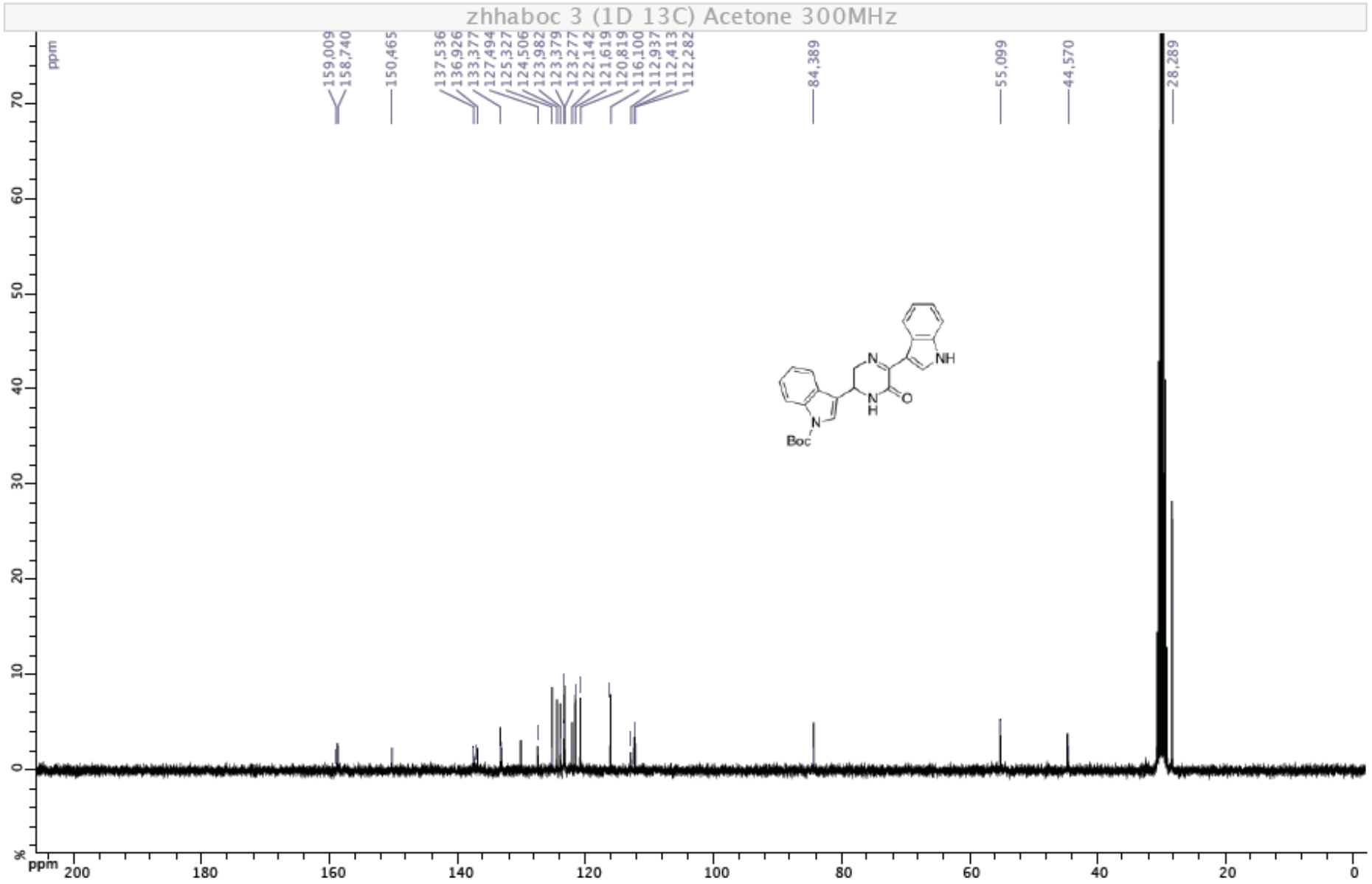
3,6-Di(1*H*-indol-3-yl)-5,6-dihydropyrazin-2(1*H*)-one (8bb)




EL1036C 1 (1D 13C) DMSO 300MHz
ppm
158,352
158,178
136,946
136,619
132,364
126,539
126,081
123,987
123,070
122,547
121,892
120,910
119,470
119,209
113,314
112,151
112,053
111,514
54,012
46,903
NH
HN
N
N
H
O
%
ppm
180
160
140
120
100
80
60
40
20
0

tert-Butyl 3-(5-(1*H*-indol-3-yl)-6-oxo-1,2,3,6-tetrahydropyrazin-2-yl)-1*H*-indole-1-carboxylate (8bd)




zhhaboc 3 (1D 13C) Acetone 300MHz
ppm
159,009
158,740
150,465
137,536
136,926
133,377
127,494
125,327
124,506
123,982
123,379
123,277
122,142
121,619
120,819
116,100
112,937
112,413
112,282
84,389
55,099
44,570
28,289
NH
N
N
H
O
N
Boc
%
ppm
200
180
160
140
120
100
80
60
40
20
0