Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

AITF (4-acetamidophenyl triflimide) mediated synthesis of amides, peptides and esters

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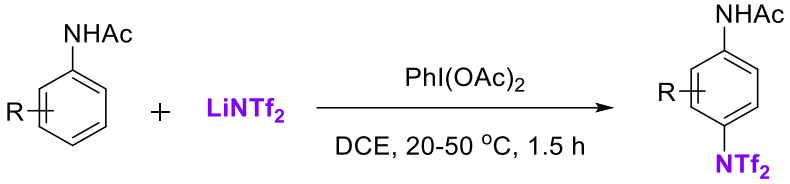
General Experimental Information

All commercially available reagents were used as received without further purification. The solvents were purified and dried by standard procedures prior to use. Reaction progress was monitored by MERCK thin layer chromatography (TLC) performed on aluminium plates coated with silica gel 60 F254. Chromatograms were visualized by UV light at 254 nm or by staining using $KMnO_4$, Iodine. High resolution mass spectra were recorded on a Micromass Q-TOF micromass spectrometer using electron spray ionization mode. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 400 MHz and 100 MHz spectrometer, respectively in DMSO-d_6 using TMS as internal standard. Chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm and coupling constants (J) quoted in Hz. ^{1}H NMR splitting patterns were designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. The RP-HPLC analysis of isomers was carried out by using an Agilent instrument at λ = 254 nm; column: Phenomenex Lux Cellulose-1, pore size-5 μm, diameter × length = 4.6 × 250 mm. For purification of products, column chromatography was performed on silica gel (100-200 mesh) using ethyl acetate and hexane mixture as eluent. Evaporation of solvents was performed under reduced pressure with a Büchi rotary evaporator. Melting points were determined in an open capillary using VEEGO, model: VMP-DS. Differential scanning calorimetry (DSC) was recorded on a Perkin Elmer Differential scanning calorimeter 8000.

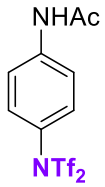
Experimental section:

Procedure for synthesis of coupling reagents:



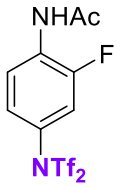
R = H (**III**); *meta*-fluoro **(IV)**; *ortho*-fluoro **(V)**

To a solution of acetanilide (0.5 mmol, 1.0 equiv) and $LiNTf_2$ (0.6 mmol, 1.2 equiv) in DCE (8 mL, 0.06 M) in a Schlenk flask under argon was added (diacetoxyiodo)benzene (DIB) (0.6 mmol, 1.2 equiv). The resulting mixture was stirred for 1.5 hours at 50 °C then filtered through a short plug of celite and concentrated under reduced pressure. The crude product was purified by silica gel chromatography.



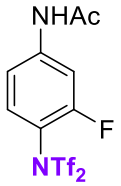
N-(4-((1,1,1-trifluoro-N-((trifluoromethyl)sulfonyl)methyl)sulfonamido)phenyl)acetamide **(III)**

White solid; Yield 78 %; M.p.154-162 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 142.8, 131.8, 128.6, 124.4, 120.4, 119.7, 118.9, 117.1, 24.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_8F_6N_2O_5S_2$ 414.9857, found 414.9845.



N-(2-fluoro-4-((1,1,1-trifluoro-N-((trifluoromethyl)sulfonyl)methyl)sulfonamido)phenyl)acetamide **(IV)**

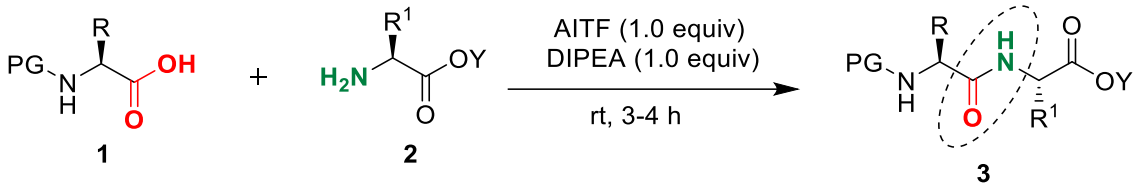
White solid; Yield 59 %; M.p.136-137 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.28 (t, J = 8.7 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.54 (d, J = 8.9 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 154.8, 152.4, 131.5, 131.4, 131.3, 131.2, 128.42 (2), 125.4, 125.2, 123.6, 123.5, 119.45 (2), 111.1, 110.9, 23.8.



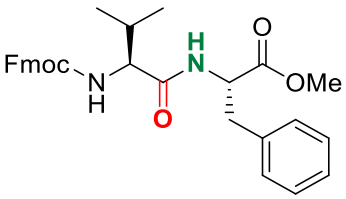
N-(3-fluoro-4-((1,1,1-trifluoro-N-((trifluoromethyl)sulfonyl)methyl)sulfonamido)phenyl)acetamide **(V)**

White solid; Yield 50 %; M.p.137-138 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.27 (t, J = 8.7 Hz, 1H), 7.92 (d, J = 10.8 Hz, 1H), 7.54 (d, J = 8.9 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 154.8, 152.4, 131.5, 131.4, 131.3, 131.2, 128.4, 125.4, 125.2 (2), 121.7, 119.4 (2), 118.5, 111.1, 110.9, 23.8.

Procedure for synthesis of peptides:



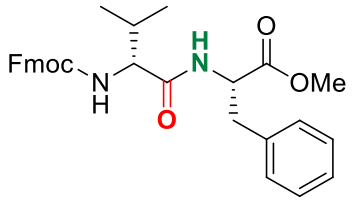
AITF (1.0 equiv) was added to a stirred solution of N^{α}-protected amino acid **1** (1.0 equiv) and DIPEA (1.0 equiv) in CH_3CN (3 mL) at room temperature. Then the reaction mixture was stirred for 20 min and amino acid ester (1.2 equiv) was added and the reaction mixture was stirred for 2.5 h at room temperature. The progress of the reaction was monitored by TLC. Thereafter, the reaction mixture was concentrated using rotary evaporator and then diluted with 15 mL of ethyl acetate and washed with 5% HCl (10 mL x 2) 5% Na_2CO_3 (10 mL x 2), saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting crude product was purified by silica gel column chromatography using the mixture of hexane and ethyl acetate as eluents to afford **3**.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-methylbutanamido)-3-phenylpropanoate (**3a**)

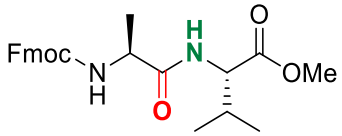
White solid; Yield 93 %; M.p. 168-172 ˚C; $[\alpha]_D^{25}$ = -11.00 (c 1.0, CH_3OH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, J = 8Hz, 1H), 7.89 (d, J = 8Hz, 2H), 7.73 (dd, J = 8Hz, J = 4Hz, 2H), 7.42 (t, J = 8Hz, 2H), 7.31 (dd, J = 16Hz, J = 4Hz, 3H), 7.23-7.16 (m, 5H), 4.48 (dd, J = 12Hz, J = 8Hz, 1H), 4.30-4.21 (m, 3H), 3.87 (t, J = 8Hz, 1H), 3.55 (s, 3H), 3.02 (dd, J = 12Hz, J = 8Hz, 1H), 2.92 (dd, J = 12Hz, J = 8Hz, 1H), 1.99 (dd, J = 12Hz, J = 8Hz, 1H), 0.82 (d, J = 4Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.7, 171.2, 155.9, 143.9, 143.7, 140.6, 137.0, 128.9, 128.1,

127.6, 127.0, 125.3, 120.0, 65.6, 59.8, 53.4, 51.6, 46.6, 36.5, 30.4, 19.0,18.1; IR (cm^{-1}): 3290, 2960, 1741, 1696, 1645, 1529, 1444, 1291, 1245, 1212, 1103, 1027, 757, 697; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_5$ 501.2389, found 501.2384.



(S)-methyl 2-((R)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-methylbutanamido)-3-phenylpropanoate (**3a***)

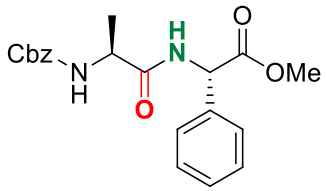
White solid; Yield 90 %; M.p. 193-197 ˚C; $[\alpha]_D^{25}$ = +29.52 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.42 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.34 – 7.16 (m, 8H), 4.54-4.48 (m, 1H), 4.32 – 4.17 (m, 3H), 3.89 (dd, *J* = 8.0,8.0 Hz, 1H), 3.61 (s, 3H), 3.06 (dd, *J* = 16, 8 Hz, 1H), 2.87 (dd, *J* = 12, 12 Hz, 1H), 1.87-1.78 (m, 1H), 0.66 (dd, *J* = 8.0, 8.0 Hz, 6H);^{13}C NMR (101 MHz, DMSO-d_6) δ 171.9, 171.1, 156.0, 143.8, 143.7, 140.6 (2), 137.1, 129.0, 128.1, 127.6, 127.0, 126.4, 125.4, 125.3, 120.0, 65.7, 59.7, 53.4, 51.8, 46.6, 36.7, 30.4, 19.0, 17.6; HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_5$ 501.2389, found 501.2386.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanamido)-3-methylbutanoate (**3b**)

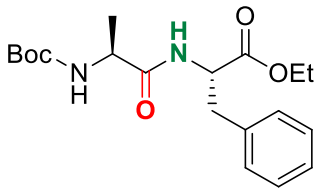
White solid; Yield 91%; M.p. 149-153 ˚C; $[\alpha]_D^{25}$ = +207.70 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, *J* = 12Hz, 1H), 7.89 (d, *J* = 8Hz, 2H), 7.72 (t, *J* = 8Hz, 2H), 7.53 (d, *J* = 8Hz, 1H), 7.41 (t, *J* = 8Hz, 2H), 7.32 (t, *J* = 8Hz, 2H), 4.27-4.15 (m, 5H), 3.62 (s, 3H), 2.05-1.99 (m, 1H), 1.21 (d, *J* = 8Hz, 3H), 0.87 (t, *J* = 4Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.9, 171.9, 155.5, 143.8, 143.7, 140.6, 127.6, 127.0, 125.2 (2), 120.0, 65.5, 57.2, 51.6, 49.5, 46.5, 29.9, 18.8, 18.1 (2); IR (cm^{-1}): 3304, 2927, 1733, 1686, 1650, 1549, 1447, 1255, 1208,

1016, 794, 664; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{28}N_2NaO_5$ 447.1896, found 447.1873.



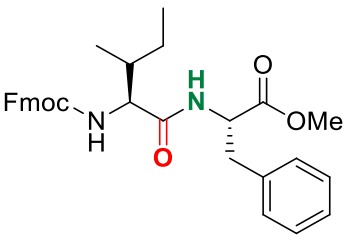
methyl (S)-2-((S)-2-(((benzyloxy)carbonyl)amino)propanamido)-2-phenylacetate (**3c**)

White solid; Yield 92%; M.p. 122-125 ˚C; $[\alpha]_D^{25}$ = +226.46 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.66 (d, *J* = 4Hz, 1H), 7.45 (d, *J* = 8Hz, 1H), 7.39-7.27 (m, 10H), 5.41 (d, *J* = 4Hz, 1H), 5.00 (s, 2H), 4.24-4.17 (m, 1H), 3.62 (s, 3H), 1.24 (d, *J* = 4Hz, 3H); ^{13}C NMR(101 MHz, DMSO-d_6) δ 172.6, 170.9, 155.5, 137.0, 135.9, 128.6, 128.3, 127.7, 127.6, 65.3, 56.1, 52.2, 49.5, 18.1; IR (cm^{-1}): 3304, 2952, 1735, 1693, 1650, 1527, 1496, 1210, 1122, 1060, 731, 694; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{22}N_2NaO_5$ 393.1426, found 393.1424.



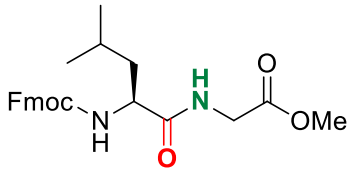
(S)-ethyl 2-((S)-2-((tert-butoxycarbonyl)amino)propanamido)-3-phenylpropanoate (**3d**)

White solid; Yield 86%; M.p. 100.5-102 ˚C; $[\alpha]_D^{25}$ = -98.97 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, *J* = 8Hz, 1H), 7.29-7.20 (m, 5H), 6.86 (d, *J* = 8Hz, 1H), 4.42 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 4.04-3.95 (m, 3H), 3.01-2.94 (m, 2H), 1.36 (s, 9H), 1.13-1.06 (m, 6H); ^{13}C NMR(101 MHz, DMSO-d_6) δ 172.8, 171.3, 154.8, 137.0, 129.1, 128.1, 126.5, 77.9, 60.4, 53.4, 49.4, 36.6, 28.1, 18.1, 13.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{28}N_2NaO_5$ 387.1896, found 387.1857.



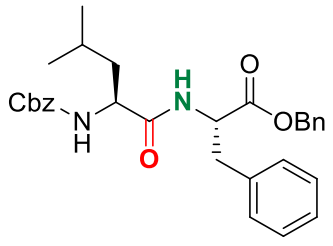
S)-methyl 2-((2S,3R)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-methylpentanamido)-3-phenylpropanoate(**3e**)

White solid; Yield 89%; M.p. 175-178 ˚C; $[\alpha]_D^{25}$ = -139.96 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.41 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 6.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.24 – 7.17 (m, 5H), 4.52 – 4.46 (m, 1H), 4.32 – 4.22 (m, 3H), 3.91 (t, *J* = 8.7 Hz, 1H), 3.56 (s, 3H), 3.03 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.94 (dd, *J* = 13.8, 8.8 Hz, 1H), 1.72-1.66 (m, 1H), 1.13 – 1.05 (m, 2H), 0.83 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.7, 171.3, 155.8, 143.9, 143.7, 140.6, 137.0, 128.9, 128.1, 127.6, 127.0, 126.4, 125.3, 120.0, 65.5, 58.7, 53.4, 51.6, 46.6, 36.5, 36.3 24.2, 15.0, 10.7; IR (cm^{-1}): 2964, 1751, 1691, 1649, 1536, 1449, 1289, 1206, 1121, 1031, 757; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{34}N_2NaO_5$ 537.2365, found 537.2351.



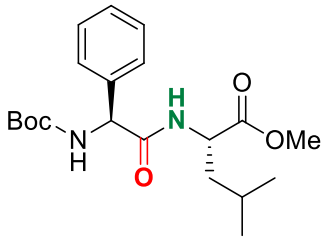
(S)-methyl 2-(2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-methylpentanamido)acetate (**3f**)

White solid; Yield 91%; M.p. 125-128 °C; $[\alpha]_D^{25}$ = -268.94 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.35 (t, *J* = 5.8 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.74 (dd, *J* = 7.3, 3.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.33 (td, *J* = 7.2, 3.5 Hz, 2H), 4.33 – 4.20 (m, 3H), 4.11 – 4.05 (m, 1H), 3.84 (qd, *J* = 17.4, 5.9 Hz, 2H), 3.62 (s, 3H), 1.69 – 1.60 (m, 1H), 1.55 – 1.41 (m, 2H), 0.88 (dd, *J* = 15.3, 6.6 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.4, 170.7, 156.3, 144.3 (2), 141.1, 128.1, 127.5, 125.8, 120.5, 66.0, 53.2, 52.1, 47.1, 41.1, 40.9, 24.5, 23.4, 21.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{34}N_2NaO_5$ 425.2076, found 425.2075.



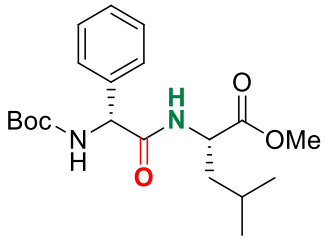
(S)-benzyl 2-((S)-2-(((benzyloxy)carbonyl)amino)-4-methylpentanamido)-3-phenylpropanoate (**3g**)

White solid; Yield 90%; M.p. 96-102 ºC; $[\alpha]_D^{25}$ = -312.26 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.10 (m, 15H), 5.11 – 4.97 (m, 4H), 4.60 – 4.47 (m, 1H), 4.10 – 4.04 (m, 1H), 3.08 – 2.96 (m, 2H), 1.67 – 1.45 (m, 2H), 1.41 – 1.33 (m, 1H), 0.85 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.9, 171.7, 156.2, 137.5, 136.1, 129.5, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 126.9, 66.4, 65.7, 54.0, 53.2, 41.1, 36.9, 24.5, 23.4, 21.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{34}N_2NaO_5$ 525.2365, found 525.2369.



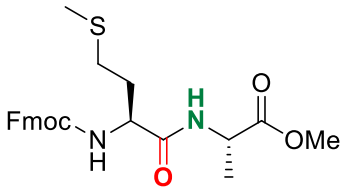
(S)-methyl 2-((S)-2-((tert-butoxycarbonyl)amino)-2-phenylacetamido)-4-methylpentanoate (**3h**)

White solid; Yield 92%; M.p. 81-82 ˚C; $[\alpha]_D^{25}$ = -69.86 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6): δ 8.52 (d, *J* = 8Hz, 1H), 7.39 (t, *J* = 8Hz, 2H), 7.34-7.27 (m, 4H), 5.23 (d, *J* = 8Hz, 1H), 4.33-4.27 (m, 1H), 3.53 (s, 3H), 1.60-1.53 (m, 3H), 1.38 (s, 9H), 0.85 (dd, *J* = 20Hz, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.5, 170.0, 154.8, 138.3, 128.0, 127.4, 127.1, 78.3, 57.3, 51.7, 50.2, 40.1, 28.1, 24.0, 22.7, 21.2; IR (cm^{-1}): 2964, 2888, 1725, 1670, 1522, 1377, 1152, 700; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{31}N_2O_5$ 379.2233, found 379.2223.



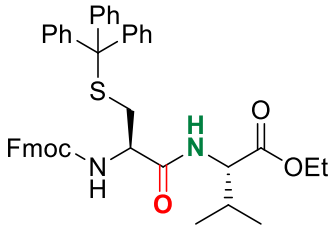
(S)-methyl 2-((R)-2-((tert-butoxycarbonyl)amino)-2-phenylacetamido)-4-methylpentanoate (**3h***)

White solid; Yield 89 %; M.p. 110-114 ˚C; $[\alpha]_D^{25}$ = -162.88 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.54 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.19 (d, *J* = 12 Hz, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 4.25-4.19 (m, 1H), 3.62 (s, 3H), 1.58-1.42 (m, 3H), 1.38 (s, 9H), 0.71 (dd, *J* = 44.4, 6.3 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.7, 170.1, 154.7, 138.8, 128.1, 127.4, 127.0, 78.4, 57.5, 51.8, 50.2, 40.2, 28.0, 24.0, 22.6, 20.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{30}N_2NaO_5$ 401.2052, found 401.2052.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino(methylthio)butanamido)propanoate (**3i**)

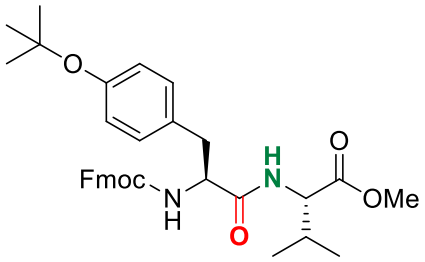
White solid; Yield 88 %; M.p. 155-158 ˚C; $[\alpha]_D^{25}$ = +46.31 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.39 (d, *J* = 8Hz, 1H), 7.89 (d, *J* = 8Hz, 2H), 7.73 (t, *J* = 4Hz, 2H), 7.58 (d, *J* = 8Hz, 1H), 7.44-7.31 (m, 4H), 4.28-4.19 (m, 4H), 4.14-4.09 (m, 1H), 3.61 (s, 3H), 2.47 (d, *J* = 8Hz, 2H), 2.05 (s, 3H), 1.92-1.78 (m, 2H), 1.28 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.9, 171.4, 155.8, 143.8, 143.7, 140.6, 127.6, 127.0, 125.3, 120.1, 65.5, 53.4, 51.8, 47.5, 46.6, 31.7, 29.4, 16.7, 14.6; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}N_2O_5S$ 457.1719, found 457.1789.



(S)-ethyl 2-((R)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(tritylthio)propanamido)-3-methylbutanoate (**3j**)

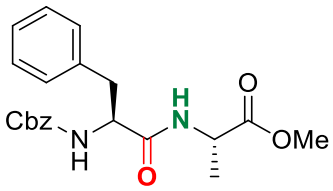
White solid; Yield 88 %; M.p. 110-132 ˚C; $[\alpha]_D^{25}$ = +219.28 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, *J* = 8Hz, 1H), 7.89 (d, *J* = 4Hz, 2H), 7.72 (t, *J* = 8Hz, 2H), 7.42-7.22 (m, 20H), 4.30-4.17 (m, 4H), 4.08-3.95 (m, 3H), 2.41-2.33 (m, 2H), 2.03-1.95 (m, 1H), 1.05 (t, *J* = 8Hz, 3H), 0.82 (t, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.8, 170.2, 155.6, 144.2,

143.7, 143.6, 140.6, 129.0, 128.0, 127.6, 127.0, 126.7, 125.3, 120.0, 65.7, 60.2, 57.4, 53.3, 46.5, 33.9, 29.8, 18.7, 18.0, 13.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{44}N_2NaO_5S$ 735.2869, found 735.2848.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(4-(tert-butoxy)phenyl)propanamido)-3-methylbutanoate (**3k**)

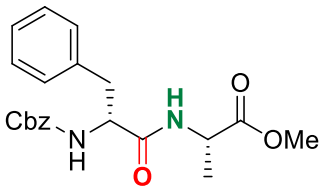
White solid; Yield 90%; M.p. 80.2-82.5 ˚C; $[\alpha]_D^{25}$ = +13.77 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, *J* = 8Hz, 1H), 7.87 (d, *J* = 8Hz, 2H), 7.66-7.61 (m, 3H), 7.40 (t, *J* = 8Hz, 2H), 7.32-7.21 (m, 4H), 6.82 (d, *J* = 8Hz, 2H), 4.39-4.34 (m, 1H), 4.22-4.08 (m, 4H), 3.63 (s, 3H), 2.92 (dd, *J* = 12Hz, *J* = 4Hz, 1H), 2.72 (dd, *J* = 12Hz, *J* = 12Hz, 1H), 2.09-2.01 (m, 1H), 1.19 (s, 9H), 0.89 (dd, *J* = 12Hz, *J* = 4Hz, 6H); ^{13}C NMR(101 MHz, DMSO-d_6) δ 172.0, 171.8, 155.7, 153.3, 143.7, 140.6 (2), 132.5, 129.7, 127.5, 127.0, 125.3, 125.2, 123.2, 120.0, 77.5, 65.6, 57.3, 55.7, 51.6, 46.5, 36.7, 29.9, 28.4, 18.9, 18.2; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{34}H_{41}N_2O_6$ 573.2965, found 573.2932.



(S)-methyl 2-((S)-2-(((benzyloxy)carbonyl)amino)-3-phenylpropanamido)propanoate (**3l**)

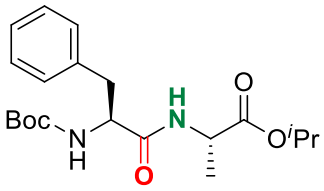
White solid; Yield 93%; M.p. 126-128 ˚C; $[\alpha]_D^{25}$ = -47.79 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.52 (d, *J* = 8Hz, 1H), 7.51 (d, *J* = 8Hz, 1H), 7.34-7.20 (m, 10H), 4.92 (s, 2H), 4.33-4.25 (m, 2H), 3.62 (s, 3H), 3.00 (dd, *J* = 8Hz, *J* = 4Hz, 1H), 2.71 (dd, *J* = 12Hz, *J* = 12Hz, 1H), 1.31 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.9, 171.6, 155.8, 138.0, 136.9, 129.1, 128.2, 128.0, 127.6, 127.4, 126.2, 65.1, 55.7, 51.8, 47.5, 37.3, 16.8; IR (cm^{-1}): 2950, 1742,

1650, 1536, 1257, 745, 696; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O_5$ 385.1763, found 385.1760.



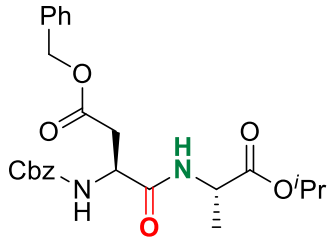
(S)-methyl 2-((R)-2-(((benzyloxy)carbonyl)amino)-3-phenylpropanamido)propanoate (**3l***)

White solid; Yield 92%; M.p. 132-135 ˚C; $[\alpha]_D^{25}$ = +60.22 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.42 (d, *J* = 8Hz, 1H), 7.45 (d, *J* = 12Hz, 1H), 7.34-7.18 (m, 10H), 4.95 (d, *J* = 4Hz, 2H), 4.34-4.24 (m, 2H), 3.63 (s, 3H), 2.95 (dd, *J* = 12Hz, *J* = 4Hz, 1H), 2.76 (t, *J* = 12Hz, 1H), 1.23 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.8, 171.2, 155.6, 137.8, 137.0, 129.2, 128.2, 127.9, 127.6, 127.3, 126.2, 66.1, 55.8, 51.8, 47.5, 37.8, 17.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O_5$ 385.1763, found 385.1759.



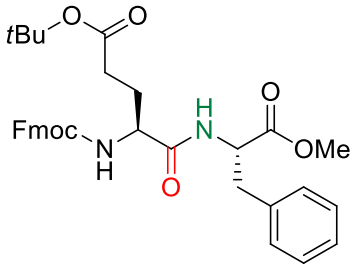
(S)-isopropyl 2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)propanoate (**3m**)

White solid; Yield %; M.p. 98-102 ˚C; $[\alpha]_D^{25}$ = -224.80 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6): δ 8.32 (d, *J* = 4Hz, 1H), 7.28-7.17 (m, 5H), 6.85 (d, *J* = 8Hz, 1H), 4.92-4.85 (m, 1H), 4.25-4.16 (m, 2H), 2.98 (dd, *J* = 12Hz, *J* = 4Hz, 1H), 2.71 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 1.28 (s, 9H), 1.19 (dd, *J* = 12Hz, *J* = 8Hz, 9H); ^{13}C NMR (101 MHz, DMSO-d_6): 171.9, 171.7, 155.2, 138.3, 129.1, 127.9, 126.1, 77.8, 67.7, 55.3, 47.8, 37.3, 28.1, 21.4 (2), 16.8; HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{30}N_2NaO_5$ 401.2052, found 401.2042.



(S)-benzyl 3-(((benzyloxy)carbonyl)amino)-4-(((S)-1-isopropoxy-1-oxopropan-2-yl)amino)-4-oxobutanoate (**3n**)

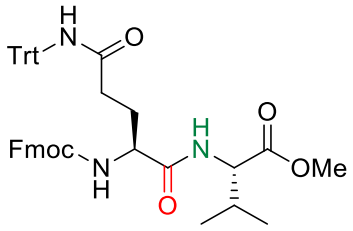
White solid; Yield 90%; M.p. 98-105 ˚C; $[\alpha]_D^{25}$ = -60.77 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, *J* = 4Hz, 1H), 7.58 (d, *J* = 8Hz, 1H), 7.38-7.29 (m, 10H), 5.10 (d, *J* = 4Hz, 2H), 5.02 (s, 2H), 4.89-4.83 (m, 1H), 4.51-4.45 (m, 1H), 4.20-4.13 (m, 1H), 2.78 (dd, *J* = 16Hz, *J* = 4Hz, 1H), 2.62 (dd, *J* = 20Hz, *J* = 8Hz, 1H), 1.25 (d, *J* = 8Hz, 3H), 1.16 (t, *J* = 4Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.8, 170.5, 169.8, 155.7, 136.8, 136.0, 128.3, 128.3, 127.9, 127.7, 127.6, 67.8, 65.6, 65.4, 50.9, 47.9, 36.3, 21.4, 21.3, 16.6; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{31}N_2O_7$ 471.2131, found 471.2118.



(S)-tert-butyl 4-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-5-(((S)-1-methoxy-1-oxo-phenylpropan-2-yl)amino)-5-oxopentanoate (**3o**)

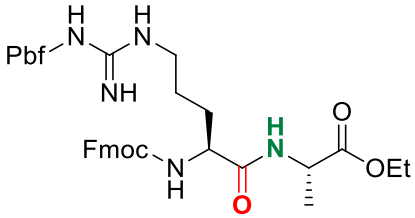
White solid; Yield 83%; M.p. 85-109 ˚C; $[\alpha]_D^{25}$ = -153.60 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, *J* = 8Hz, 1H), 7.89 (d, *J* = 8Hz, 2H), 7.72 (t, *J* = 8Hz, 2H), 7.49-7.40 (m, 3H), 7.34-7.18 (m, 7H), 4.47 (dd, *J* = 12Hz, *J* = 8Hz, 1H), 4.30-4.18 (m, 3H), 4.04 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 3.58 (s, 3H), 3.02 (dd, *J* = 16Hz, *J* = 4Hz, 1H), 2.94 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 2.19 (t, *J* = 8Hz, 2H), 1.87-1.78 (m, 1H), 1.75-1.65 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.7, 171.6, 171.4, 155.7, 143.8, 143.7, 140.6, 136.9, 129.0, 128.1, 127.6, 127.0, 126.5, 125.2, 120.0, 79.6, 65.6, 53.5, 51.8, 46.6, 40.1, 36.4, 31.1, 27.7, 27.3; IR (cm^{-1}):

2977, 1730, 1693, 1645, 1530, 1204, 1153, 1083, 737, 697; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{38}N_2NaO_7$ 609.2577, found 609.2508.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-5-oxo-5-(tritylamino)pentanamido)-3-methylbutanoate (**3p**)

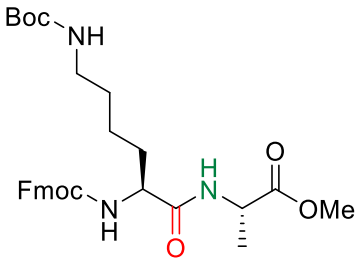
White solid; Yield 87%; M.p. 102-106 ˚C; $[\alpha]_D^{25}$ = +224.60 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.35 – 7.16 (m, 18H), 4.31 – 4.15 (m, 4H), 4.10 - 4.04 (m, 1H), 3.60 (s, 3H), 2.46 – 2.35 (m, 1H), 2.34 – 2.25 (m, 1H), 2.08 – 1.98 (m, 1H), 1.86 – 1.79 (m, 1H), 1.72 – 1.64 (m, 1H), 0.85 (dd, *J* = 6.7, 4.4 Hz, 7H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.5, 172.4, 171.9, 156.3, 145.3, 144.2 (2), 141.1, 128.9, 128.1, 127.9, 127.5, 126.8, 125.7, 120.6, 69.6, 66.0, 57.7, 54.4, 52.1, 47.1, 33.3, 30.3, 28.4, 19.3, 18.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{45}H_{46}N_3O_6$ 724.3387, found 724.3328.



(S)-ethyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-5-(3-((2,2,4,6,7-pentamethyl-2,3-dihydrobenzofuran-5-yl)sulfonyl)guanidino)pentanamido)propanoate (**3q**)

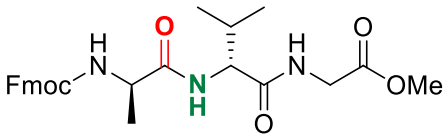
White solid; Yield 81%; M.p. 84-96˚C; $[\alpha]_D^{25}$ = -25.48 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 9.37 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 23.1, 7.5 Hz, 4H), 7.44 – 7.32 (m, 5H), 4.44 – 4.16 (m, 6H), 4.07 – 3.94 (m, 2H), 3.62 – 3.55 (m, 1H), 3.00 (s, 3H), 2.55 (s, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 2.03 (s, 6H), 1.93 – 1.65 (m, 5H), 1.42 (s, 6H), 1.29 – 1.12 (m,

3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.1, 158.7, 156.5, 154.4, 144.2 (2), 141.2, 138.4, 132.5, 128.1, 127.5, 125.6, 125.2, 120.6, 117.2, 87.2, 66.1, 60.2, 52.8, 47.0, 43.7, 42.7, 28.7, 25.2, 20.2, 19.3, 18.1, 12.7; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{50}N_5O_8S$ 748.3380, found 748.3332.



(S)-methyl 2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-6-((tert-butoxycarbonyl)amino)hexanamido)propanoate (**3r**)

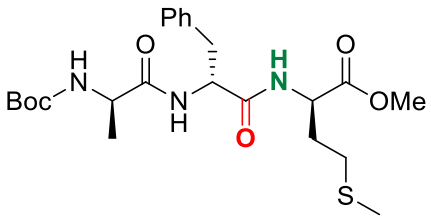
White solid; Yield 88%; M.p. 103-110 ˚C; $[\alpha]_D^{25}$ = -52.60 (c 1.0, CH_3OH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, J = 8Hz, 1H), 7.89 (d, J = 8Hz, 2H), 7.73 (dd, J = 8Hz, 2H), 7.47-7.30 (m, 6H), 4.28-4.20 (m, 4H), 4.03-3.97 (m, 1H), 3.61 (s, 3H), 2.91-2.85 (m, 2H), 1.64-1.51 (m, 4H), 1.36 (s, 9H), 1.28 (d, J = 8Hz, 3H), 1.22-1.10 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.9, 171.9, 155.8, 155.5, 143.8, 143.7, 140.6, 127.6, 127.0, 125.3, 120.0, 77.3, 65.5, 54.1, 51.7, 47.4, 46.6, 31.6, 29.2, 28.2, 22.7, 16.8; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{30}H_{40}N_3O_7$ 554.2866, found 554.2823.



(5R,8R)-methyl 1-(9H-fluoren-9-yl)-8-isopropyl-5-methyl-3,6,9-trioxo-2-oxa-4,7,10-triazadodecan-12-oate (**6a**)

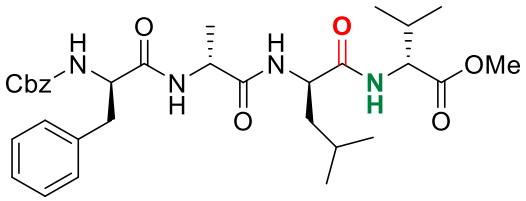
White solid; Yield 92%; M.p. 188-192 ˚C; $[\alpha]_D^{25}$ = -187.96 (c 1.0, CH_3OH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (s, 1H), 7.87 (dd, J = 18.5, 7.5 Hz, 3H), 7.72 (t, J = 6.9 Hz, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.36 (dd, J = 10.8, 4.3 Hz, 2H), 4.28 – 4.12 (m, 5H), 3.88 – 3.82 (m, 2H), 3.61 (s, 3H), 2.00 – 1.95 (m, 1H), 1.21 (d, J = 7.1 Hz, 3H), 0.88 – 0.83 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.9, 171.8, 170.6, 143.0, 141.1, 139.8, 129.4, 127.7,

121.8, 120.5, 110.2, 66.0, 57.7, 52.0, 50.7, 47.0, 31.3, 19.5, 18.3; IR (cm^{-1}): 3294, 1734, 1692, 1634, 1538, 736, 552; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{26}H_{32}N_3O_6$ 482.2291, found 482.2322.



(6R,9R,12R)-methyl 9-benzyl-2,2,6-trimethyl-12-(2-(methylthio)ethyl)-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (**6b**)

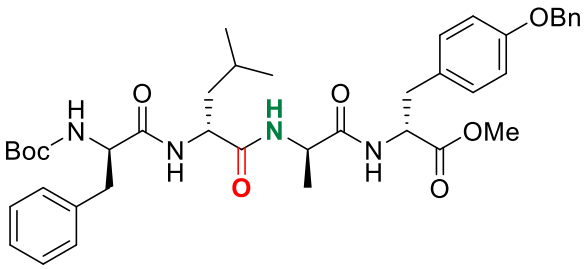
White solid; Yield 88%; M.p. 99-103 ˚C; $[\alpha]_D^{25}$ = -29.06 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.41 (d, *J* = 4Hz, 1H), 7.79 (d, *J* = 8Hz, 1H), 7.26– 7.17 (m, 5H), 6.91 (d, *J* = 8Hz, 1H), 4.58– 4.50 (m, 1H), 4.42-4.36 (m, 1H), 3.88 (dd, *J* = 16Hz, *J* = 4Hz ,1H), 3.62 (s, 3H), 3.00 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 2.81 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 2.47– 2.38 (m, 2H), 2.03 (s, 3H), 1.98 – 1.86 (m, 2H), 1.36 (s, 9H), 1.07 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.3, 171.9, 171.0, 154.9, 137.4, 129.2, 127.9, 126.2, 78.0, 53.2, 51.9, 50.8, 49.8, 37.4, 30.5, 29.3, 28.1, 18.0, 14.5; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{23}H_{36}N_3O_6S$ 482.2325, found 482.2322.



(5R,8R,11R,14S)-methyl 5-benzyl-11-isobutyl-14-isopropyl-8-methyl-3,6,9,12-tetraoxo-1-phenyl-2-oxa-4,7,10,13-tetraazapentadecan-15-oate (**6c**)

White solid; Yield 90%; M.p. 182-194 ˚C; $[\alpha]_D^{25}$ = -113.72 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, *J* = 7.3 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.12 (m, 10H), 4.93 (s, 1H), 4.44 – 4.24 (m, 3H), 4.20 - 4.13 (m, 2H), 3.62 (s, 1H), 3.00 (dd, *J* = 13.9, 3.3 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.06 – 2.01 (m, 1H), 1.66 – 1.58 (m, 1H), 1.44 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.89 – 0.85 (m, 12H).

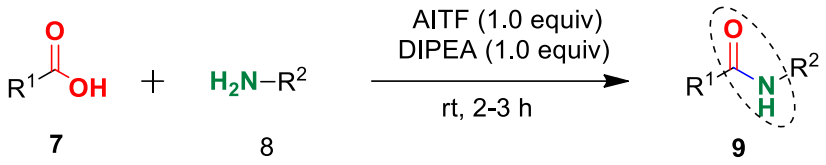
^{13}C NMR (101 MHz, DMSO-d_6) δ 172.7, 172.3, 171.7, 156.3, 138.6, 137.4, 129.8, 129.6, 128.7, 128.4, 128.4, 128.1, 127.8, 126.6, 65.6, 57.7, 56.4, 52.1, 51.2, 48.4, 41.2, 30.3, 24.5, 23.5, 22.6, 22.2, 19.3, 18.6, 18.5; IR (cm^{-1}): 3285, 2962, 1742, 1697, 1634, 1537, 696, 454; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{32}H_{45}N_4O_7$ 597.3288, found 597.3283.



(6R,9R,12R,15R)-methyl 6-benzyl-15-(4-(benzyloxy)benzyl)-9-isobutyl-2,2,12-trimethyl-4,7,10,13-tetraoxo-3-oxa-5,8,11,14-tetraazahexadecan-16-oate (**6d**)

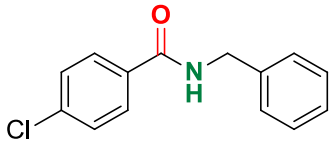
White solid; Yield 84%; M.p. 189-196 ˚C; $[\alpha]_D^{25}$ = + 25.31 (c 1.0, CH_3OH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, J = 8Hz, 1H), 8.07 (d, J = 8Hz, 1H), 7.99 (d, J = 8Hz, 1H), 7.43–7.11 (m, 12H), 6.92 (dd, J = 16Hz, J = 8Hz, 3H), 5.04 (s, 2H), 4.40–4.24 (m, 3H), 4.18–4.12 (m, 1H), 3.54 (s, 3H), 2.98–2.84 (m, 3H), 2.71 (dd, J = 12Hz, J = 12Hz, 1H), 1.64–1.57 (m, 1H), 1.44 (d, J = 4Hz, 2H), 1.28 (s, 9H), 1.18 (d, J = 4Hz, 3H), 0.84 (dd, J = 12Hz, J = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.1, 171.7, 171.4 (2), 157.0, 155.2, 138.2, 137.1, 130.1, 129.1, 129.0, 128.3, 127.9, 127.7, 127.6, 126.0, 114.5, 78.0, 69.0, 55.7, 53.8, 51.7, 50.7, 47.8, 40.9, 37.1, 35.7, 28.0, 23.9, 23.1, 21.5, 18.1; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{40}H_{52}N_4NaO_8$ 739.3683, found 739.3678.

Procedure for synthesis of amides:



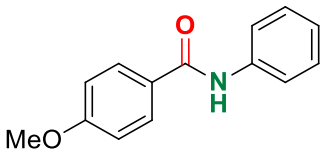
7 8 **9**

AITF (1.0 equiv) was added to a stirred solution of carboxylic acid/N^{α}-protected amino acid **7** (1.0 equiv) and DIPEA (1.0 equiv) in CH_3CN (3 mL) at room temperature. Then the reaction mixture was stirred for 20 min and amine (1.2 equiv) was added and the reaction mixture was stirred for 2.0 h at room temperature. The progress of the reaction was monitored by TLC. Thereafter, the reaction mixture was concentrated using rotary evaporator and then diluted with 15 mL of ethyl acetate and washed with 5% HCl (10 mL x 2) 5% Na_2CO_3 (10 mL x 2), saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting crude product was purified by silica gel column chromatography using the mixture of hexane and ethyl acetate as eluents to afford **9**.



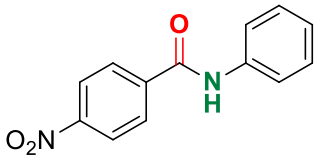
N-benzyl-4-chlorobenzamide (**9a**)

White solid; Yield 95%; M.p. 38-46 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (t, J = 8Hz, 1H), 7.93-7.90 (m, 2H), 7.57-7.54 (m, 2H), 7.35-7.22 (m, 5H), 4.48 (d, J = 4Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1, 139.4, 136.0, 133.0, 129.1, 128.3, 128.2, 127.2, 126.7, 42.6; IR (cm^{-1}) 3311, 3029, 1637, 1549, 761, 523; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{14}H_{13}ClNO$ 246.0686, found 246.0677.



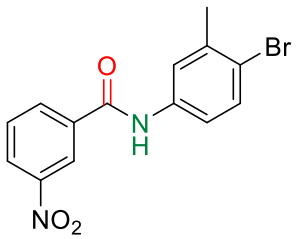
4-methoxy-N-phenylbenzamide (**9b**)

White solid; Yield 90%; M.p. 170-172 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (s, 1H), 7.98-7.95 (m, 2H), 7.77 (d, *J* = 8Hz, 2H), 7.34 (dd, *J* = 8Hz, *J* = 8Hz, 2H), 7.10-7.04 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.8, 161.8, 139.3, 129.5, 128.5, 126.9, 123.3, 120.3, 113.5, 55.3; IR (cm^{-1}) 3335, 3015, 1653, 1594, 750, 578; HRMS (ESI-TOF): m/z [M+Na]$^{+}$ Calcd for $C_{14}H_{13}NNaO_2$ 250.0844, found 250.0823.



4-nitro-N-phenylbenzamide (**9c**)

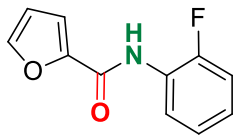
Yellow solid; Yield 84%; M.p. 207-210 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.57 (s, 1H), 8.37 (t, *J* = 8Hz, 2H), 8.18 (d, *J* = 8Hz, 2H), 7.78 (d, *J* = 8Hz, 2H), 7.38 (t, *J* = 8Hz, 2H), 7.14 (t, *J* = 8Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.8, 149.1, 140.6, 138.6, 129.1, 128.7, 124.1, 123.5, 120.4; IR (cm^{-1}) 3320, 3083, 1650, 1515, 757, 585; HRMS (ESI-TOF): m/z [M+H]$^{+}$ Calcd for $C_{13}H_{11}N_2O_3$ 243.0770, found 243.0770.



N-(4-bromo-3-methylphenyl)-3-nitrobenzamide (**9d**)

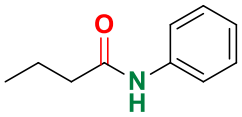
Pale Yellow solid; Yield 86%; M.p. 177-181˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53–10.45 (m, 1H), 8.81 (d, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 7.7 Hz, 2H), 7.80–7.70 (m, 2H), 7.54–7.41 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.6, 148.1, 138.5, 137.7, 136.4, 134.4,

132.4, 130.3, 126.4, 123.2, 122.8, 120.2, 118.9, 23.1; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{14}H_{12}BrN_2O_3$ 335.0031, found 335.0026.



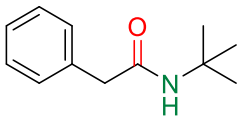
N-(2-fluorophenyl)furan-2-carboxamide (**9e**)

White solid; Yield 92%; M.p. 76-79 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.94 (dd, J = 4Hz, 1H), 7.62-7.58 (m, 1H), 7.34-7.19 (m, 4H), 6.70 (dd, J = 4Hz, J = 4Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.8, 156.2, 154.4, 147.1, 145.8, 126.9 (4), 124.9, 124.8, 124.3, 124.2, 115.8, 115.6, 114.9, 112.1; IR (cm^{-1}) 3425, 3142, 1672, 1535, 769, 581; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{11}H_9FNO_2$ 206.0617, found 206.0612.



N-phenylbutyramide (**9f**)

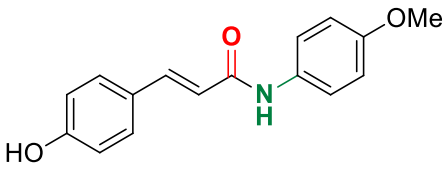
White solid; Yield 91%; M.p. 93-95 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.59 (t, J = 8Hz, 2H), 7.29-7.25 (m, 2H), 7.03-6.99 (m, 1H), 2.27 (t, J = 8Hz, 2H), 1.65-1.56 (m, 2H), 0.91 (t, J = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.0, 139.3, 128.6, 122.8, 118.9, 38.2, 18.5, 13.6; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{10}H_{14}NO$ 164.1075, found 164.1062.



N-(tert-butyl)-2-phenylacetamide (**9g**)

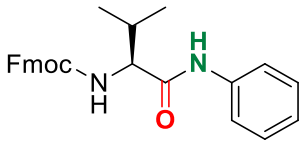
White solid; Yield 92%; M.p. 106-109 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (s, 1H), 7.32 – 7.19 (m, 5H), 3.36 (s, 2H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.5, 136.9, 128.8,

128.0, 126.0, 49.9, 43.0, 28.4; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{12}H_{18}NO$ 192.1388, found 192.1382.



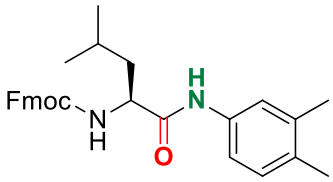
(E)-3-(4-hydroxyphenyl)-N-(4-methoxyphenyl)acrylamide (**9h**)

Pale Yellow solid; Yield 87%; M.p. 189-191 ˚C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 9.87 (s, 1H), 7.60 (d, *J* = 8Hz, 2H), 7.45 (dd, *J* = 16Hz, 3H), 6.89 (dd, *J* = 8Hz, *J* = 4Hz, 2H), 6.82 (d, *J* = 8Hz, 2H), 6.58 (d, *J* = 16Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.5, 159.0, 155.1, 139.7, 132.6, 129.3, 125.8, 120.5, 118.7, 115.8, 113.8, 55.1; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{16}H_{16}NO_3$ 270.1130, found 270.1120.



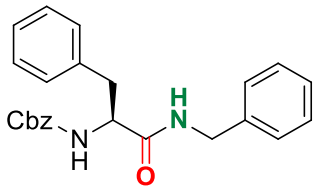
(9H-fluoren-9-yl)methyl (S)-(3-methyl-1-oxo-1-(phenylamino)butan-2-yl)carbamate (**9i**)

White solid; Yield 91%; M.p. 230-234 ˚C; $[\alpha]_D^{25}$ = -47.53 (c 1.0, CH_3OH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.02 (s, 1H), 7.88 (d, *J* = 8Hz, 2H), 7.75 (t, *J* = 8Hz, 2H), 7.60 (t, *J* = 8Hz, 3H), 7.43-7.39 (m, 2H), 7.33-7.28 (m, 4H), 7.05 (t, *J* = 8Hz, 1H), 4.29-4.20 (m, 3H), 3.99 (t, *J* = 8Hz,1H), 2.08-1.99 (m, 1H), 0.93 (t, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6): δ170.4, 156.2, 143.8, 143.7, 140.6, 138.7, 128.7, 127.6, 127.0. 125.3 (2), 120.0, 119.2, 65.7, 61.0, 46.6, 30.3, 19.1, 18.5; IR (cm^{-1}) 3286, 3064, 2960, 1694, 1246, 737, 533; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{26}H_{27}N_2O_3$ 415.2022, found 415.2021.



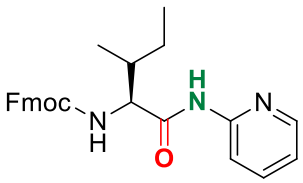
(9H-fluoren-9-yl)methyl (S)-(1-((3,4-dimethylphenyl)amino)-4-methyl-1-oxopentan-2-yl)carbamate (**9j**)

White solid; Yield 87%; M.p. 150-154 ˚C; $[\alpha]_D^{25}$ = -79.73(c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.89 (d, *J* = 8Hz, 2H), 7.73 (d, *J* = 4Hz, 2H), 7.58 (d, *J* = 8Hz, 1H), 7.41-7.32 (m, 6H), 7.04 (d, *J* = 8Hz, 1H),4.30-4.20 (m,4H), 2.17 (d, *J* = 8Hz, 6H), 1.68-1.55 (m, 2H), 1.49-1.42 (m, 1H), 0.90 (t, *J* = 4Hz, 6H) ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.1.155.9, 143.8, 143.7, 140.7, 136.6, 136.1, 130.9, 129.4, 127.6, 127.0, 125.2, 120.5, 120.0, 116.8, 65.5, 53.7, 46.6, 40.6, 24.2, 22.9, 21.4, 19.5, 18.7; IR (cm^{-1}) 3292, 3065, 2956, 1684, 1284, 737, 680; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{29}H_{33}N_2O_3$ 457.2491, found 457.2487.



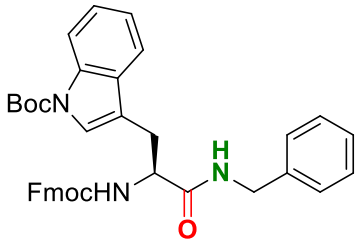
(S)-benzyl (1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)carbamate (**9k**)

White solid; Yield 90%; M.p. 146-150 ˚C; $[\alpha]_D^{25}$ = + 2.38 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.43 (t, *J* = 8Hz, 1H), 7.52 (d, *J* = 8Hz, 1H), 7.34-7.17 (m, 15H), 4.95 (s, 2H), 7.31-7.25 (m, 3H), 3.00 (dd, *J* = 12Hz, *J* = 4Hz, 1H), 2.79 (dd, *J* = 12Hz, *J* = 12Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 155.8, 139.1, 138.0, 137.0, 129.1, 128.2 (2), 128.0, 127.6, 127.4, 127.0, 126.6, 126.2, 65.2, 56.3, 42.0, 37.6; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{24}H_{24}N_2NaO_3$ 411.1685, found 411.1692.



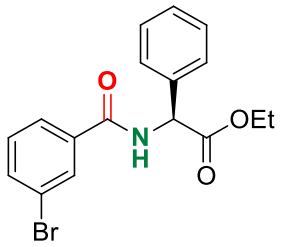
(9H-fluoren-9-yl)methyl ((2S,3R)-3-methyl-1-oxo-1-(pyridin-2-ylamino)pentan-2-yl)carbamate (**9l**)

White solid; Yield 87 %; M.p. 150-153 ˚C; $[\alpha]_D^{25}$ = -30.81 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 1H), 8.32 (d, *J* = 4Hz, 1H), 8.09 (d, *J* = 8Hz, 1H), 7.88 (d, *J* = 8Hz, 2H), 7.80-7.72 (m, 3H), 7.60 (d, *J* = 12Hz, 1H), 7.40 (dd, *J* = 8Hz, *J* = 8Hz, 2H), 7.30 (dd, *J* = 16Hz, *J* = 4Hz, 2H), 7.11 (t, *J* = 8Hz, 1H), 4.30-4.19 (m, 4H), 1.86-1.80 (m, 1H), 1.53-1.46 (m, 1H), 1.24-1.15 (m, 1H), 0.89-0.82 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.5, 156.1, 151.6, 147.9, 143.7, 140.6, 138.1, 127.6, 127.0, 125.2, 120.0, 119.5, 113.5, 65.6, 59.7, 46.6, 36.1, 24.4, 15.2, 10.7; IR (cm^{-1}) 3253, 3206, 2964, 1725, 1298, 780, 534; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{26}H_{28}N_3O_3$ 430.2131, found 430.2126.



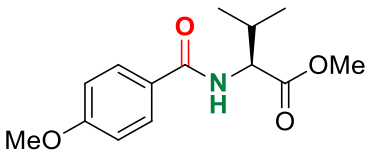
(S)-tert-butyl 3-(2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(benzylamino)-3-oxopropyl)-1H-indole-1-carboxylate (**9m**)

White solid; Yield 90%; M.p. 153-155 ˚C; $[\alpha]_D^{25}$ = -84.04 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.64 (t, *J* = 4Hz, 1H), 8.04 (d, *J* = 8Hz, 1H), 7.87-7.76 (m, 4H), 7.62 (dd, *J* = 12Hz, *J* = 4Hz, 2H), 7.39-7.17 (m, 12H), 4.45-4.38 (m, 1H), 4.31 (brs, 2H), 4.23-4.10 (m, 3H), 3.13 (dd, *J* = 16Hz, *J* = 4Hz, 1H), 3.00 (dd, *J* = 12Hz, *J* = 12Hz, 1H), 1.56 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.3, 155.8, 149.0, 143.7, 143.6, 140.6 (2), 139.1, 134.6, 130.2, 128.1, 127.5, 127.0, 126.6, 125.3, 125.2, 124.2, 124.1, 122.4, 120.0, 119.5, 116.7, 114.6, 83.4, 65.7, 54.6, 46.5, 42.1, 27.6, 27.4; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{38}H_{38}N_3O_5$ 616.2811, found 616.2769.



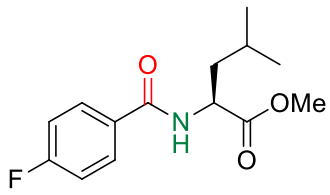
(S)-ethyl 2-(3-bromobenzamido)-2-phenylacetate (**9n**)

White solid; Yield 86%; M.p. 98-102 ˚C; $[\alpha]_D^{25}$ = + 47.50 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 9.29 (d, *J* = 4Hz, 1H), 8.12 (s, 1H), 7.91 (d, *J* = 8Hz, 1H), 7.77-7.74 (m, 1H), 7.48-7.37 (m, 6H), 5.62 (d, *J* = 8Hz, 1H), 4.18-4.10 (m, 2H), 1.16-1.17 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.3, 165.0, 135.9, 135.6, 134.2, 130.5, 130.2, 128.5, 128.4, 128.2, 127.7, 126.9, 121.5, 60.9, 57.1, 13.9; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{17}H_{16}BrNNaO_3$ 384.0211, found 384.0206.



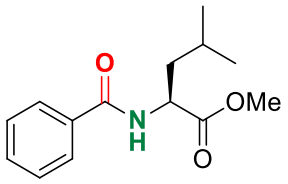
(S)-methyl 2-(4-methoxybenzamido)-3-methylbutanoate (**9o**)

White solid; Yield 86%; M.p. 100.7-101.1 ˚C; $[\alpha]_D^{25}$ = -2.49 (c 1.0, CH_3OH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 6.94-6.90 (m, 2H), 6.52 (d, *J* = 8Hz, 1H), 4.76 (dd, *J* = 8Hz, *J* = 4Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 2.29-2.21 (m, 1H), 0.98 (dd, *J* = 8Hz, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 166.8, 162.4, 128.9, 126.4, 113.8, 57.4, 55.5, 52.3, 31.7, 19.0, 18.0; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{14}H_{19}NNaO_4$ 288.1212, found 288.1200.



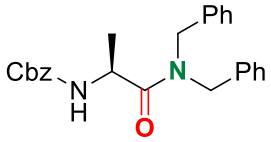
(S)-methyl 2-(4-fluorobenzamido)-4-methylpentanoate (**9p**)

White solid; M.p. 97-100˚C; $[\alpha]_D^{25}$ = -18.57 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.76 (d, *J* = 7.6 Hz, 1H), 7.97 (dd, *J* = 8.2, 5.8 Hz, 2H), 7.31 (t, *J* = 8.5 Hz, 2H), 4.53-4.48 (m, 1H), 3.65 (s, 3H), 1.82-1.75 (m, 1H), 1.72-1.66 (m, 1H), 1.61-1.54 (m, 1H), 0.90 (dd, *J* = 18.2, 6.5 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.5, 166.0, 165.7, 163.2, 130.6, 130.5, 115.7, 115.5, 52.3, 51.4, 39.6, 24.9, 23.2, 21.5; IR (cm^{-1}) 3276, 3076, 2957, 1745, 1273, 766, 503; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{14}H_{19}FNO_3$ 268.1349, found 268.1345.



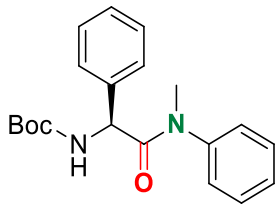
(S)-methyl 2-benzamido-4-methylpentanoate (**9q**)

White solid; Yield 89%; M.p. 102-104 ˚C; $[\alpha]_D^{25}$ = -18.08 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.70 (d, *J* = 8Hz, 1H), 7.89-7.87 (m, 2H), 7.57-7.46 (m, 3H), 4.53-4.48 (m, 1H), 3.64 (s, 3H), 1.83-1.76 (m, 1H), 1.73-1.66 (m, 1H), 1.61-1.54 (m, 1H), 0.90 (dd, *J* = 16Hz, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.0, 166.5, 133.7, 131.4, 128.2, 127.4, 51.8, 50.9, 39.2, 24.4, 22.8, 21.1; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{14}H_{20}NO_3$ 250.1443, found 250.1429.



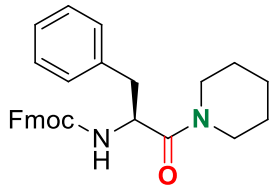
(S)-benzyl (1-(dibenzylamino)-1-oxopropan-2-yl)carbamate (**11a**)

White solid; Yield 88%; M.p. 82-88 ˚C; $[\alpha]_D^{25}$ = -69.44 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8Hz, 1H), 7.39-7.15 (m, 15H), 5.03 (s, 2H), 4.65-4.48 (m, 4H), 4.29 (d, *J* = 16Hz, 1H), 1.20 (d, *J* = 4Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.0, 155.8, 137.3, 137.0, 136.9, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.3 (2), 126.9, 65.3, 49.4, 47.7, 46.7, 17.5; IR (cm^{-1}) 3290, 2982, 1716, 1645, 729, 578; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{25}H_{27}N_2O_3$ 403.2022 , found 403.2027.



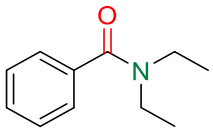
(S)-tert-butyl (2-(methyl(phenyl)amino)-2-oxo-1-phenylethyl)carbamate (**11b**)

Gel; Yield 86%; $[\alpha]_D^{25}$ = + 164.13 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 4Hz, 2H), 7.21 (dd, *J* = 28Hz, *J* = 52Hz, 7H), 6.88 (d, *J* = 4Hz, 2H), 5.21 (d, *J* = 8Hz, 1H), 3.15 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.7, 154.7, 142.4, 137.2, 129.4, 128.1, 127.8, 127.6, 78.2, 55.1, 37.4, 28.1; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{20}H_{24}N_2NaO_3$ 363.1685, found 363.1654.



(S)-(9H-fluoren-9-yl)methyl (1-oxo-3-phenyl-1-(piperidin-1-yl)propan-2-yl)carbamate (**11c**)

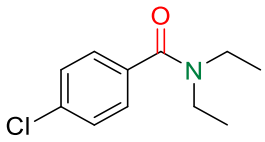
White solid; Yield 81%; M.p. 99-105˚C; $[\alpha]_D^{25}$ = -137.64 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 8Hz, 1H), 7.68 (dd, *J* = 8Hz, *J* = 4Hz, 2H), 7.41 (t, *J* = 8Hz, 2H), 7.34-7.19 (m, 9H), 4.63 (dd, *J* = 12Hz, *J* = 8Hz, 1H), 4.19-4.13 (m, 3H), 2.90 (dd, *J* = 12Hz, *J* = 8Hz, 1H), 2.82 (dd, *J* = 16Hz, *J* = 8Hz, 1H), 1.50-1.33 (m, 6H), 1.26-1.10 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.1, 155.6, 143.7, 140.6, 137.7, 129.3, 128.0, 127.6, 127.0, 126.3, 125.3, 120.0, 65.6, 51.7, 46.5, 45.8, 42.4, 37.5, 25.7, 25.2, 23.9; IR (cm^{-1}) 3259, 2932, 1713, 1623, 757, 540; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{29}H_{30}N_2NaO_3$ 477.2154 , found 477.2078.



N,N-diethylbenzamide **(11d)**

Colorless oil; Yield 91%; ^1H NMR (400 MHz, DMSO-d_6) δ 7.45-7.33 (m, 5H), 3.46 (s, 2H), 3.17 (s, 2H), 1.08 (d, *J* = 41.7 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.4, 137.7, 129.3,

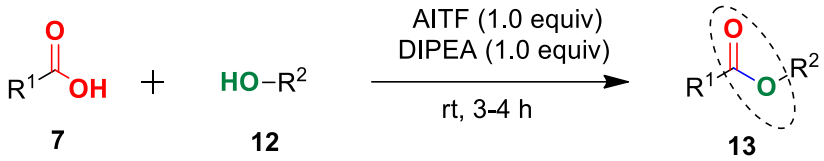
128.7, 126.4, 43.2, 39.1, 14.4, 13.2; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{11}H_{16}NO$178.1232 , found 178.1238.



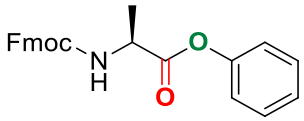
4-chloro-N,N-diethylbenzamide (**11e**)

Colourless oil; Yield 90%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48-7.45 (m, 1H), 7.38-7.36 (m, 1H), 3.41 (s, 2H), 3.16 (s, 2H), 1.08 (d, J = 21.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 136.0, 133.6, 128.3, 128.0, 42.7, 38.7, 13.8, 12.7; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{11}H_{14}ClNNaO$234.0662, found 234.0657.

Procedure for synthesis of esters:

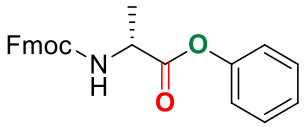


AITF (1.0 equiv) was added to a stirred solution of carboxylic acid/N^{α}-protected amino acid **7** (1.0 equiv) and DIPEA (1.0 equiv) in CH_3CN (3 mL) at room temperature. Then the reaction mixture was stirred for 20 min and alcohol (1.2 equiv) was added and the reaction mixture was stirred for 3.0 h at room temperature. The progress of the reaction was monitored by TLC at room temperature. Thereafter, the reaction mixture was concentrated using rotary evaporator and then diluted with 15 mL of ethyl acetate and washed with 5% HCl (10 mL x 2) 5% Na_2CO_3 (10 mL x 2), saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting crude product was purified by silica gel column chromatography using the mixture of hexane and ethyl acetate as eluents to afford **13**.



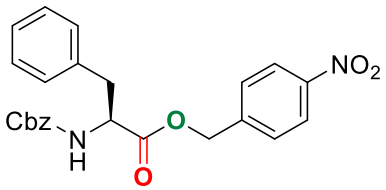
(S)-phenyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanoate (**13a**)

White solid; Yield 87%; M.p. 135-139 ˚C; $[\alpha]_D^{25}$ = + 61.04 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 4Hz, 1H), 7.89 (d, *J* = 8Hz, 2H), 7.72 (dd, *J* = 8Hz, *J* = 4Hz, 2H), 7.44 -7.25 (m, 8H), 7.09 (d, *J* = 8Hz, 1H), 4.41-4.23 (m, 4H), 1.44 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.8, 155.9, 150.4, 143.7 (2), 140.7, 129.5, 127.6, 127.0, 125.9, 125.1 (2), 121.5, 120.1, 65.6, 49.5, 46.5, 16.7; IR (cm^{-1}) 2928, 1762, 1531, 1450, 1302, 1260, 1161, 1064, 757, 690; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{24}H_{21}NNaO_4$ 410.1368, found 410.1384.



(R)-phenyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanoate (**13a***)

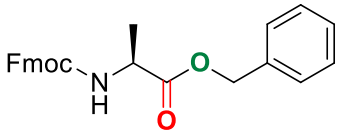
White solid; Yield 85%; M.p 134-137.$[\alpha]_D^{25}$ = + 486.20 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 8.0 Hz, 2H), 7.44-7.25 (m, 7H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.41-4.23 (m, 4H), 1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.7, 155.9, 150.4, 143.7 (2), 140.7, 129.5, 127.6, 127.0, 125.9, 125.1 (2), 121.4, 120.1, 65.6, 49.5, 46.6, 16.7; HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{24}H_{22}NO_4$ 388.1549, found 388.1558.



(S)-benzyl (1-((4-nitrobenzyl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate (**13b**)

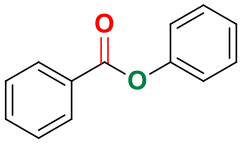
White solid; Yield 78%; M.p. 102-110 ˚C; $[\alpha]_D^{25}$ = - 8.60 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 8.19 (d, *J* = 8Hz, 2H), 7.96 (d, *J* = 8Hz, 1H), 7.53 (d, *J* = 8Hz, 2H), 7.33-7.22 (m, 10H), 5.26 (s, 2H), 5.00 (d, *J* = 8Hz, 2H), 4.42-4.36 (m, 1H), 3.09 (dd, *J* = 16Hz, *J* = 4Hz, 1H), 2.94 (dd, *J* = 12Hz, *J* = 12Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.6, 156.0, 147.0,

143.5, 137.2, 136.8, 129.1, 128.2 (2), 127.7, 127.5, 126.5, 123.4, 65.4, 64.7, 55.6, 36.3; IR (cm^{-1}) 2921, 1707, 1511, 1450, 1347, 1285, 1035, 1011, 752, 661; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{24}H_{22}N_2NaO_6$ 457.1376, found 457.1333.



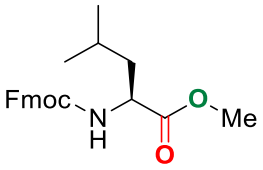
(S)-benzyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanoate (**13c**)

White solid; Yield 84%; M.p. 69-102 ˚C; $[\alpha]_D^{25}$ = + 2.08 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.88 (dd, *J* = 12Hz, *J* = 8Hz, 3H), 7.71 (dd, *J* = 4Hz, *J* = 4Hz, 2H), 7.43-7.30 (m, 9H), 5.12 (s, 2H), 4.32-4.14 (m, 4H), 1.31 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.7, 155.8, 143.8, 143.7, 140.7, 135.9, 128.3, 127.9, 127.6, 127.0, 125.1 (2), 120.1, 65.8, 65.6, 49.4, 46.5, 16.8; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{25}H_{23}NNaO_4$ 424.1525, found 424.1490.



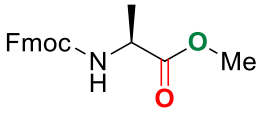
phenyl benzoate (**13d**)

White solid; Yield 89%; M.p. 62-68 ˚C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.14 (t, *J* = 8Hz, 2H), 7.35 (t, *J* = 8Hz, 1H), 7.61 (t, *J* = 8Hz, 2H), 7.50-7.45 (m, 2H), 7.31 (dd, *J* = 16Hz, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.5, 150.6, 134.0, 129.7, 129.5, 128.9, 126.0, 121.9; IR (cm^{-1}) 2982, 1734, 1593, 1471, 1262, 1192, 1062, 811, 747, 689; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{13}H_{10}NaO_2$ 221.0578, found 221.0576.



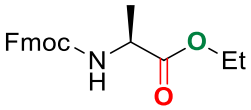
(S)-methyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-methylpentanoate (**13e**)

White solid; Yield 91%; M.p. 59-64 ˚C; $[\alpha]_D^{25}$ = -29.04 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 4Hz, 2H), 7.75 (dd, *J* = 28Hz, *J* = 8Hz, 3H), 7.44-7.31 (m, 4H), 4.32-4.21 (m, 3H), 4.08-4.03 (m, 1H), 3.62 (s, 3H), 1.66-1.55 (m, 2H), 1.48-1.42 (m, 1H), 0.86 (dd, *J* = 16Hz, *J* = 8Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.2, 156.0, 143.8, 143.7, 140.7, 127.6, 127.0, 125.2, 120.1, 65.5, 52.1, 51.8, 46.6, 39.4, 24.1, 22.7, 21.0; IR (cm^{-1}): 2955, 1751, 1534, 1447, 1263, 1120, 1081, 756, 538; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{22}H_{25}NNaO_4$ 390.1681, found 390.1646.



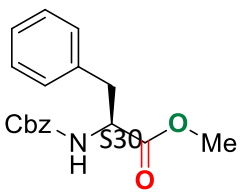
(S)-methyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanoate (**13f**)

White solid; Yield 86%; M.p. 112-114 ˚C; $[\alpha]_D^{25}$ = - 390.20 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 8Hz, 2H), 7.80-7.70 (m, 3H), 7.44-7.32 (m, 4H), 4.35-4.21 (m, 3H), 4.14-4.07 (m, 1H), 3.63 (s, 3H), 1.29 (d, *J* = 8Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.3, 155.8, 143.8, 143.7, 140.7, 127.6, 127.0, 125.1, 120.0, 65.5, 51.8, 49.2, 46.6, 16.9; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{19}H_{19}NNaO_4$ 348.1212, found 348.1232.



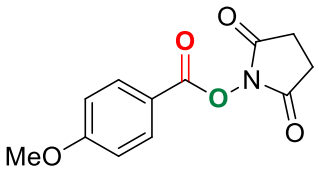
(S)-ethyl 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanoate (**13g**)

White solid; Yield 89%; M.p. 103-105 ˚C; $[\alpha]_D^{25}$ = - 181.08 (1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, *J* = 8Hz, 2H), 7.77-7.70 (m, 3H), 7.44-7.32 (m, 4H), 4.36-4.21 (m, 3H), 4.11-4.03 (m, 3H), 1.28 (d, *J* = 8Hz, 3H), 1.17 (t, *J* = 4Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.8, 155.8, 143.8, 143.7, 140.7, 127.6, 127.0, 125.2, 125.1, 120.0, 65.5, 60.4, 49.3, 46.6, 16.8, 14.0; IR (cm^{-1}) 2982, 1748, 1527, 1449, 1298, 1255, 1179, 1029, 758, 583; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO_4$ 362.1368, found 362.1370.



(S)-methyl 2-(((benzyloxy)carbonyl)amino)-3-phenylpropanoate (**13h**)

Colorless oil; Yield 84%; $[\alpha]_D^{25}$ = +143.90 (c 1.0, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8Hz, 1H), 7.37-7.22 (m, 10H), 5.02 (s, 2H), 4.38-4.32 (m, 1H), 3.64 (s, 3H), 3.10 (dd, *J* = 12Hz, *J* = 8Hz, 1H), 2.94 (dd, *J* = 16Hz, *J* = 8Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.3, 155.9, 137.4, 136.9, 129.0, 128.2 (2), 127.7, 127.5, 126.4, 65.4, 55.5, 51.8, 36.5; IR (cm^{-1}) 2952, 1707, 1585, 1497, 1349, 1207, 1049, 1027, 742, 696; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{18}H_{19}NNaO_4$ 336.1212, found 336.1185.



2,5-dioxopyrrolidin-1-yl 4-methoxybenzoate (**13i**)

White solid; Yield 84%; M.p. 138-141 ˚C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8Hz, 2H), 7.17 (d, *J* = 8Hz, 2H), 3.89 (s, 3H), 2.88 (s, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.4, 164.7, 161.2, 132.3, 116.2, 114.8, 55.8, 25.4; IR (cm^{-1}) 2981, 1790, 1513, 1426, 1375, 1210, 1071, 1020, 756, 689; HRMS (ESI-TOF): m/z $[M+Na]^+$ Calcd for $C_{12}H_{11}NNaO_5$ 272.0535, found 272.0535.

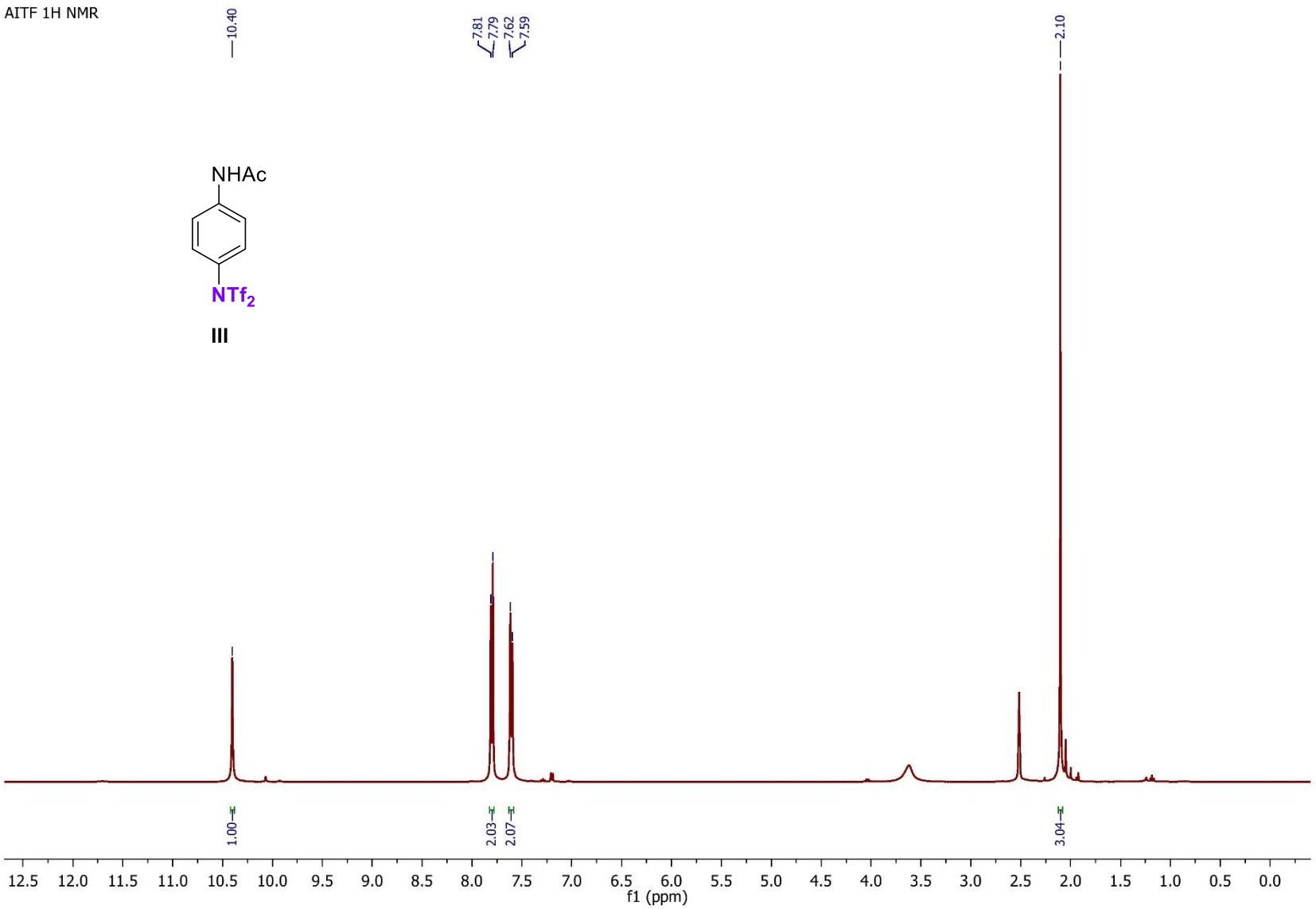


Figure S1. ^{1}H NMR Spectrum of **III (400MHz, DMSO-d$_6$)**

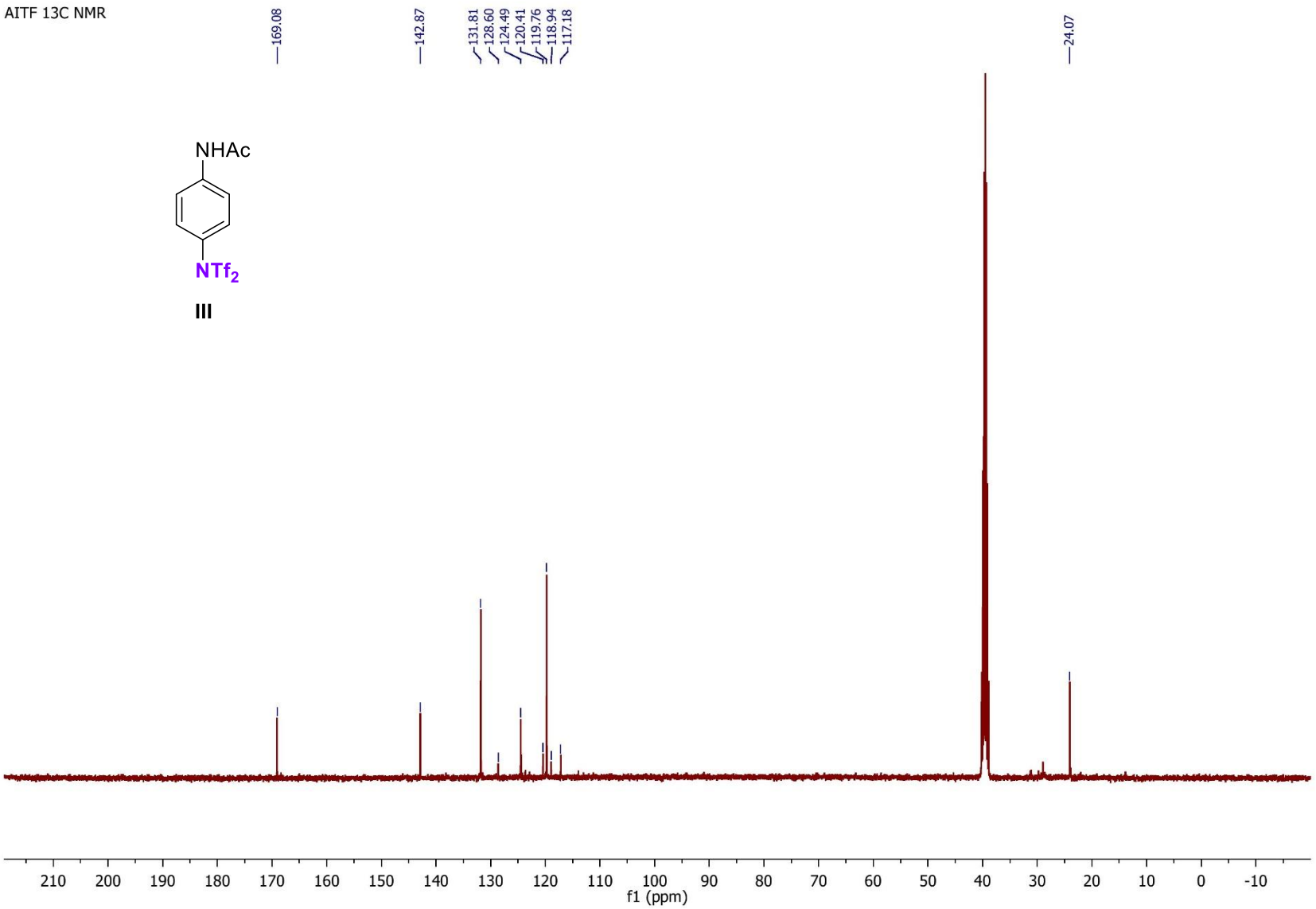


Figure S2. ^{13}C NMR Spectrum of **III (400MHz, DMSO-d$_6$)**

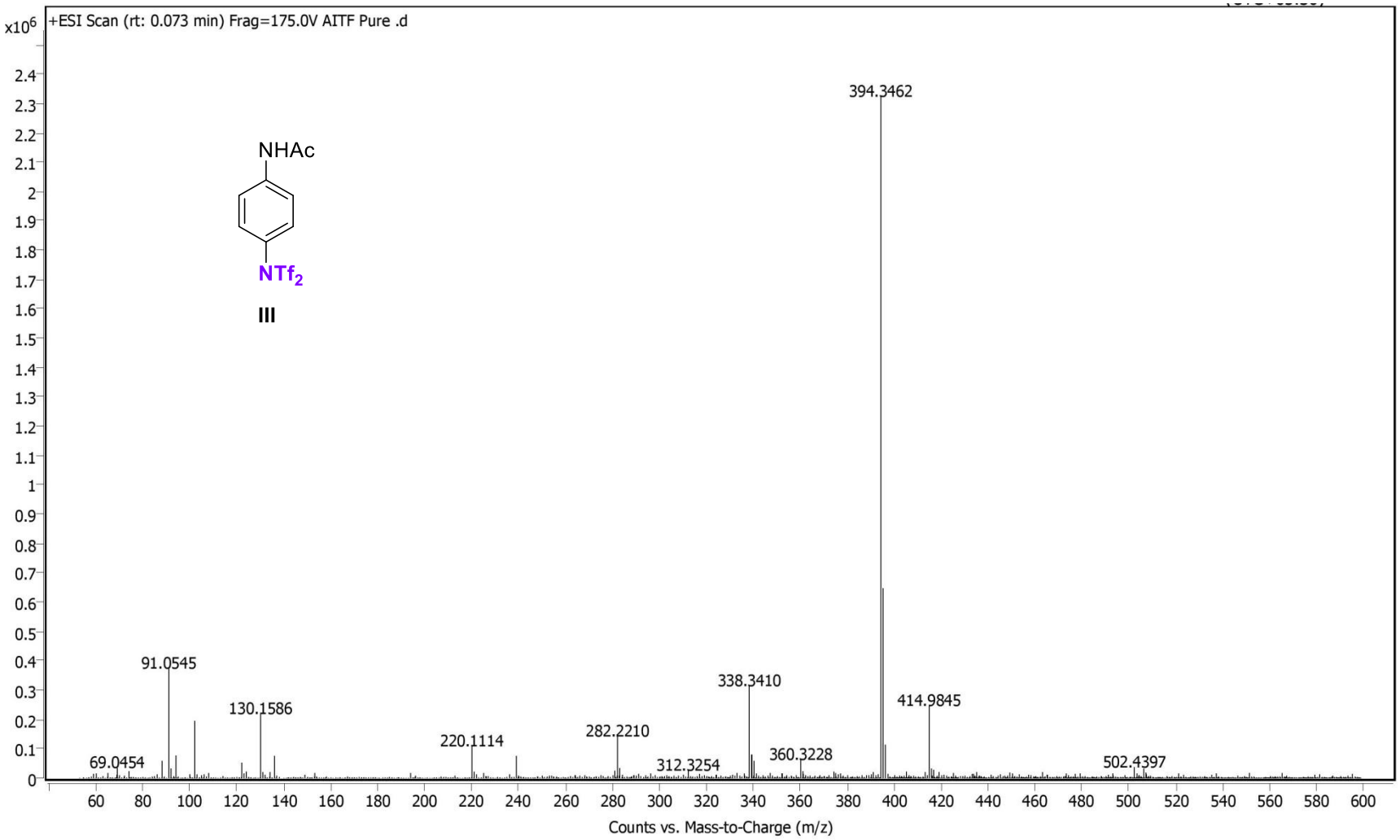


Figure S3. HRMS Spectrum of **III (AITF)**

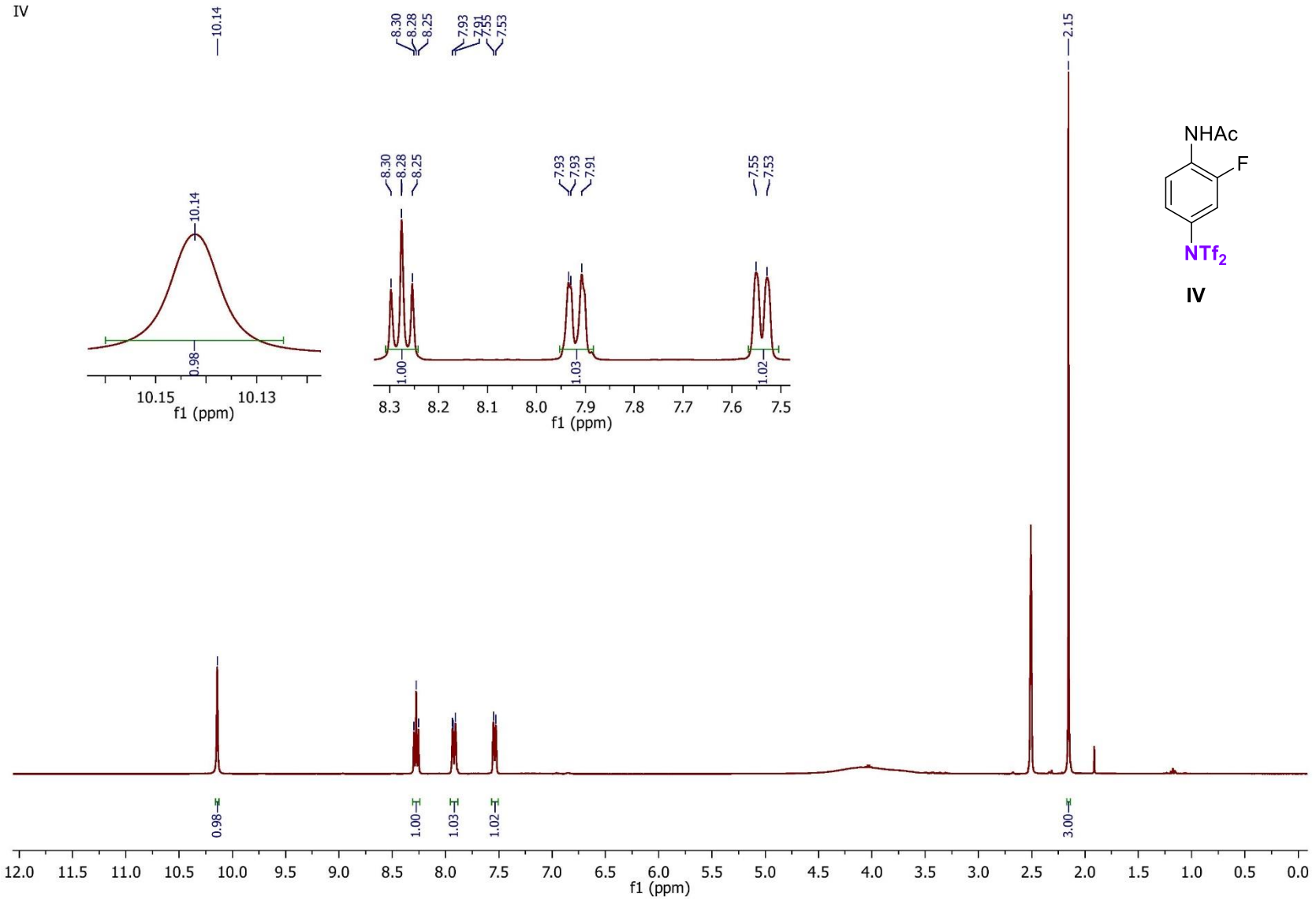


Figure S4. ^{1}H NMR Spectrum of **IV (400MHz, DMSO-d$_6$)**

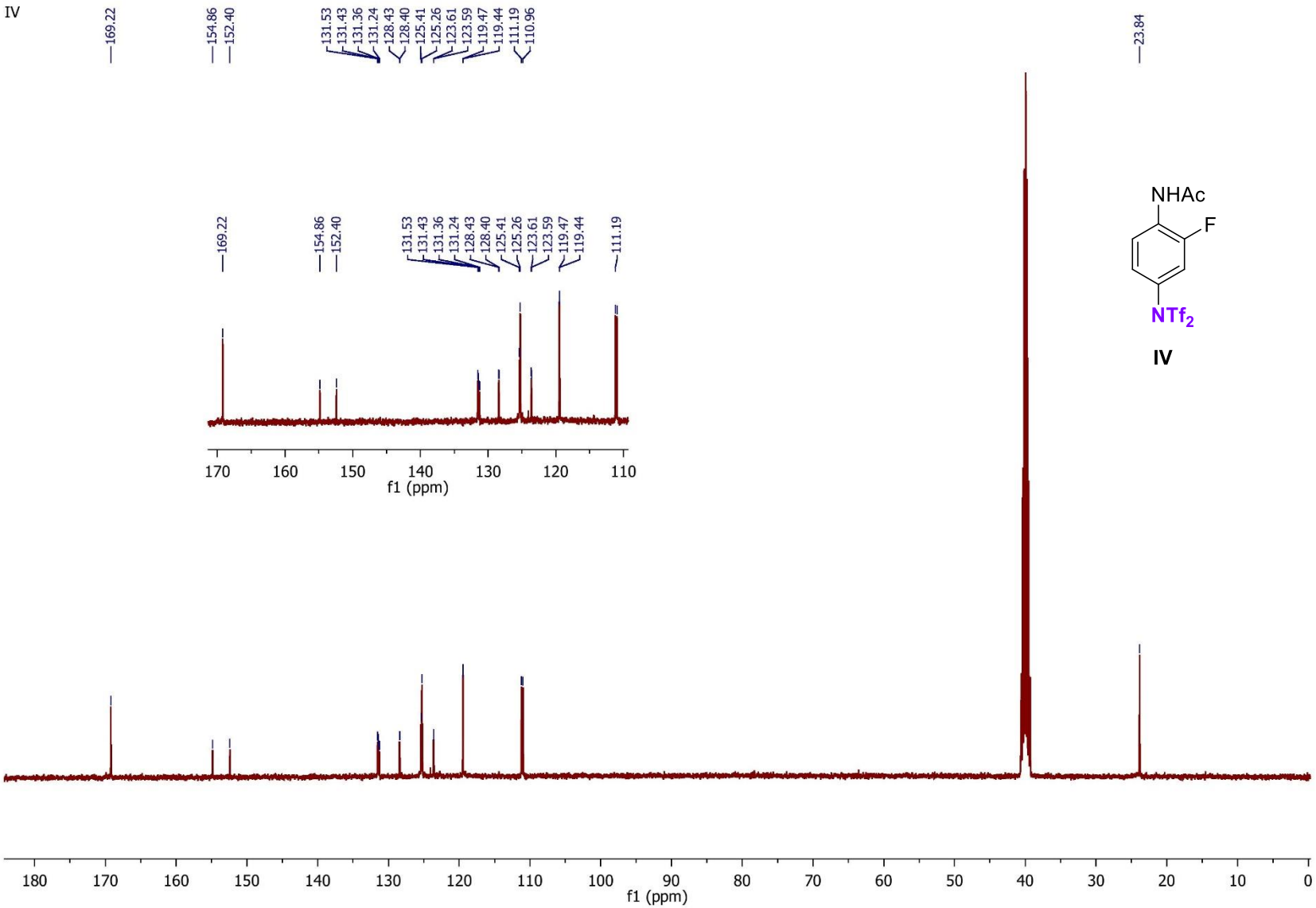


Figure S5. ^{13}C NMR Spectrum of **IV (400MHz, DMSO-d$_6$)**

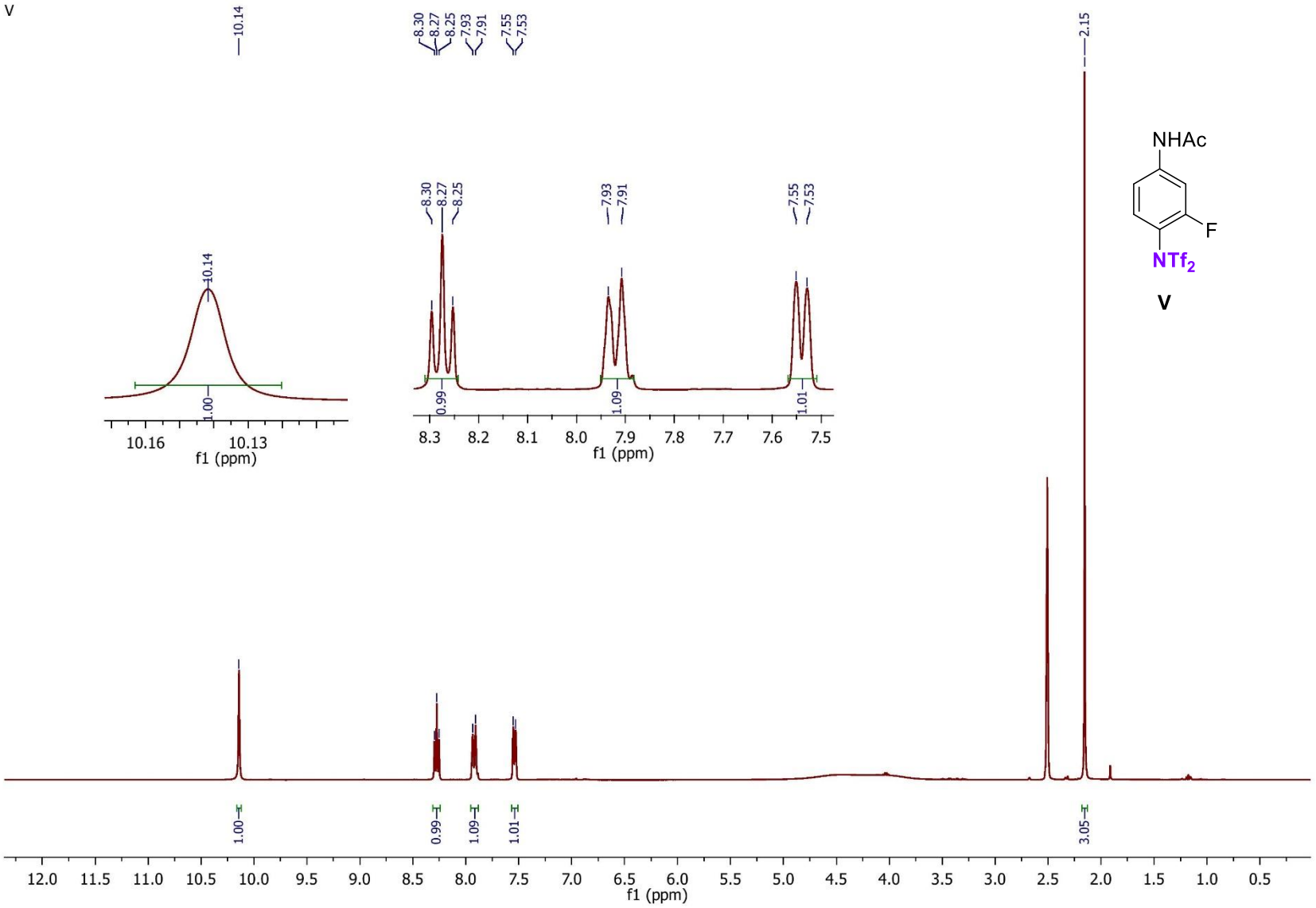


Figure S6. ^{1}H NMR Spectrum of **V (400MHz, DMSO-d$_6$)**

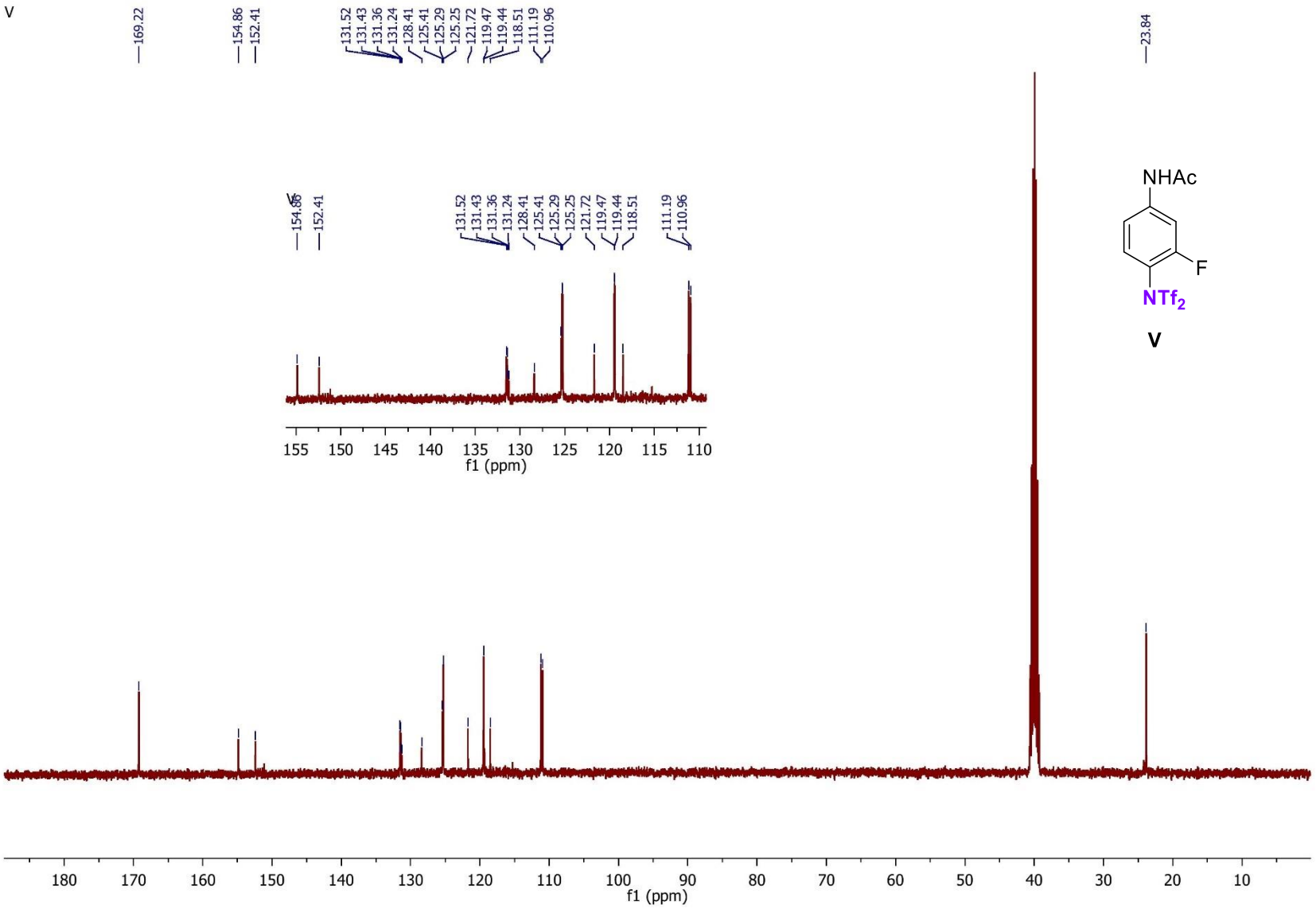


Figure S7. ^{13}C NMR Spectrum of **V (400MHz, DMSO-d$_6$)**

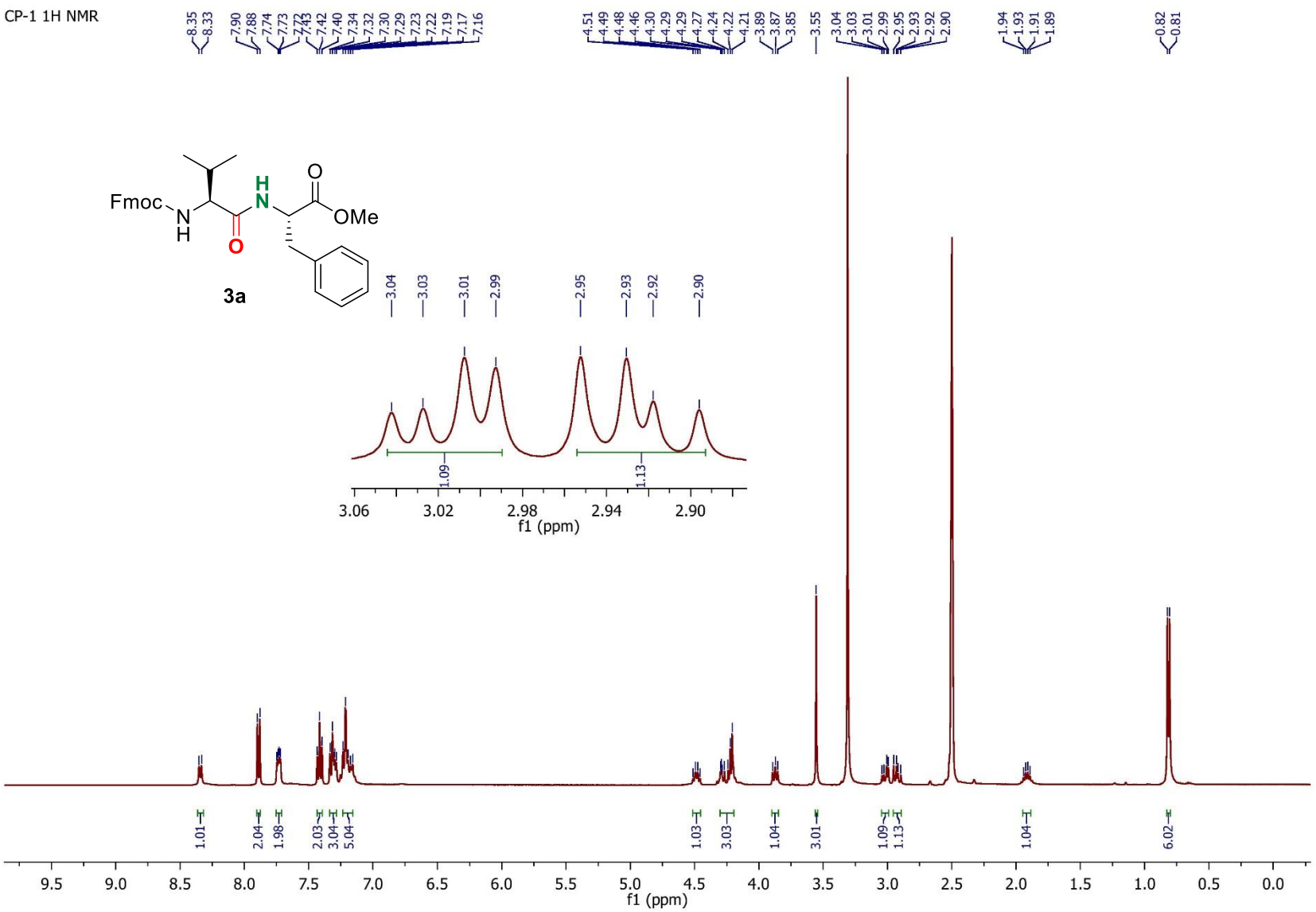


Figure S8. ^{1}H NMR Spectrum of **3a (400MHz, DMSO-d$_6$)**

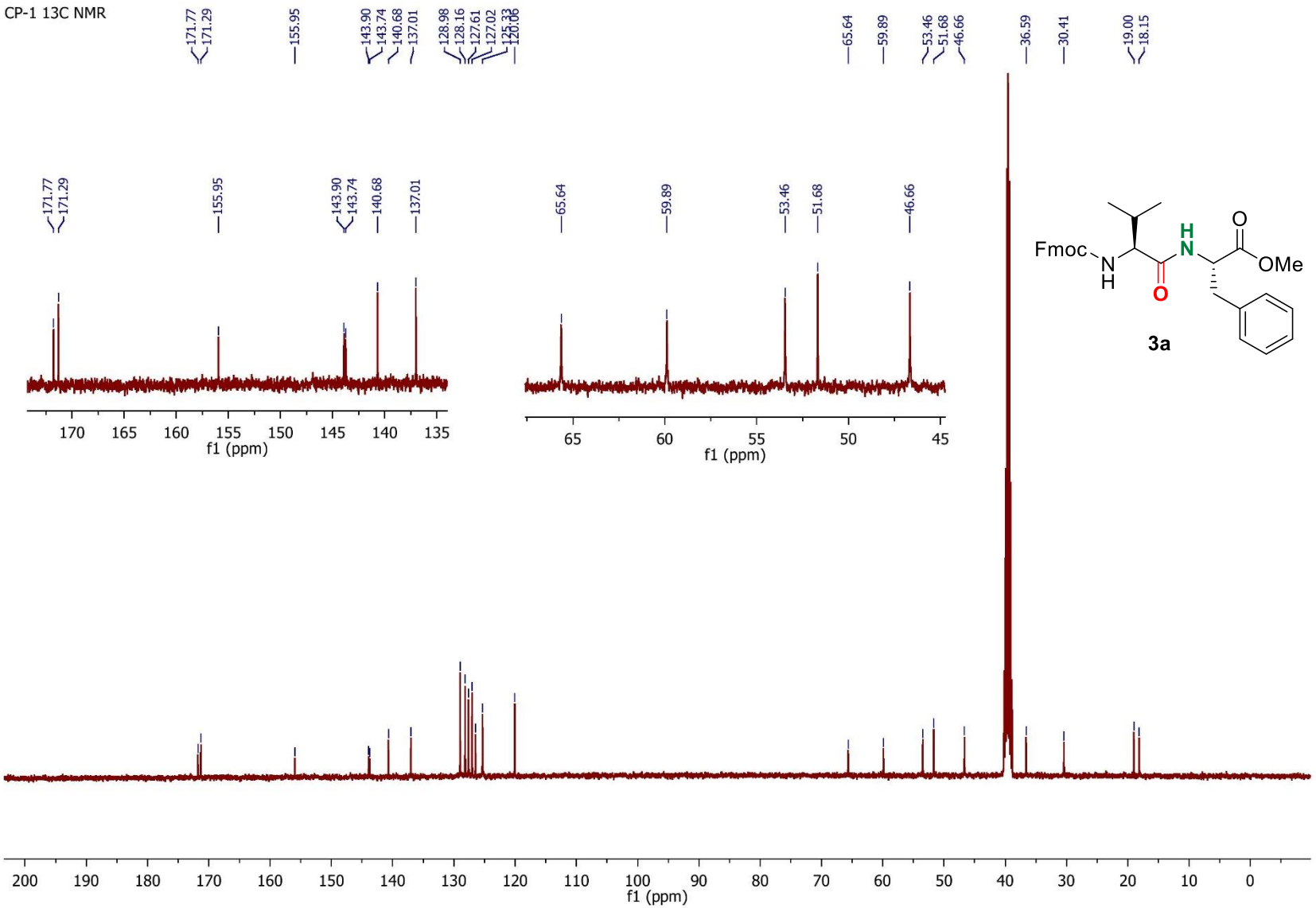


Figure S9. ^{13}C NMR Spectrum of **3a (101MHz, DMSO-d$_6$)**

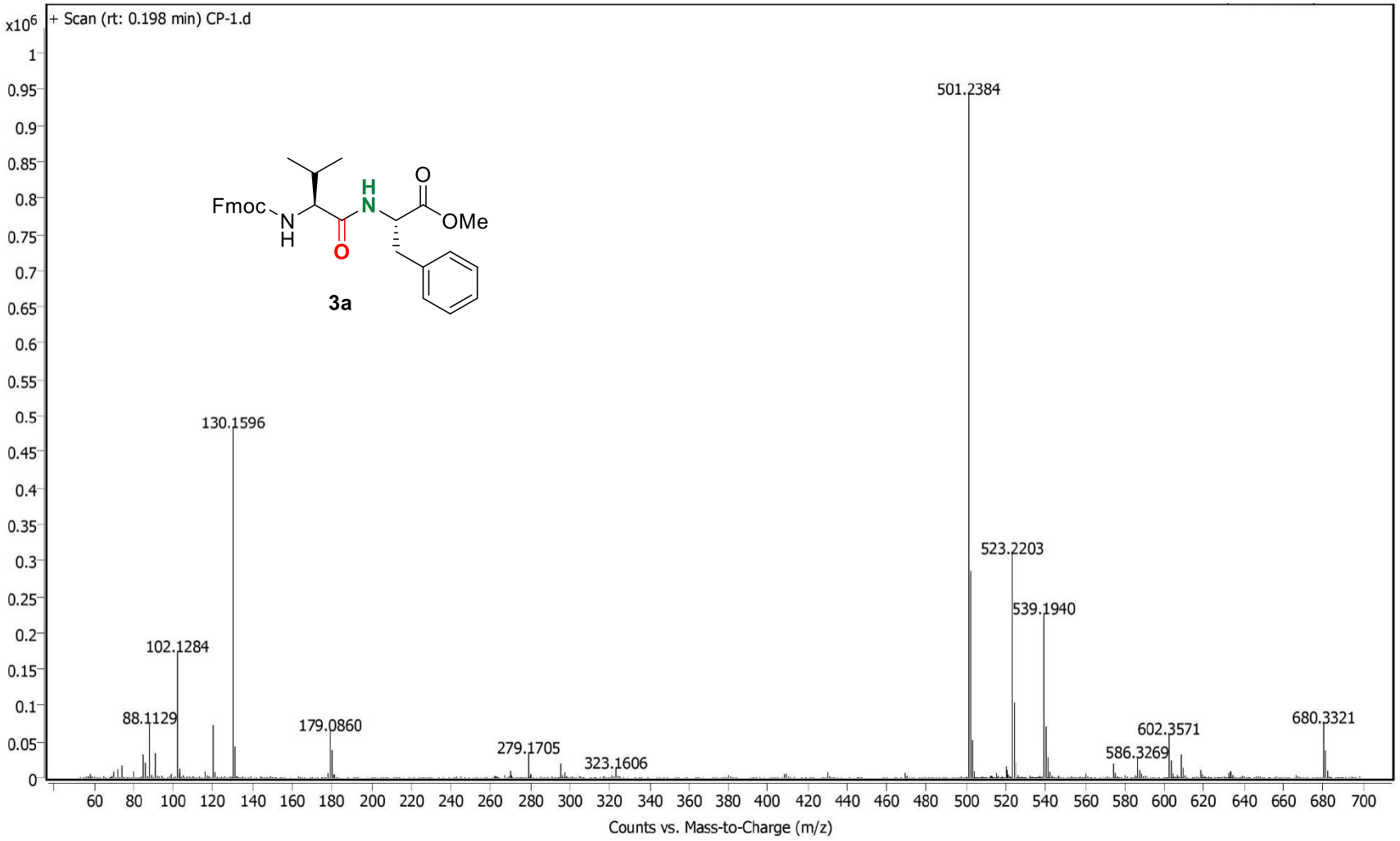


Figure S10. HRMS Spectrum of **3a**

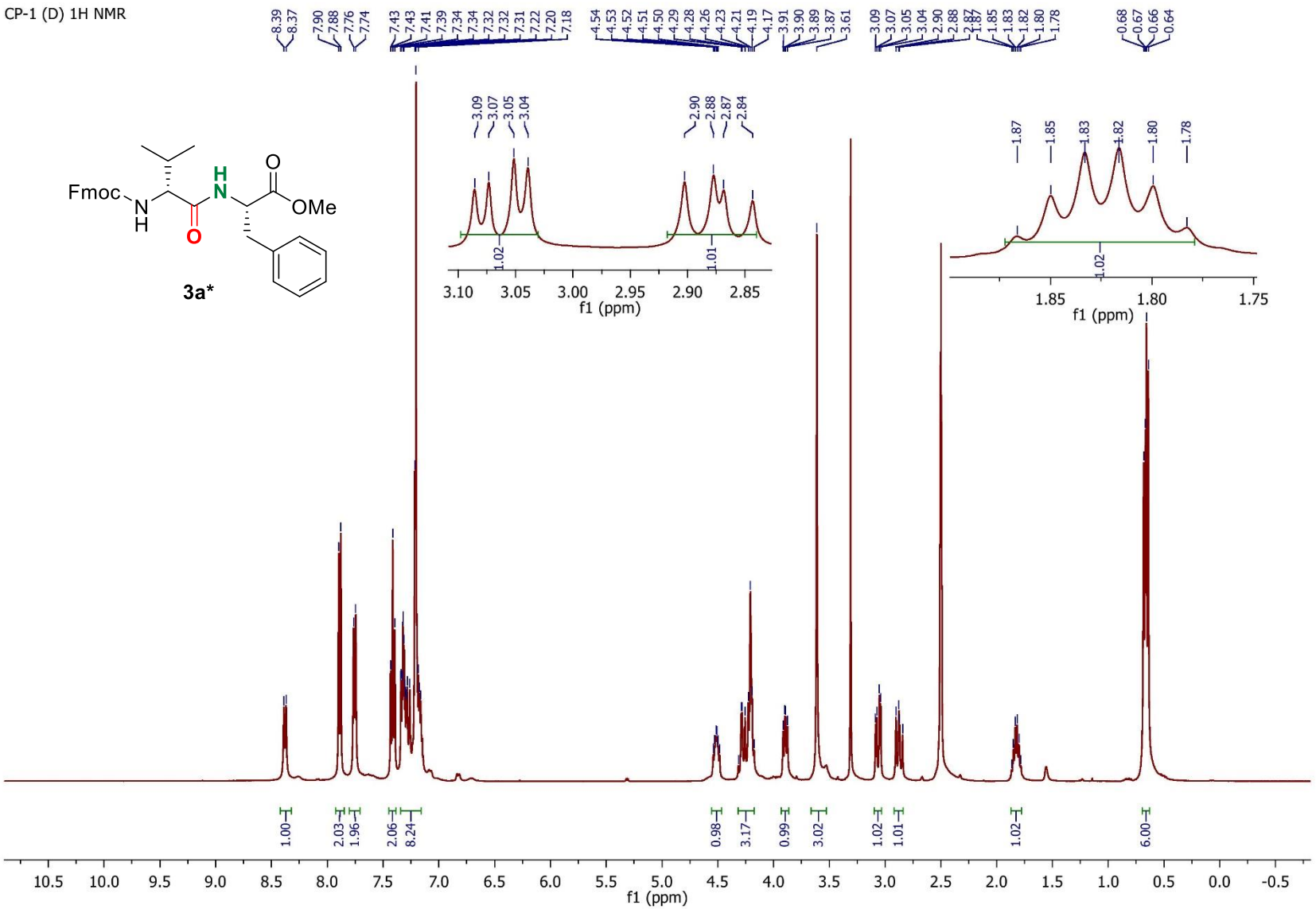


Figure S11. ^{1}H NMR Spectrum of **3a* (400MHz, DMSO-d$_6$)**

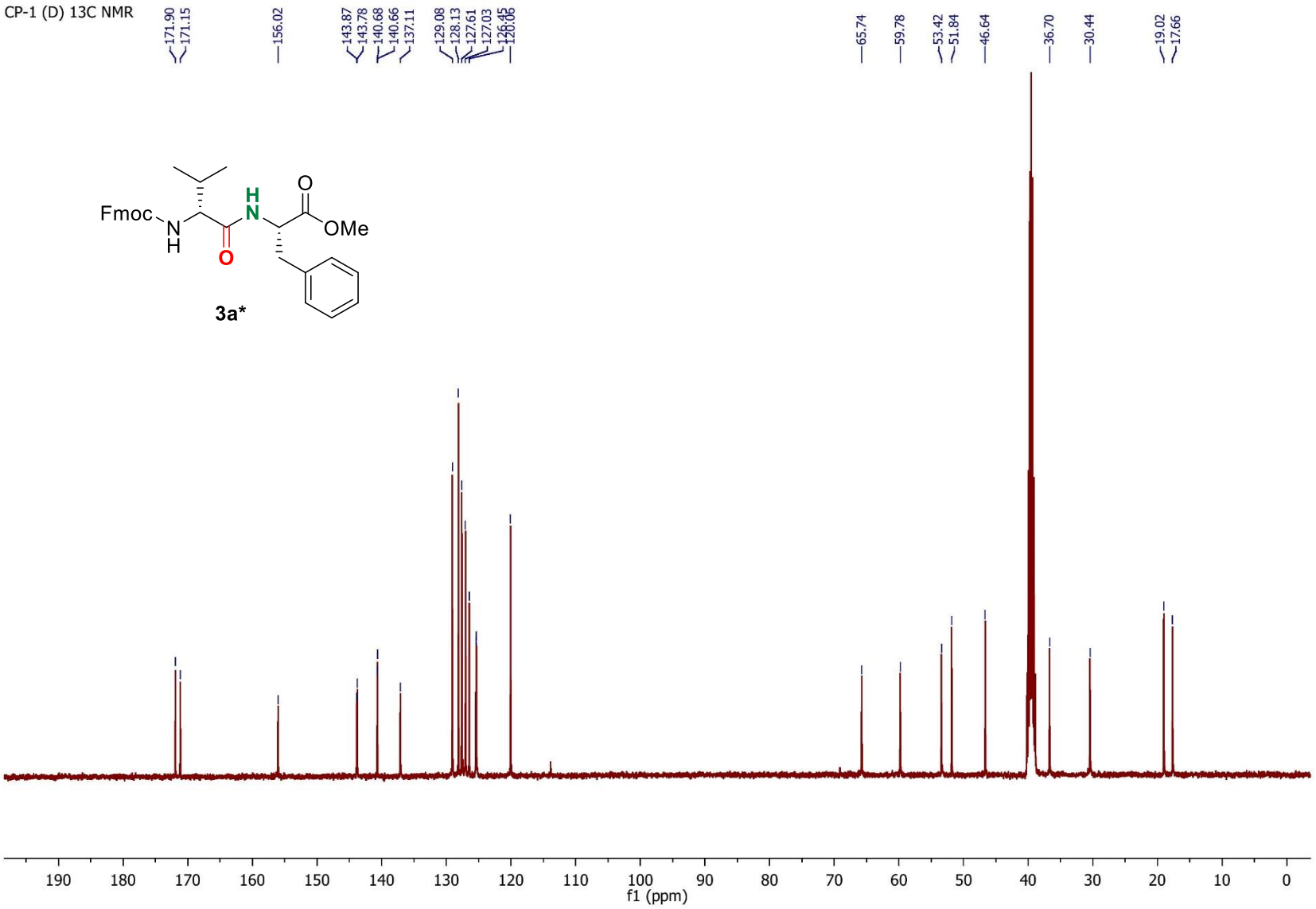


Figure S12. ^{13}C NMR Spectrum of **3a* (101MHz, DMSO-d$_6$)**

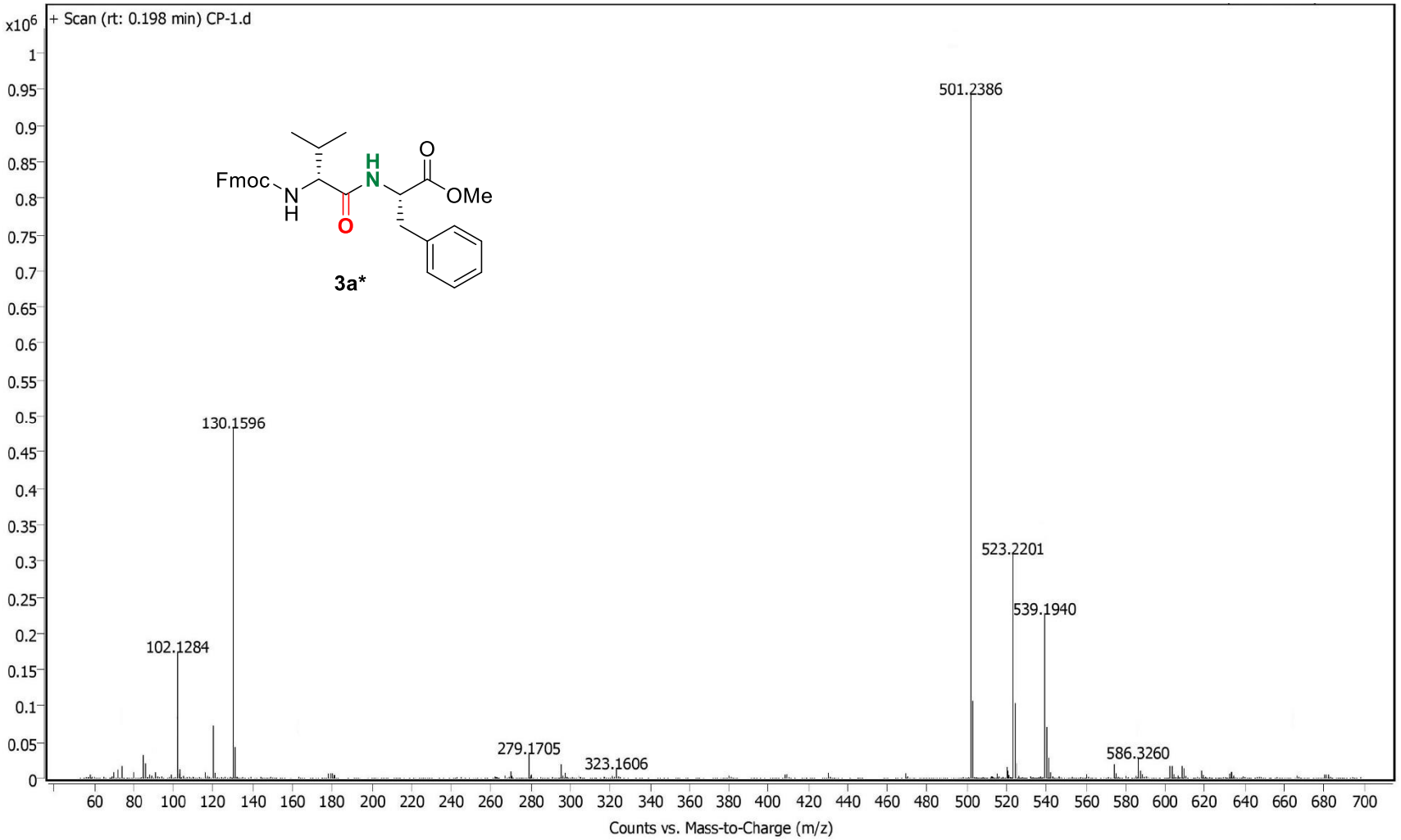


Figure S13. HRMS Spectrum of **3a***

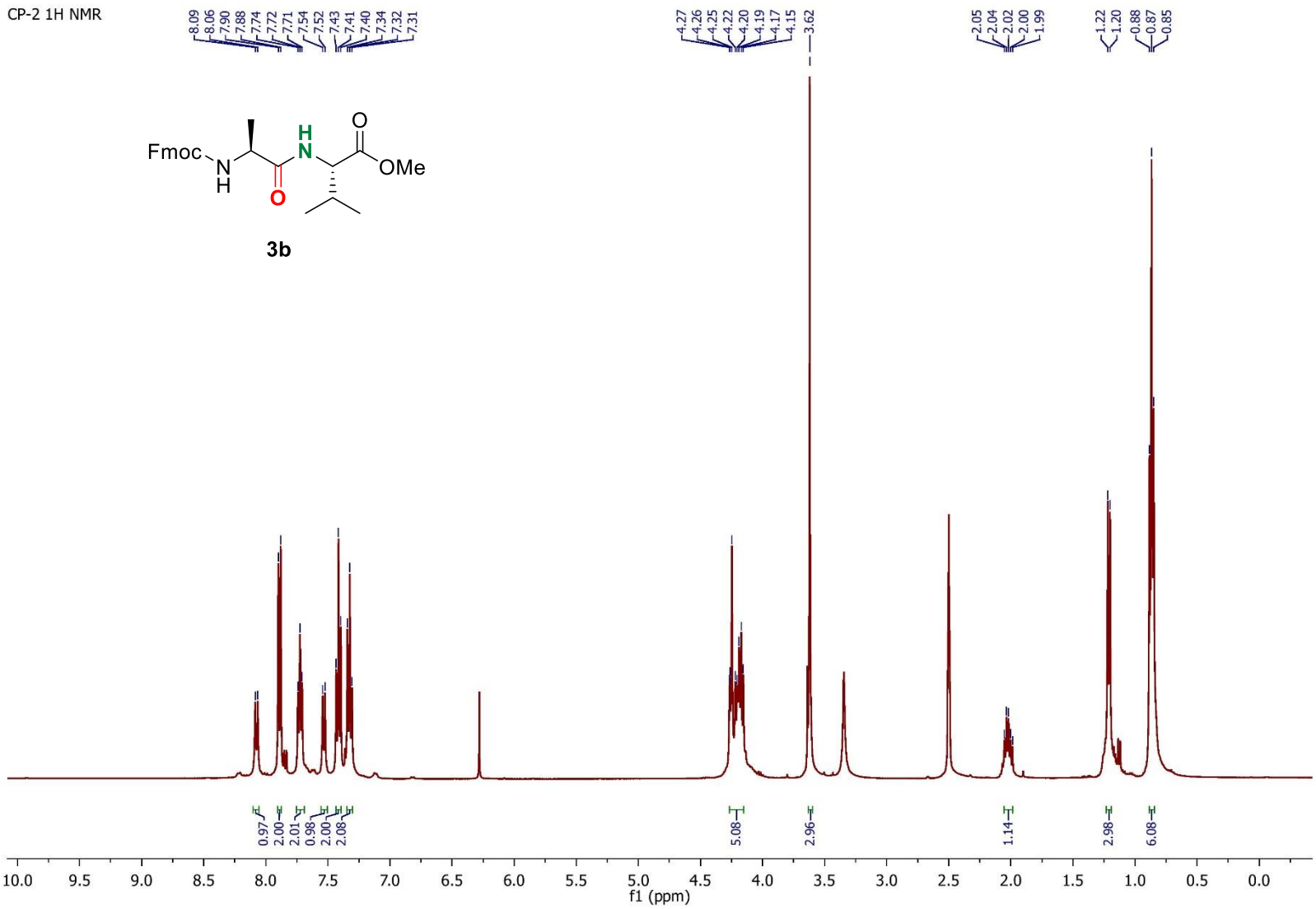


Figure S14. ^{1}H NMR Spectrum of **3b (400MHz, DMSO-d$_6$)**

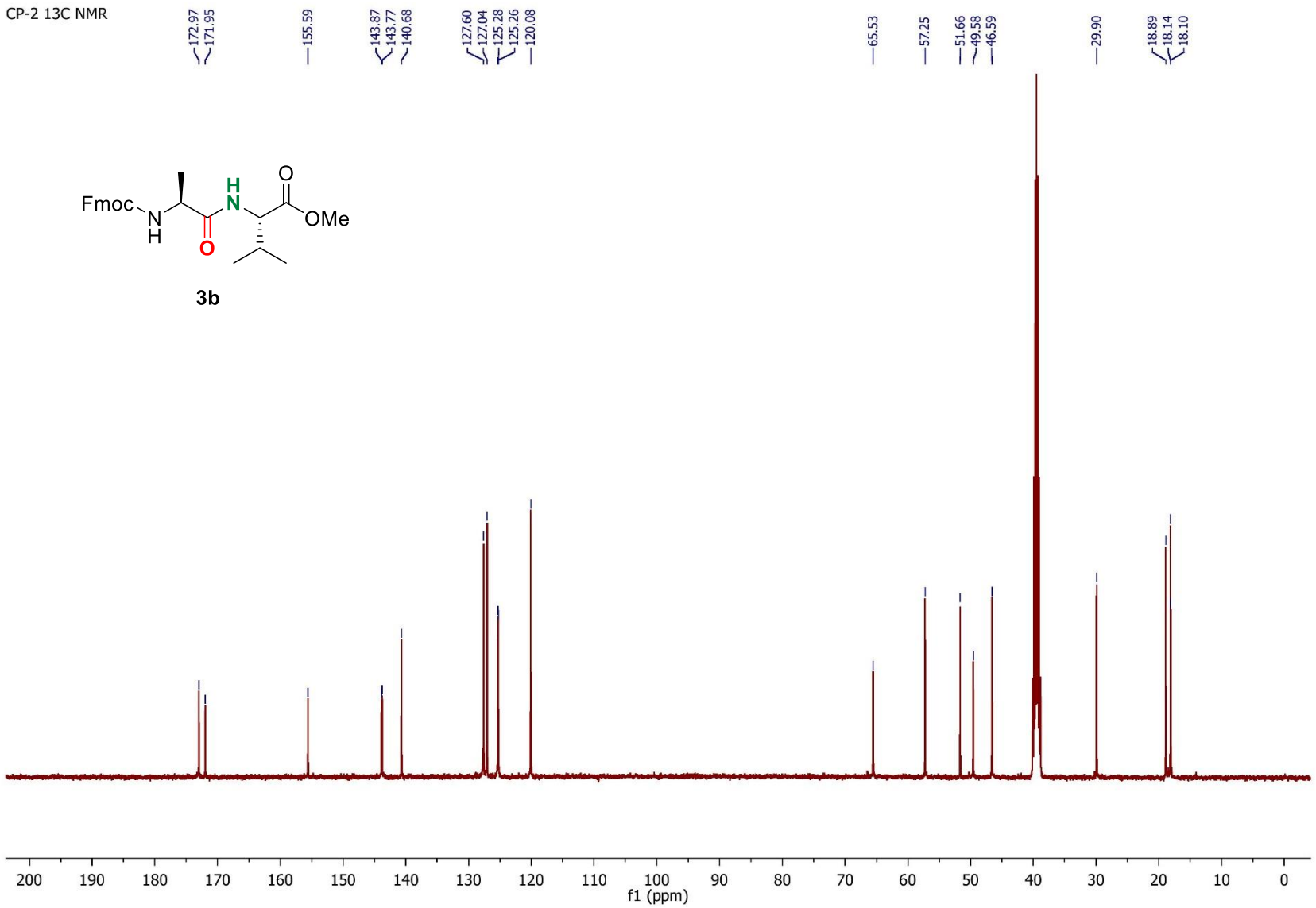


Figure S15. ^{13}C NMR Spectrum of **3b (101MHz, DMSO-d$_6$)**

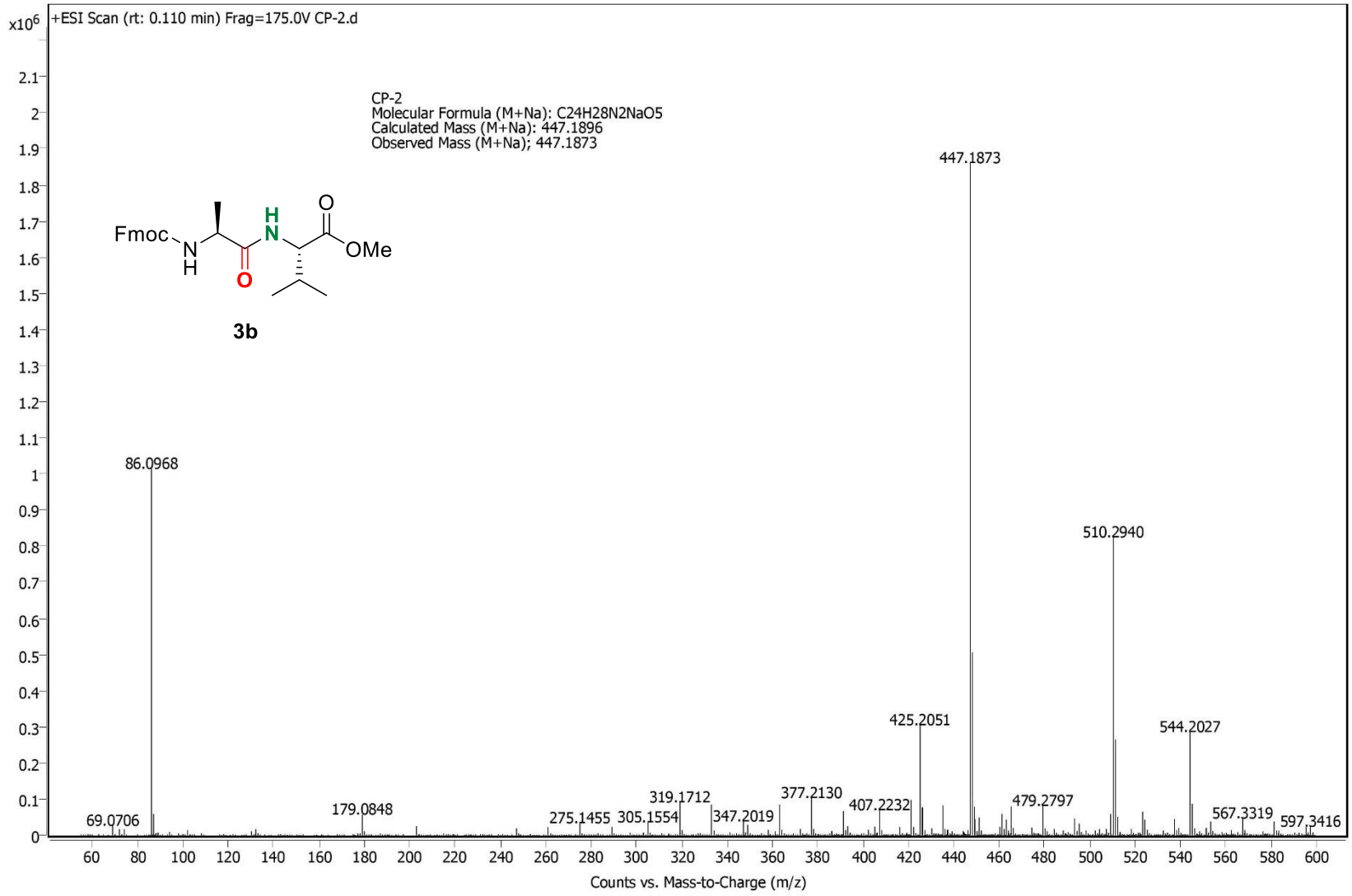


Figure S16. HRMS Spectrum of **3b**

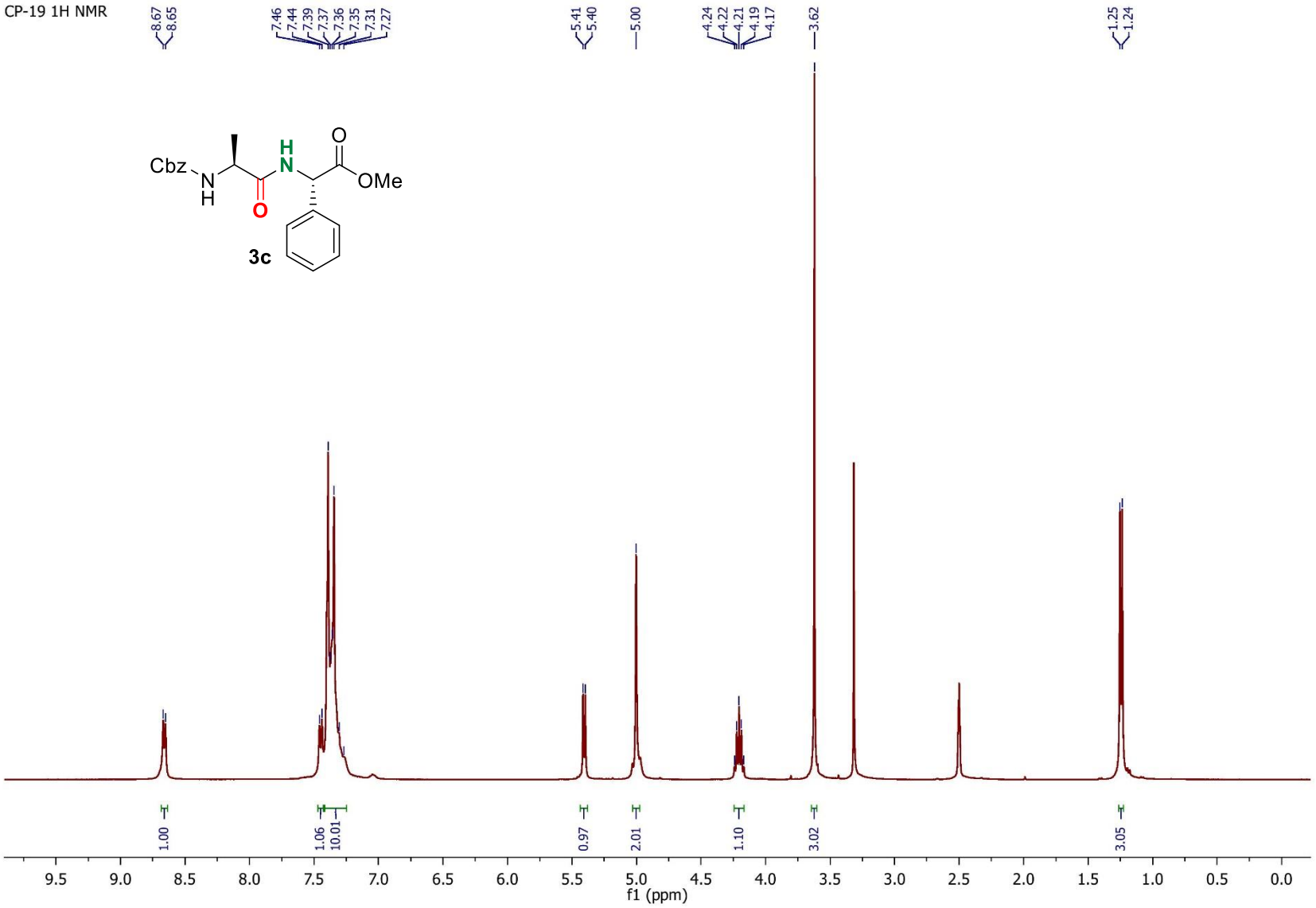


Figure S17. ^{1}H NMR Spectrum of **3c (400MHz, DMSO-d$_6$)**

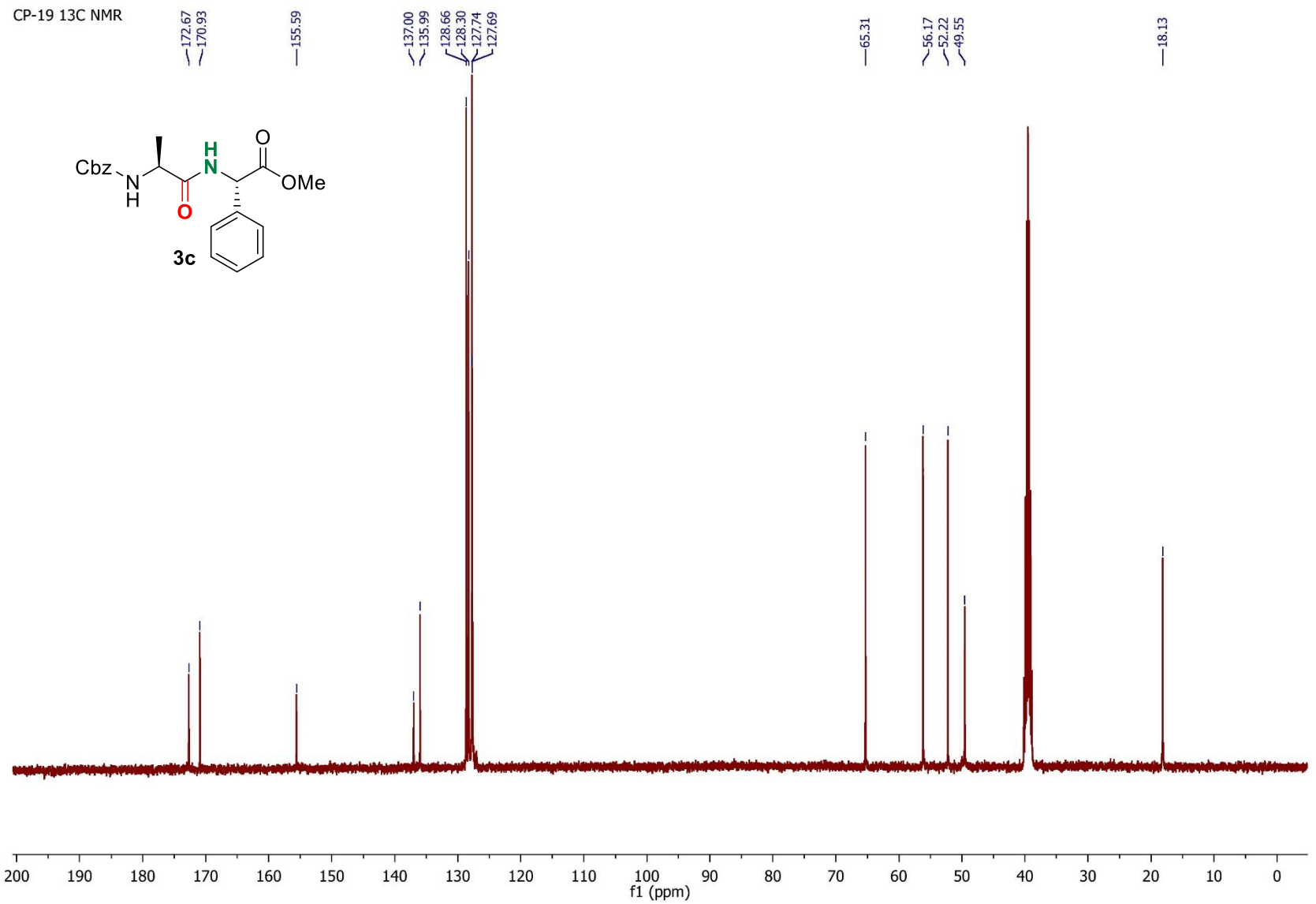


Figure S18. ^{13}C NMR Spectrum of **3c (101MHz, DMSO-d_6)**

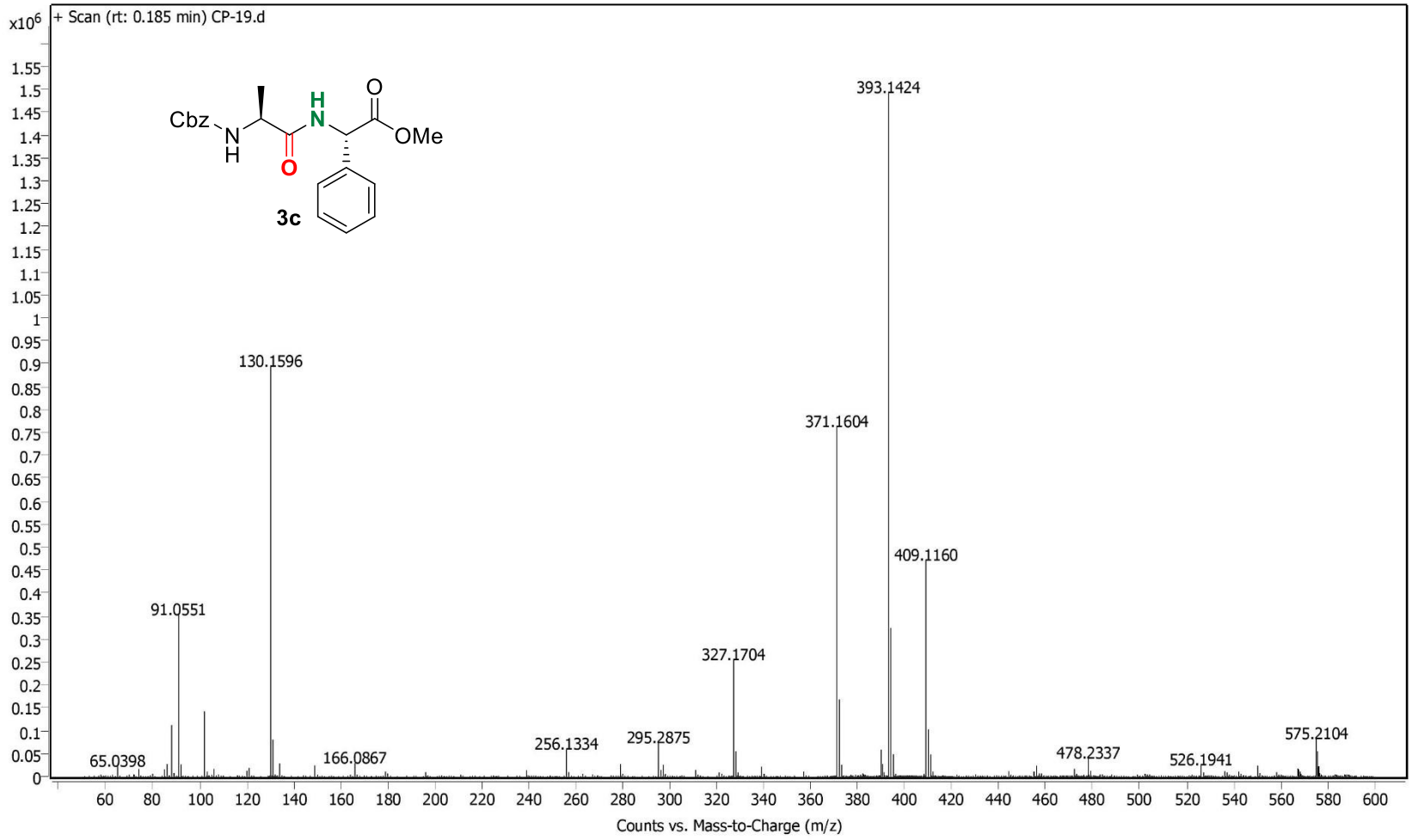


Figure S19. HRMS Spectrum of **3c**

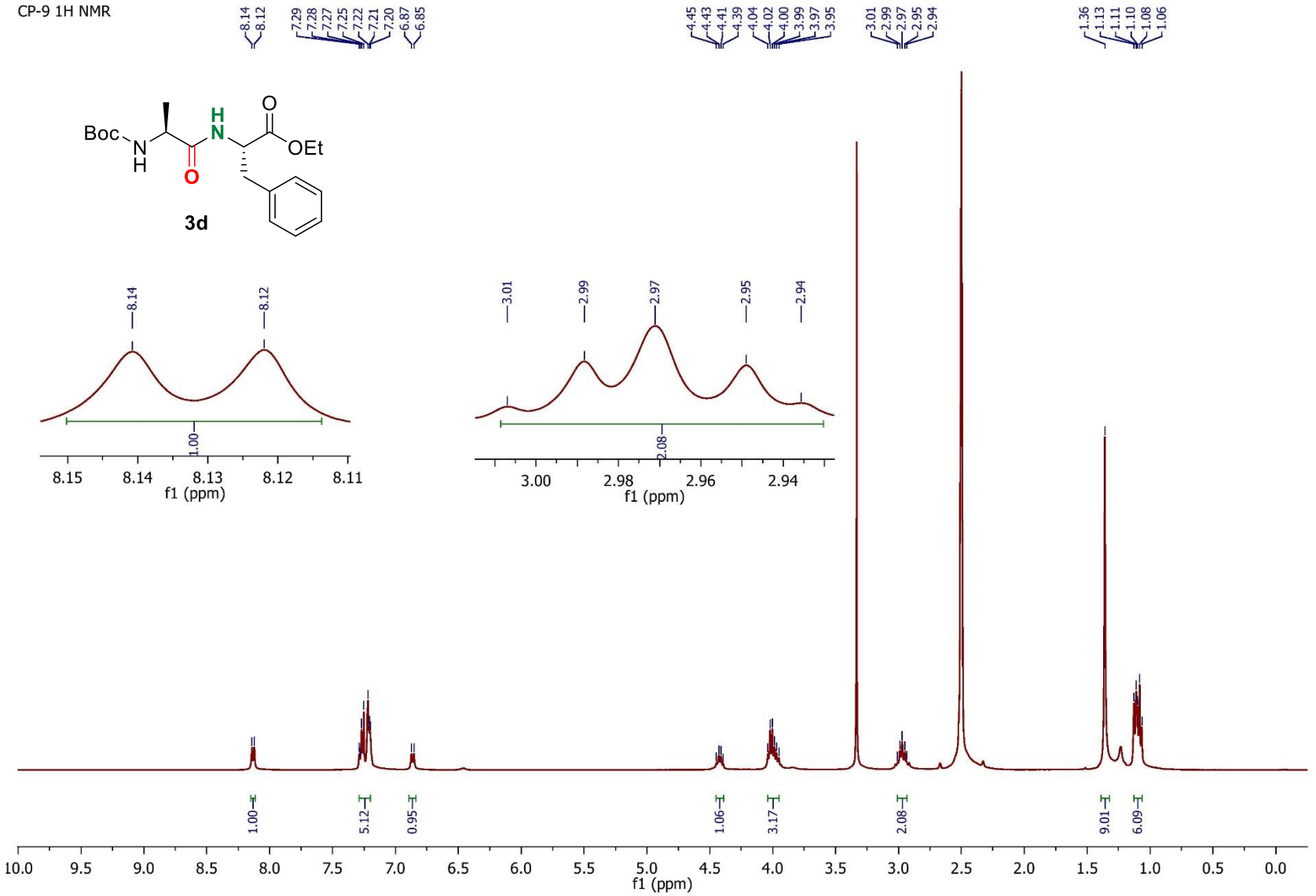


Figure S20. ^{1}H NMR Spectrum of **3d (400MHz, DMSO-d$_6$)**

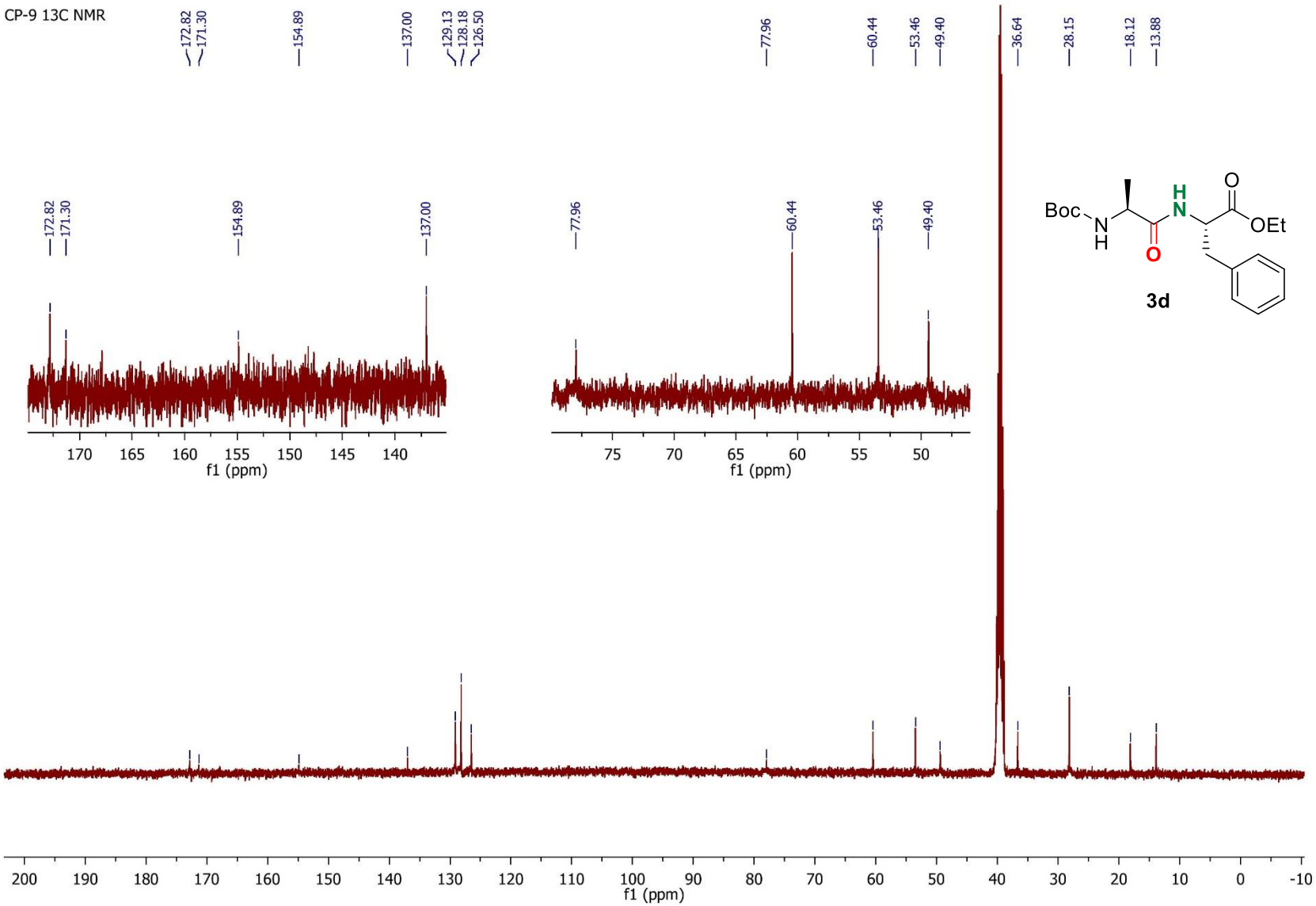


Figure S21. ^{13}C NMR Spectrum of **3d (101MHz, DMSO-d$_6$)**

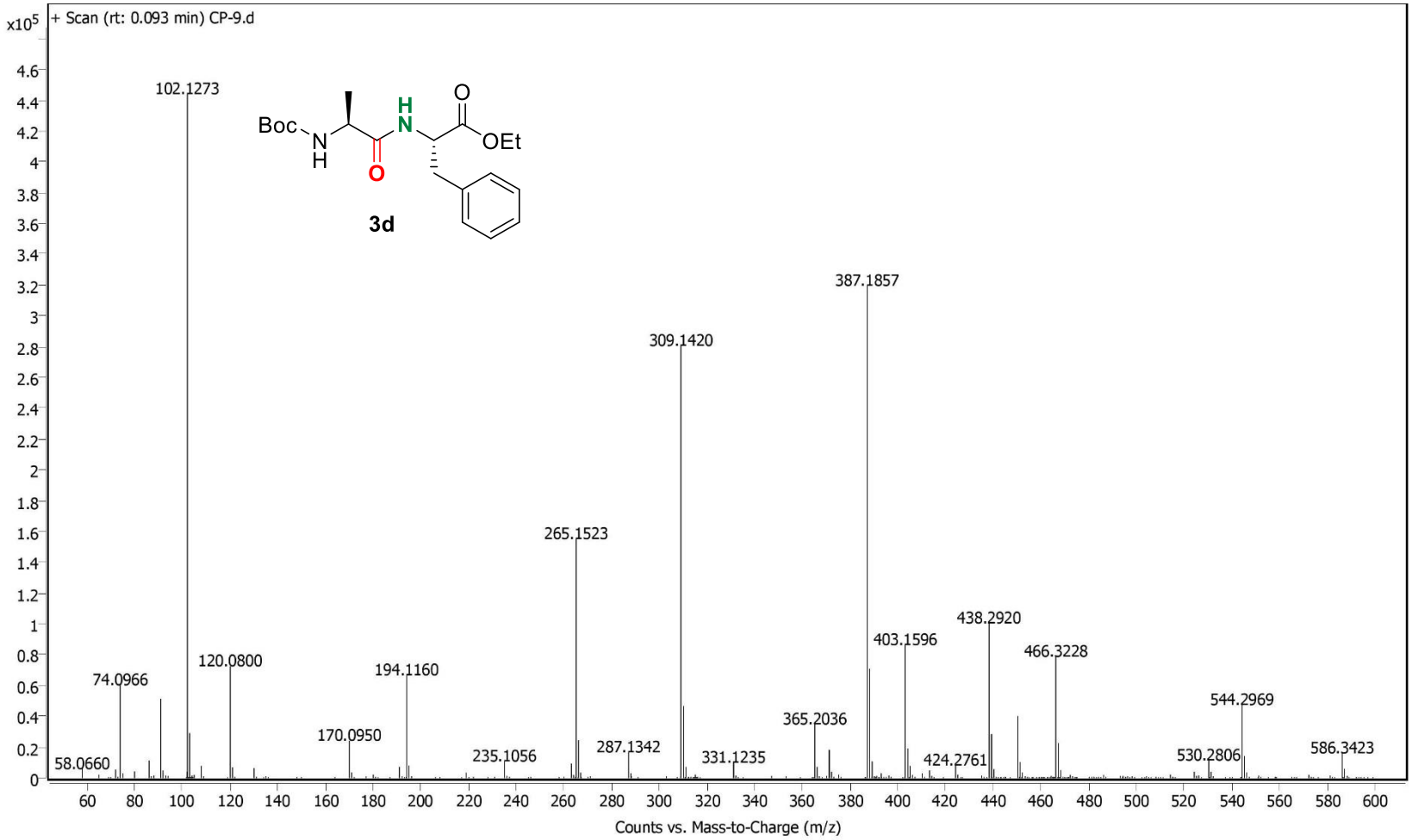


Figure S22. HRMS Spectrum of **3d**

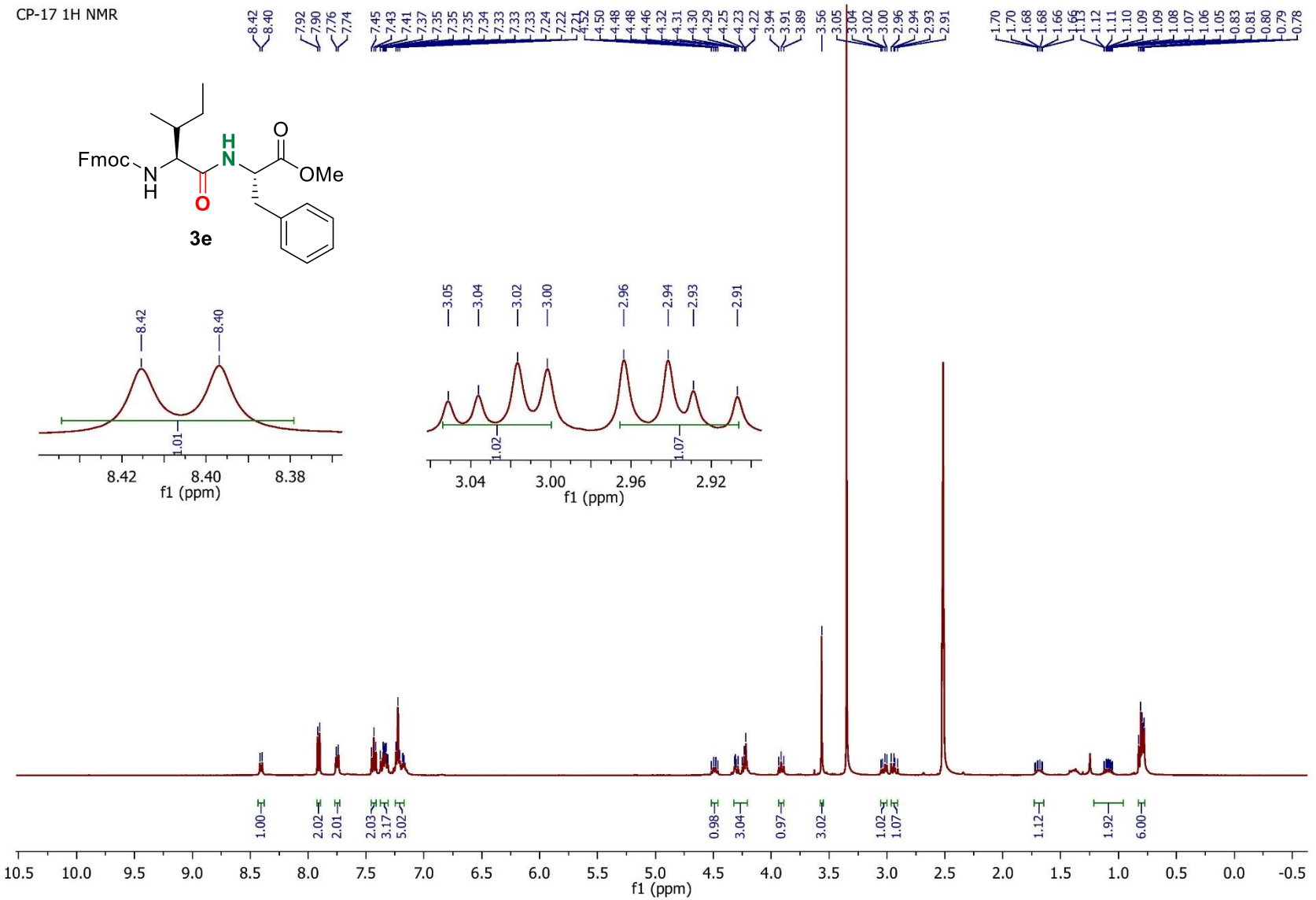


Figure S23. ^{1}H NMR Spectrum of **3e (400MHz, DMSO-d$_6$)**

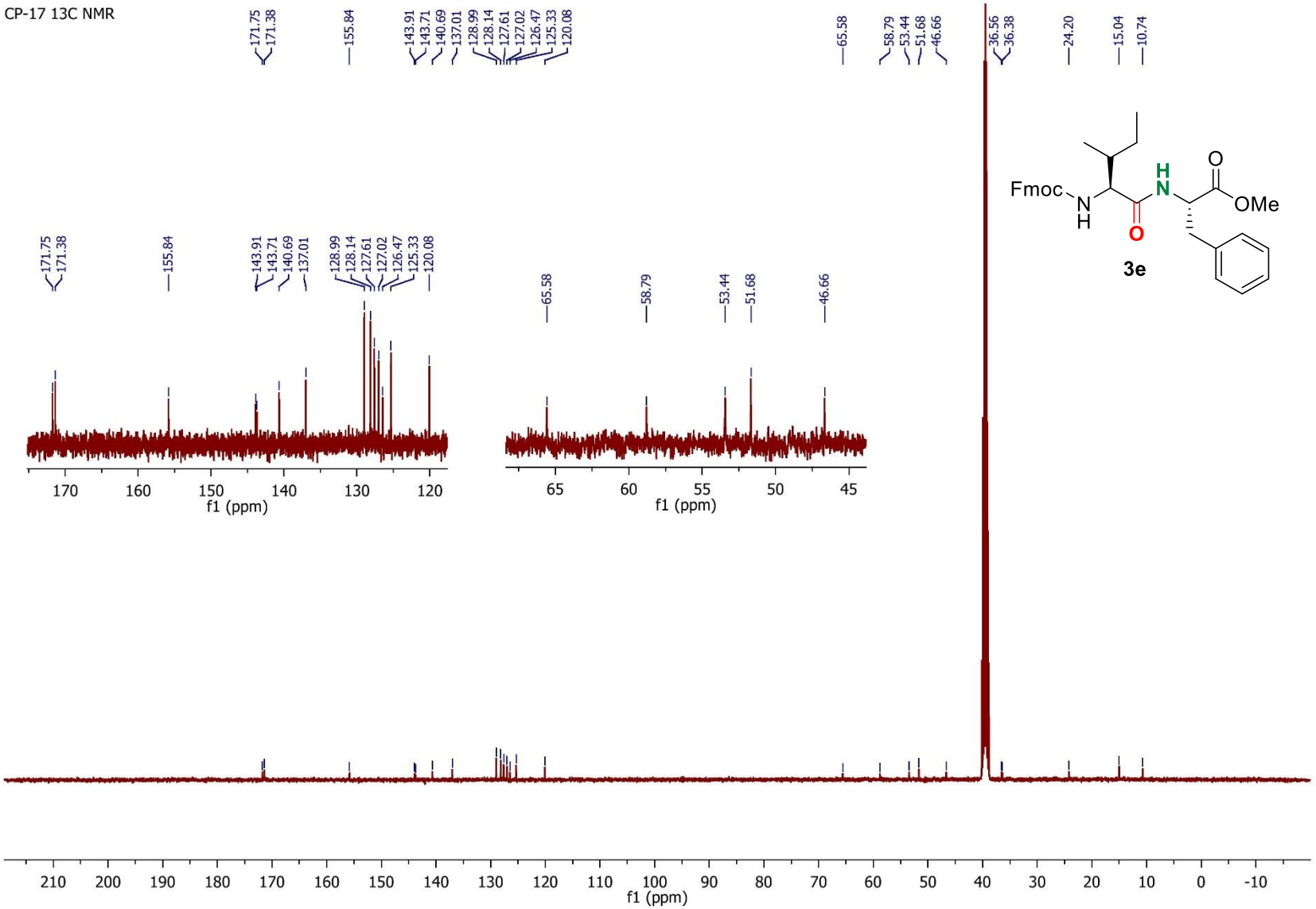


Figure S24. ^{13}C NMR Spectrum of **3e (101MHz, DMSO-d$_6$)**

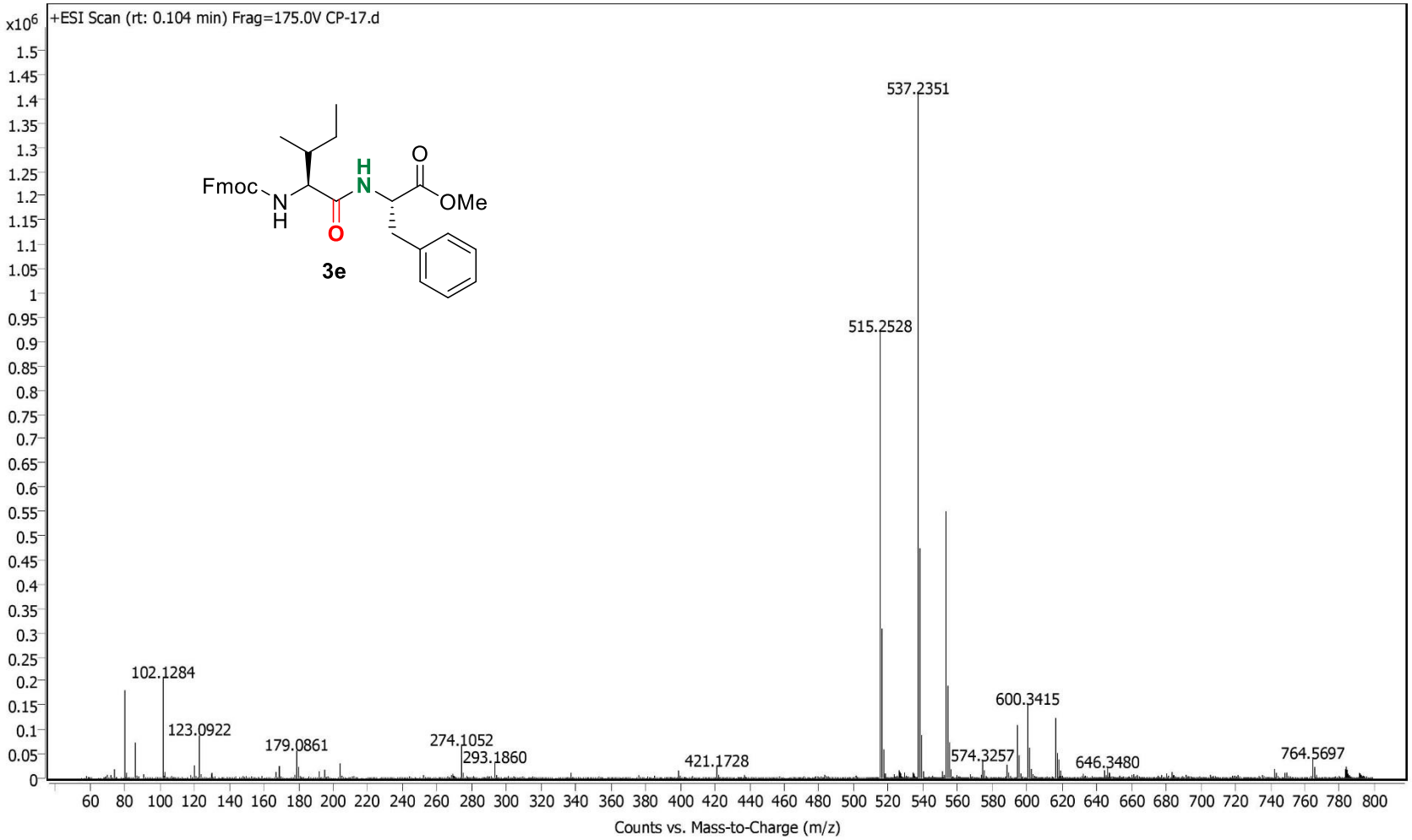


Figure S25. HRMS Spectrum of **3e**

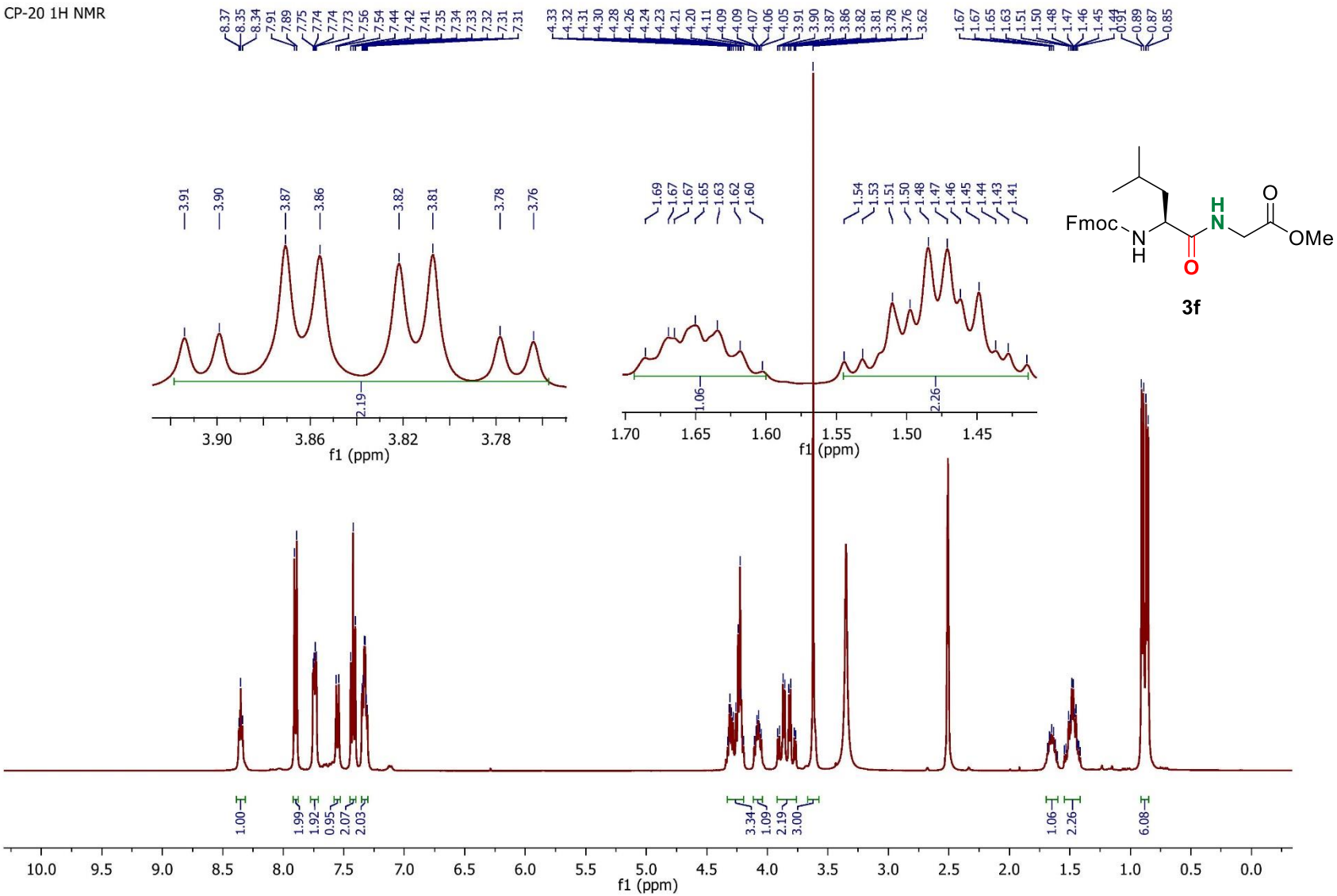


Figure S26. ^{1}H NMR Spectrum of **3f (400MHz, DMSO-d$_6$)**

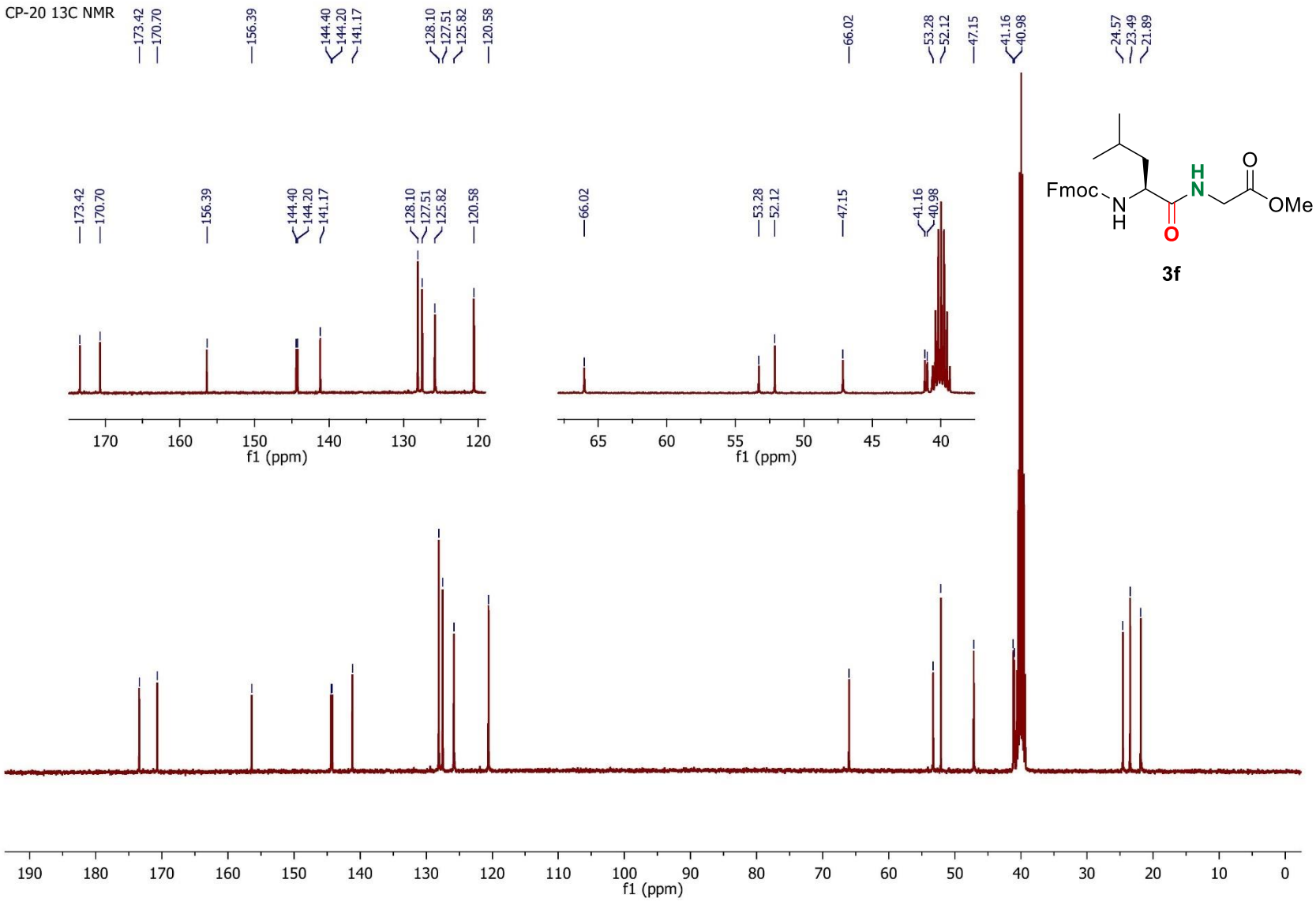


Figure S27. ^{13}C NMR Spectrum of **3f (101MHz, DMSO-d$_6$)**

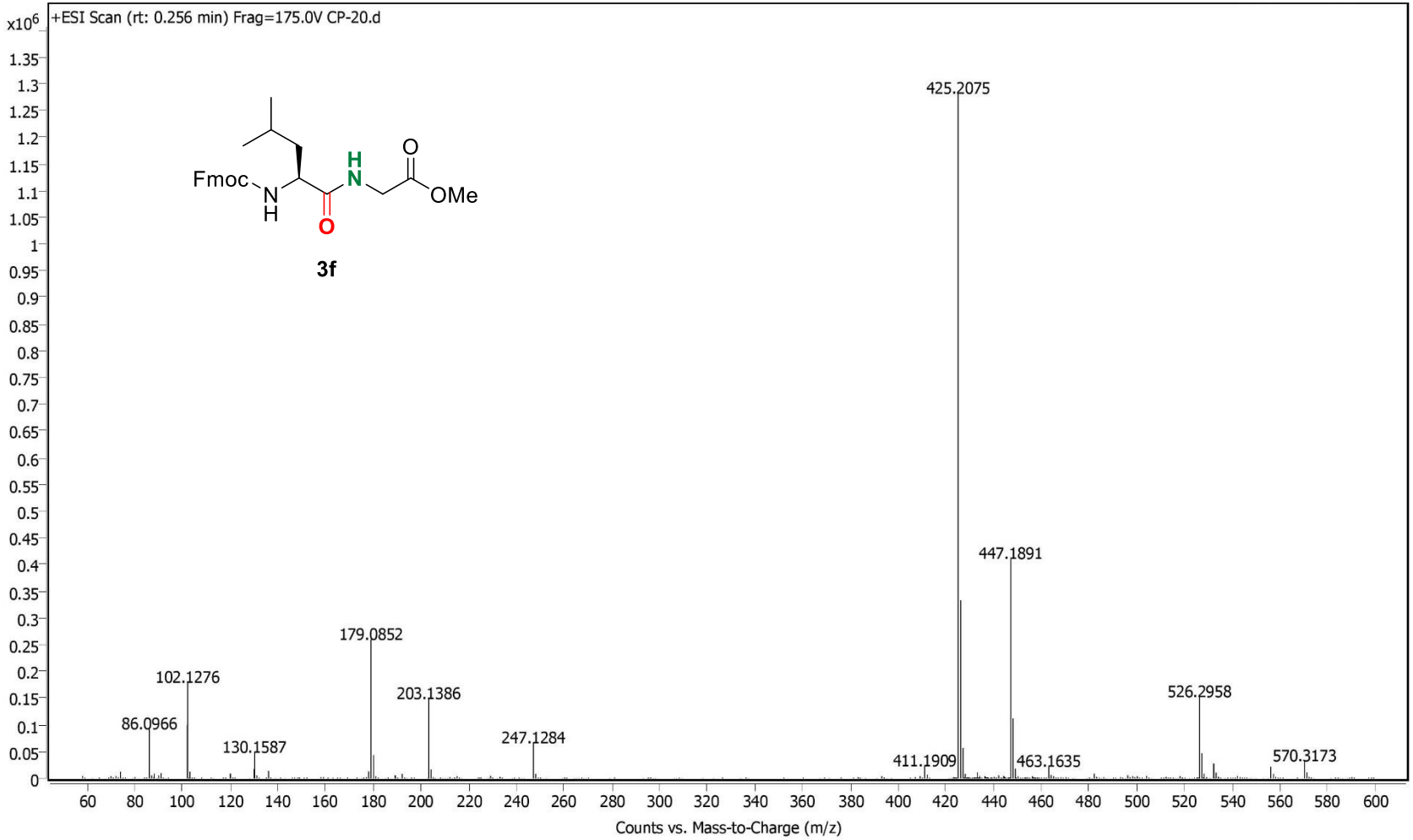


Figure S28. HRMS Spectrum of **3f**

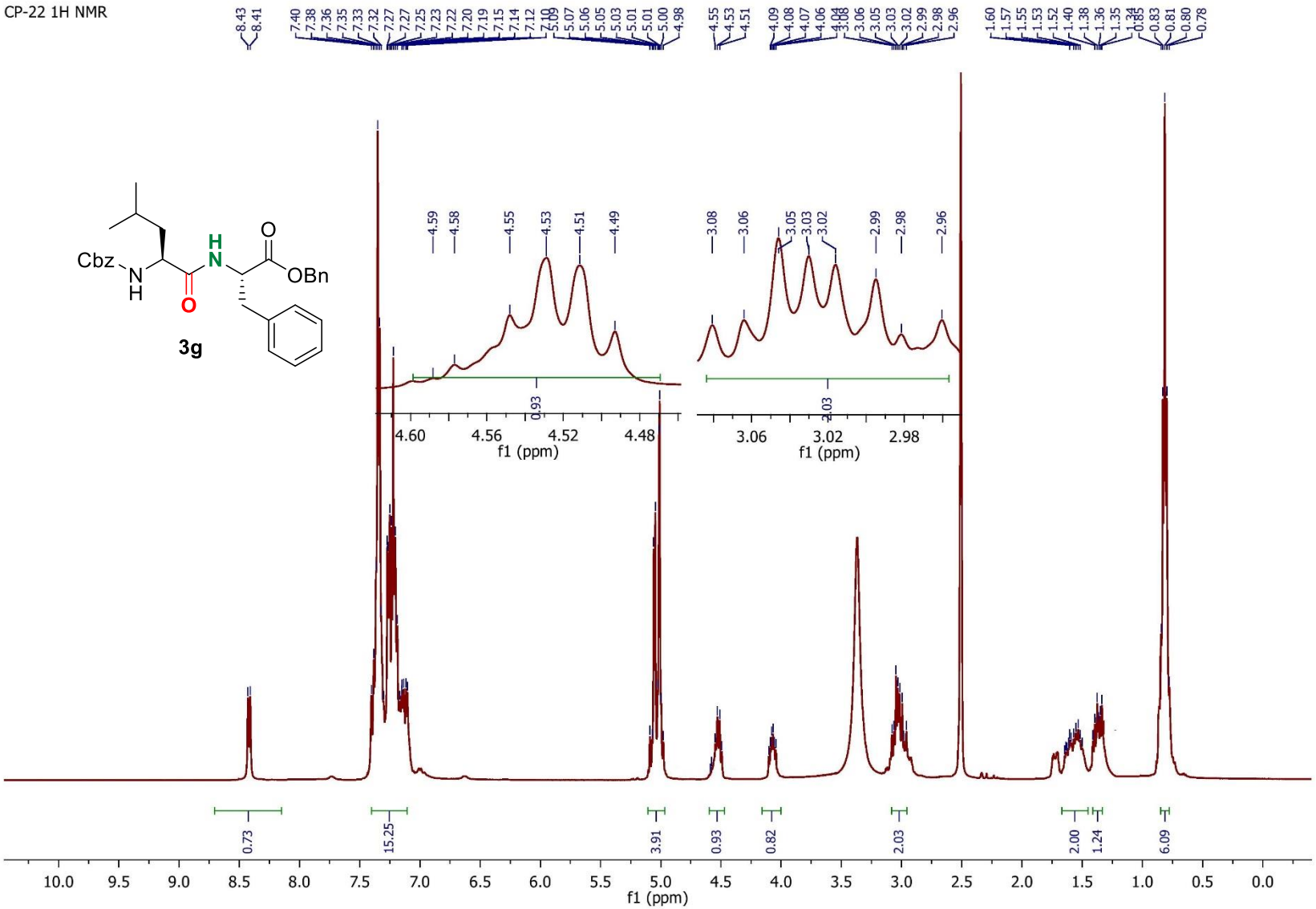


Figure S29. ^{1}H NMR Spectrum of **3g (400MHz, DMSO-d$_6$)**

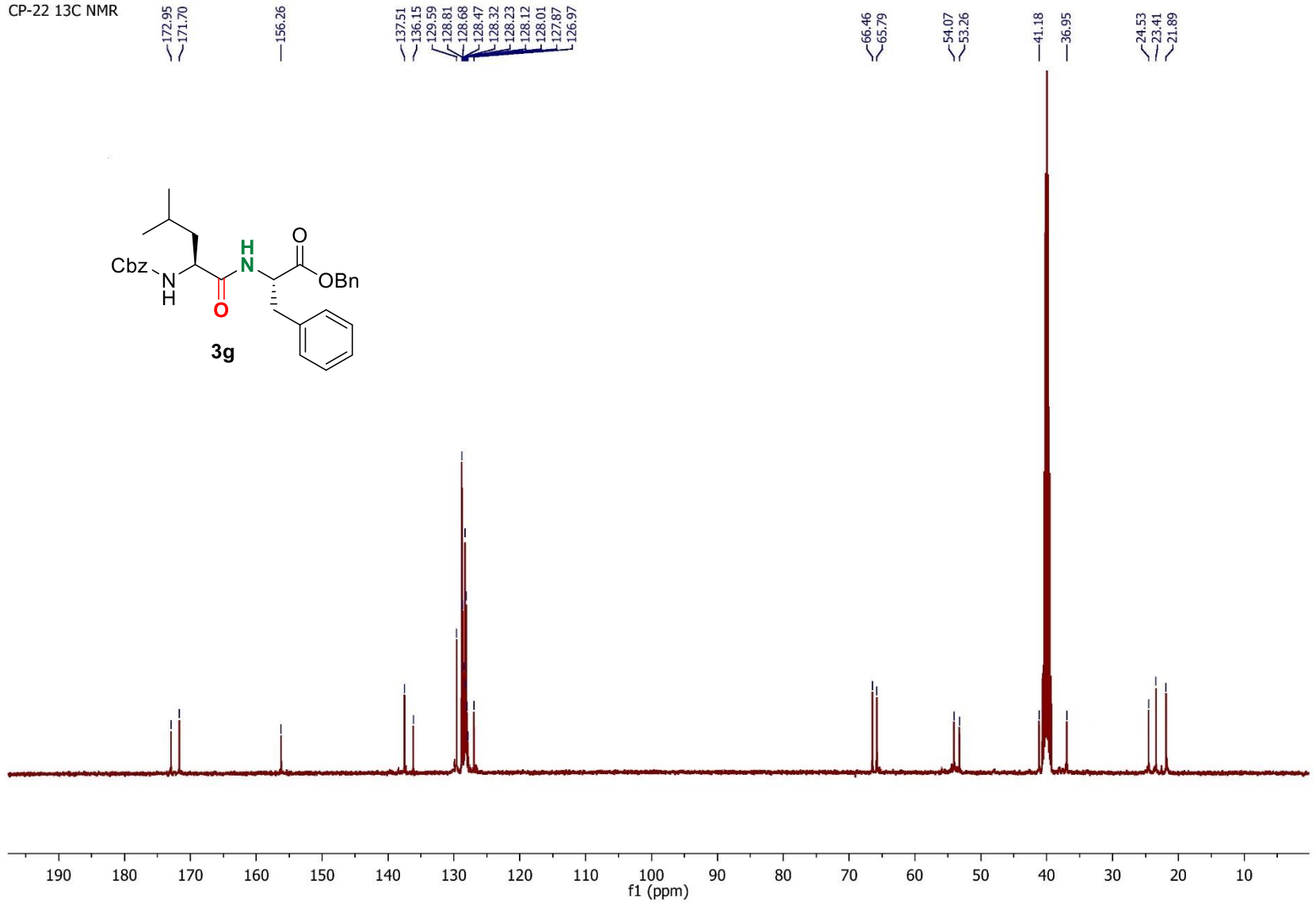


Figure S30. ^{13}C NMR Spectrum of **3g (101MHz, DMSO-d$_6$)**

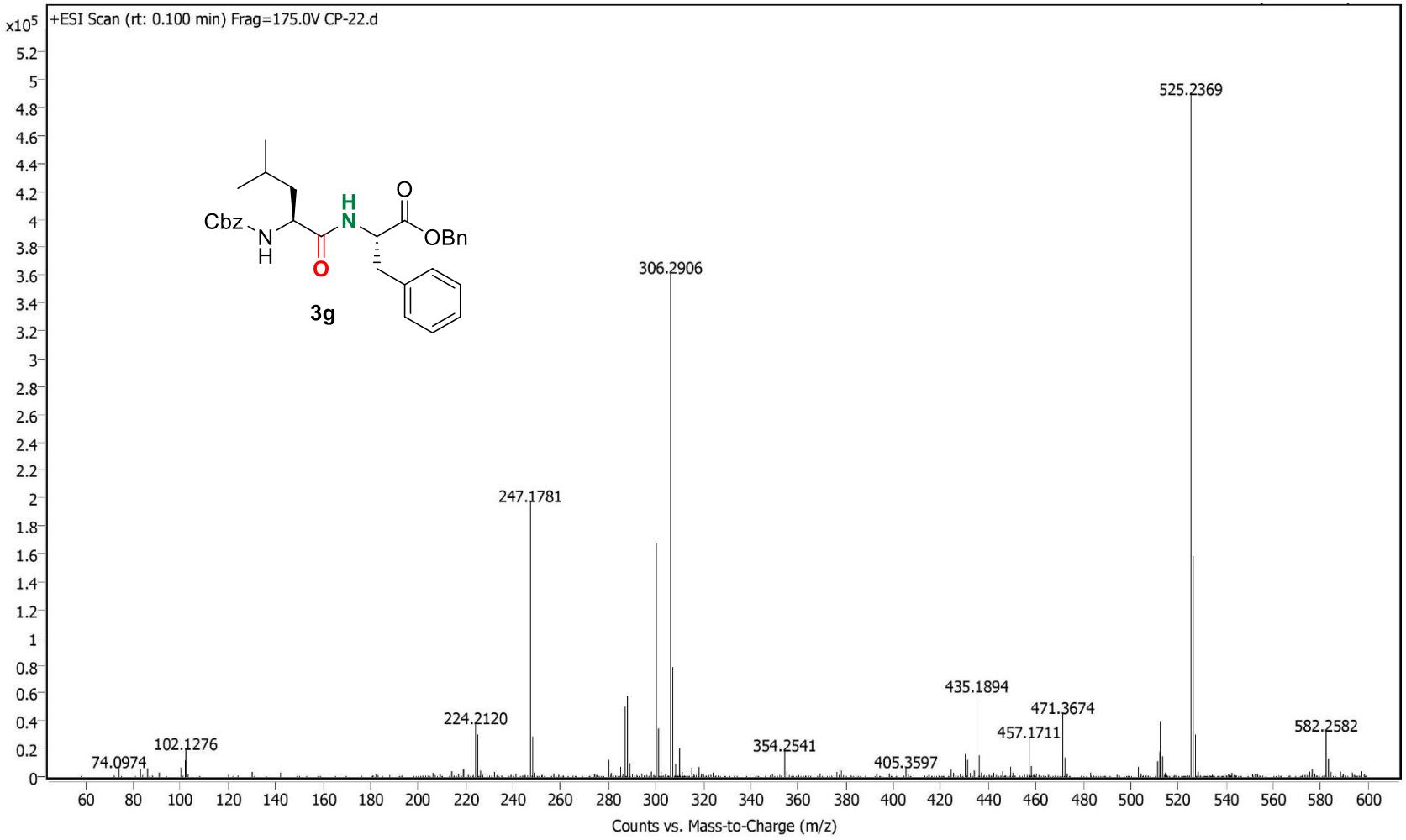


Figure S31. HRMS Spectrum of **3g**

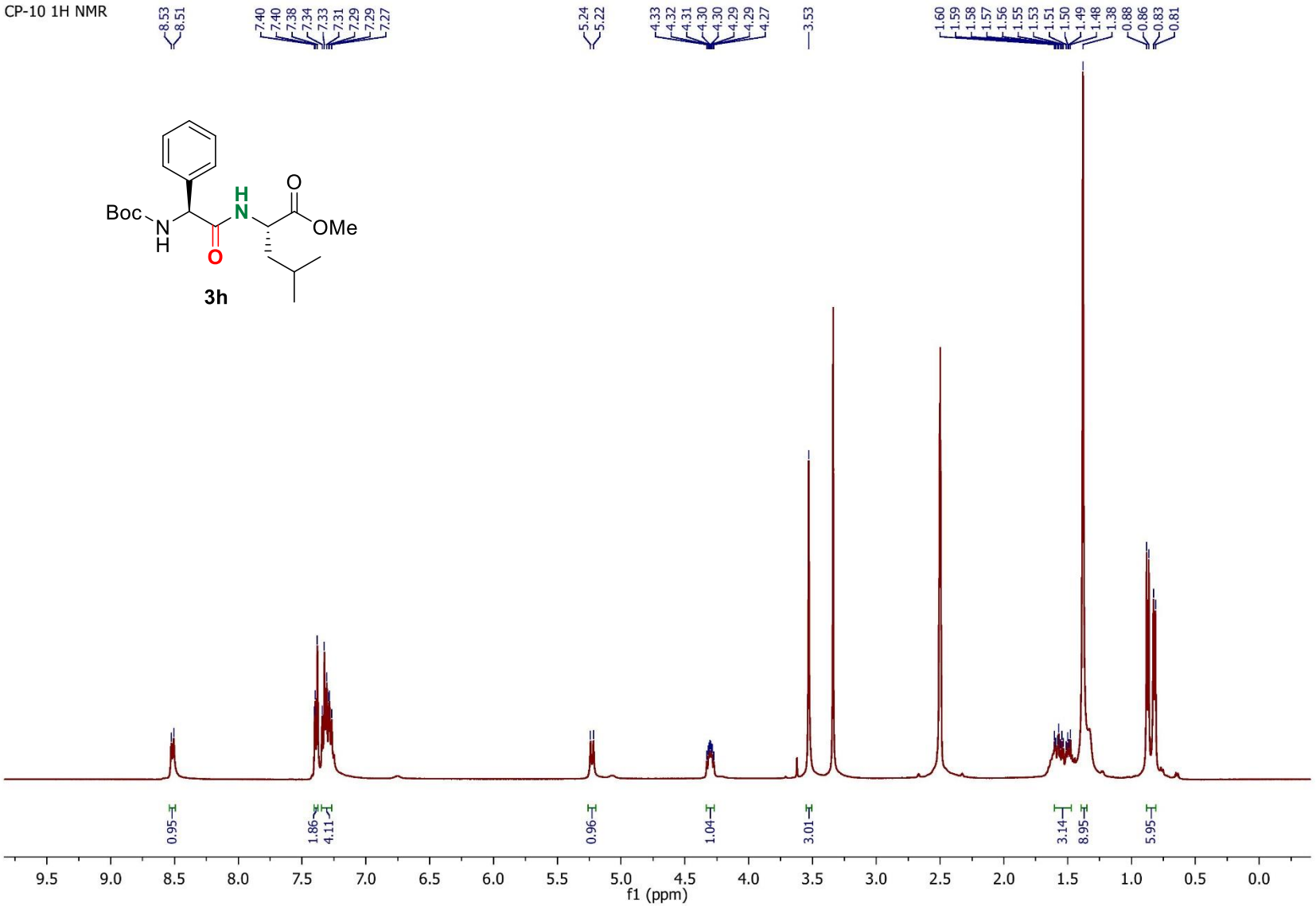


Figure S32. ^{1}H NMR Spectrum of **3h (400MHz, DMSO-d$_6$)**

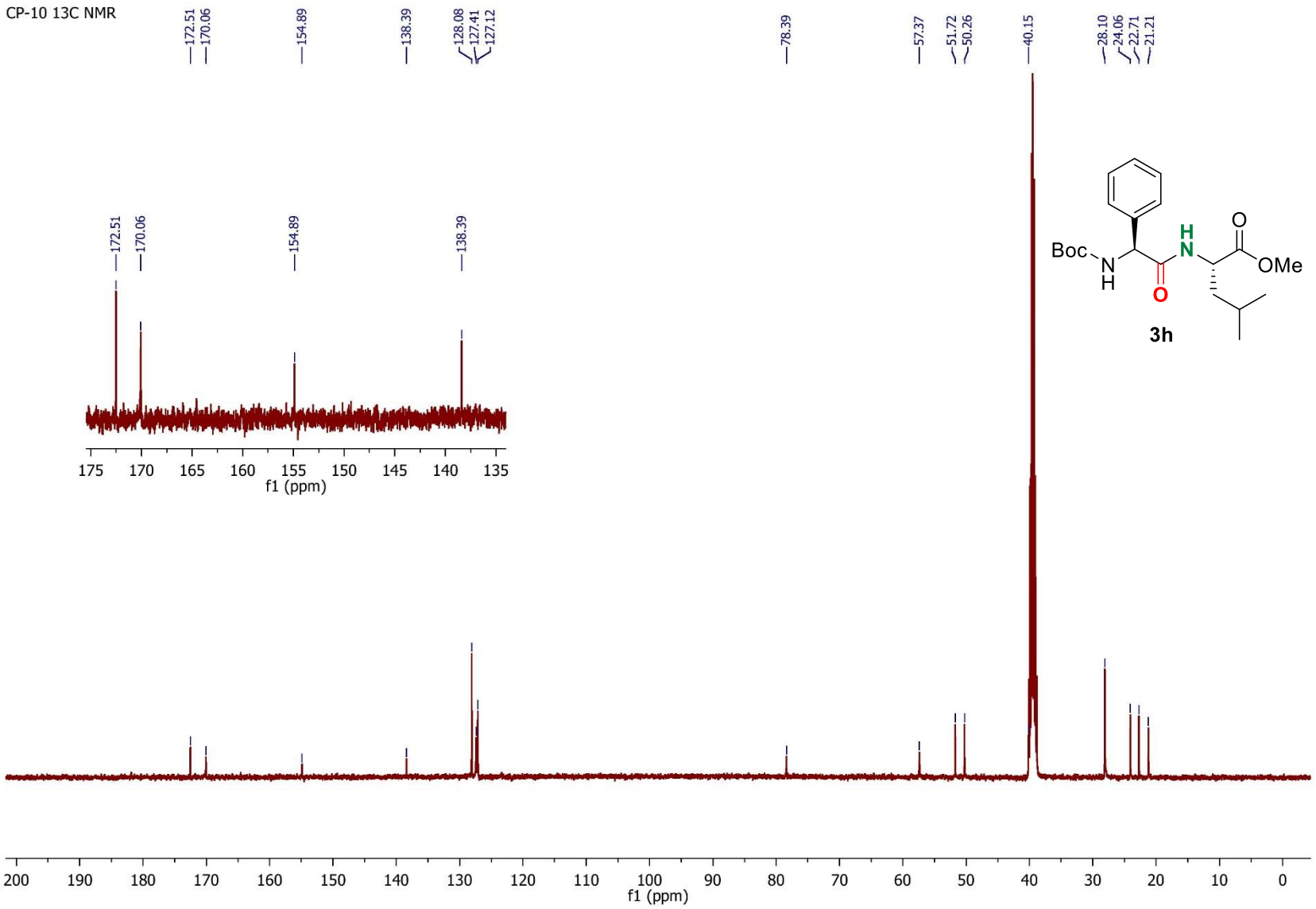


Figure S33. ^{13}C NMR Spectrum of **3h (101MHz, DMSO-d$_6$)**

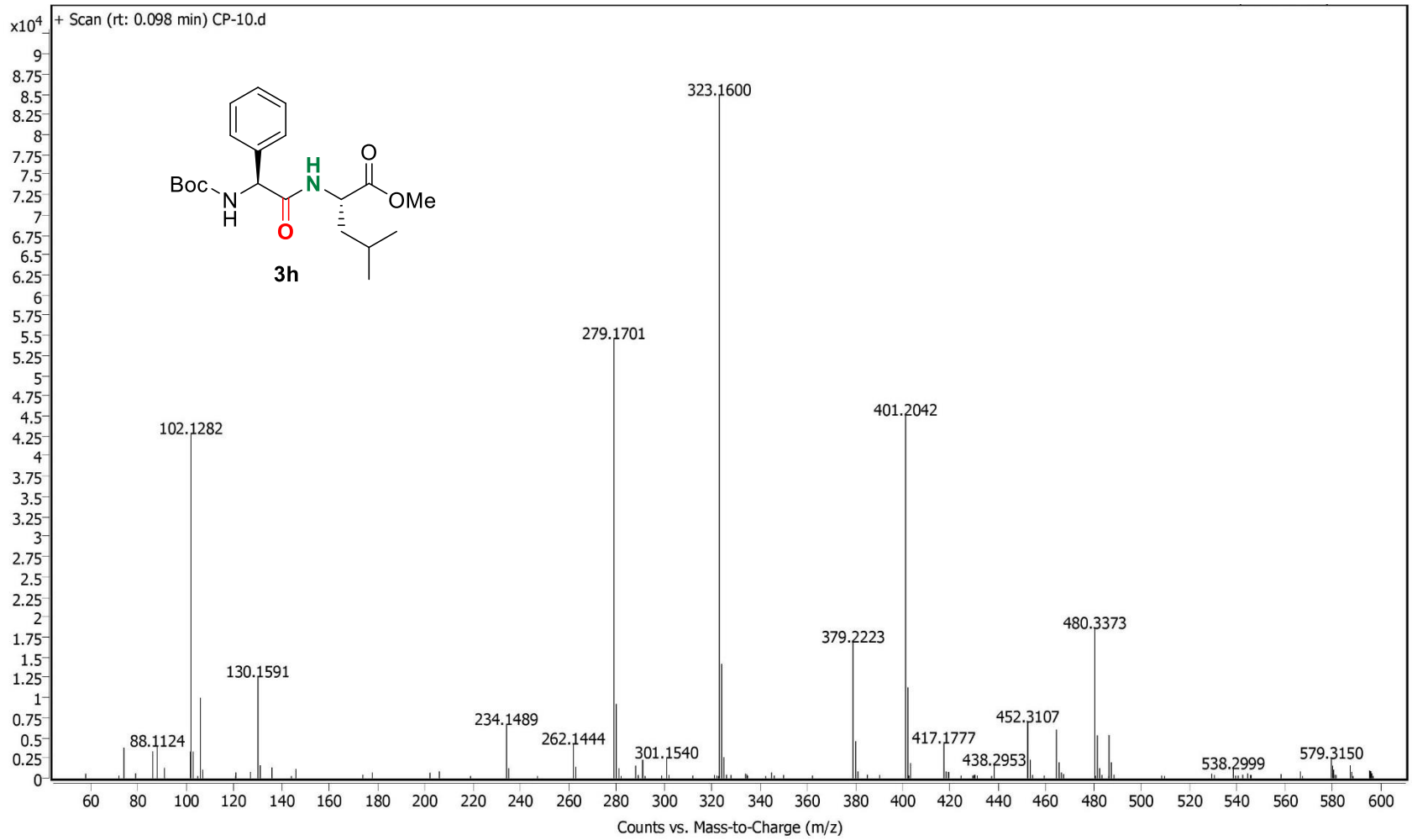


Figure S34. HRMS Spectrum of **3h**

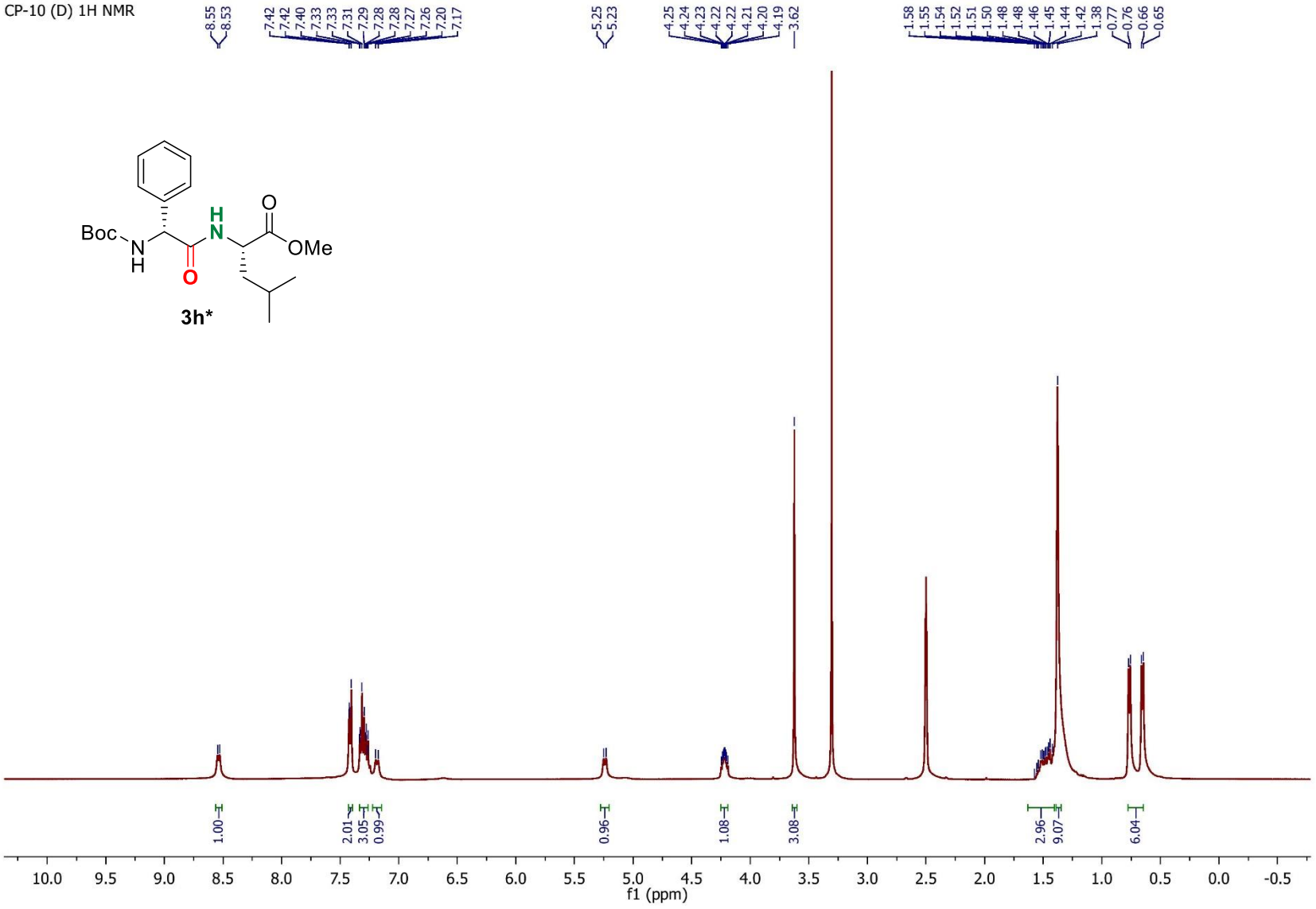


Figure S35. ^{1}H NMR Spectrum of **3h* (400MHz, DMSO-d$_6$)**

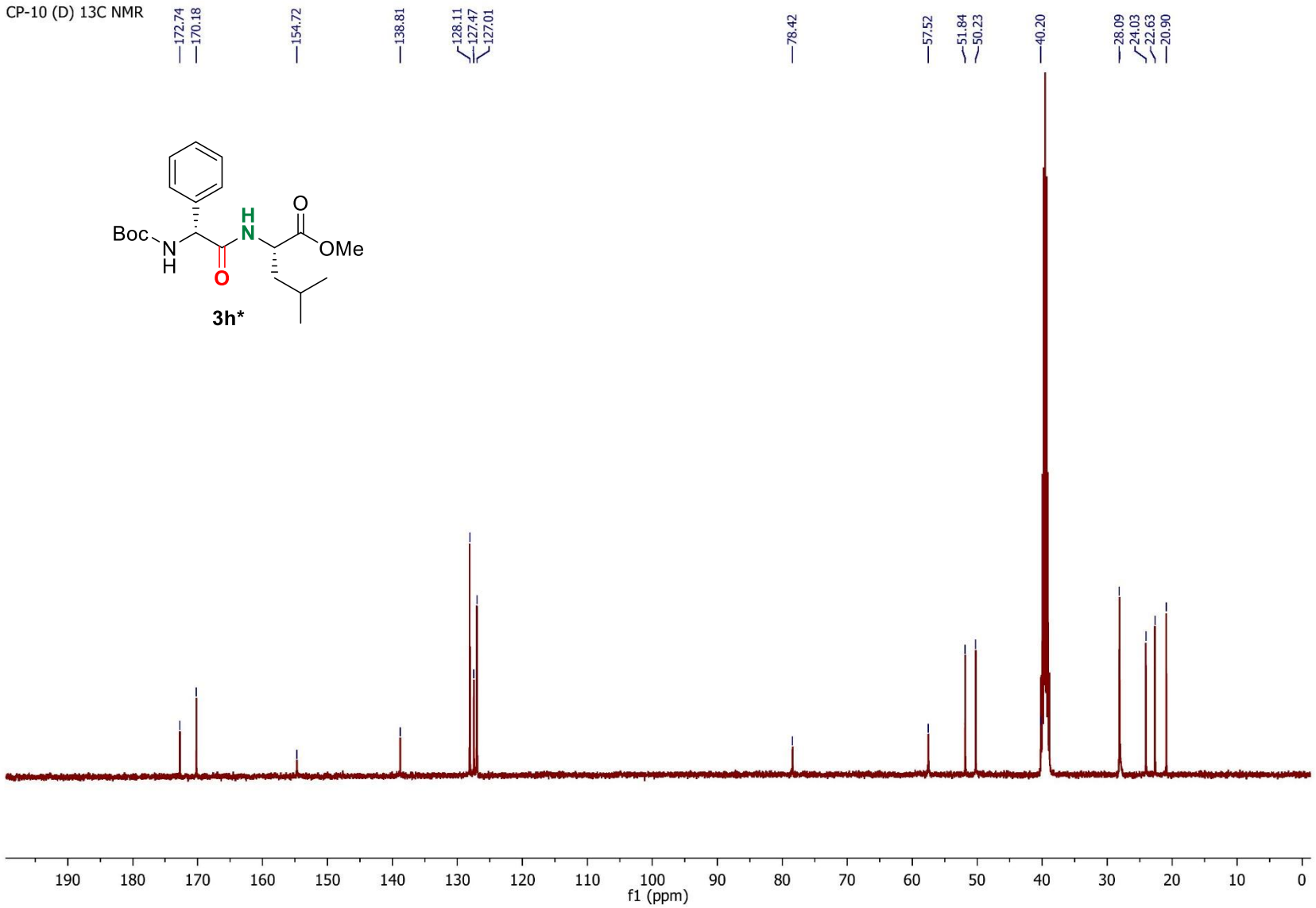


Figure S36. ^{13}C NMR Spectrum of **3h* (101MHz, DMSO-d$_6$)**

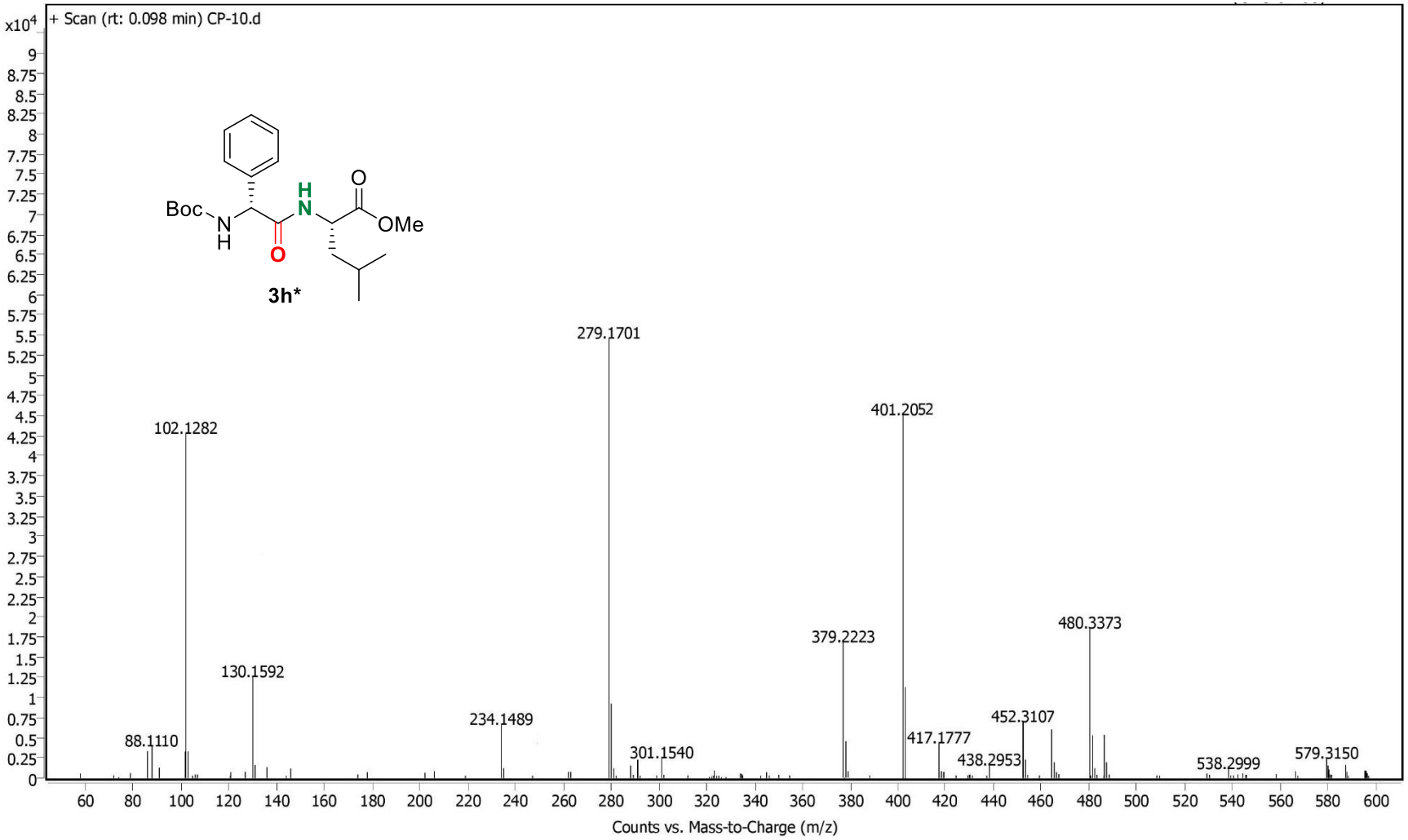


Figure S37. HRMS Spectrum of **3h***

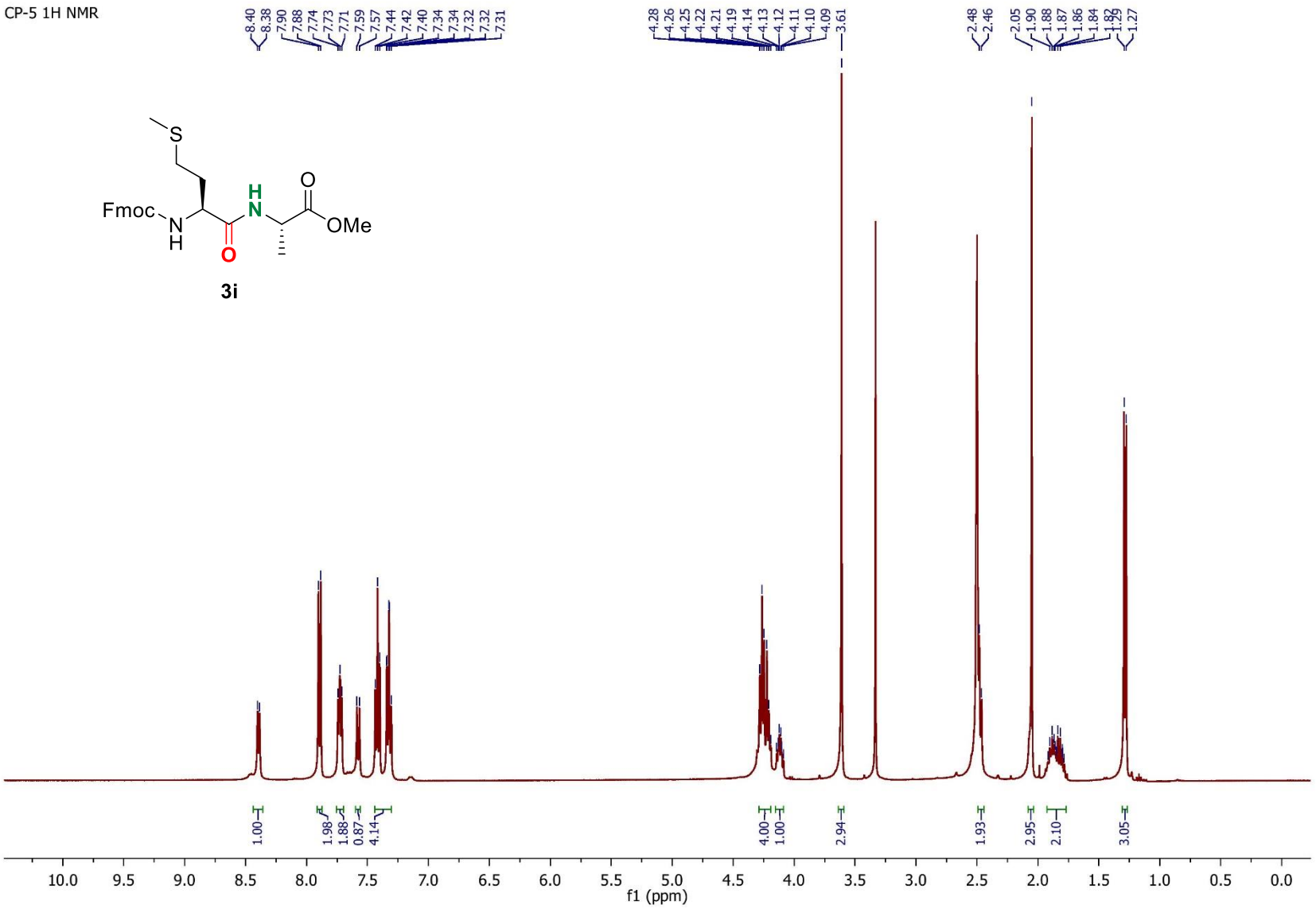


Figure S38. ^{1}H NMR Spectrum of **3i (400MHz, DMSO-d$_6$)**

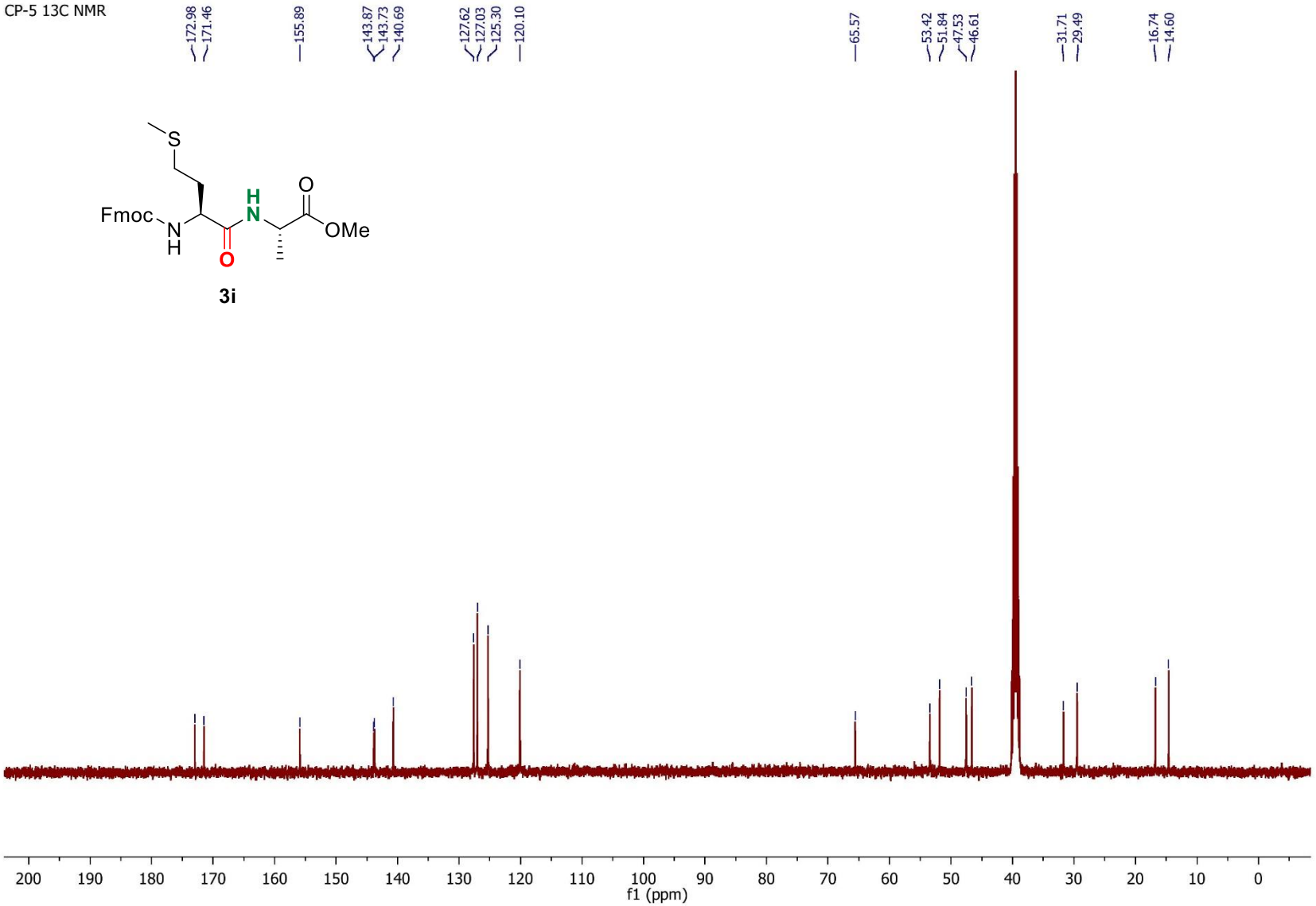


Figure S39. ^{13}C NMR Spectrum of **3i (101MHz, DMSO-d$_6$)**

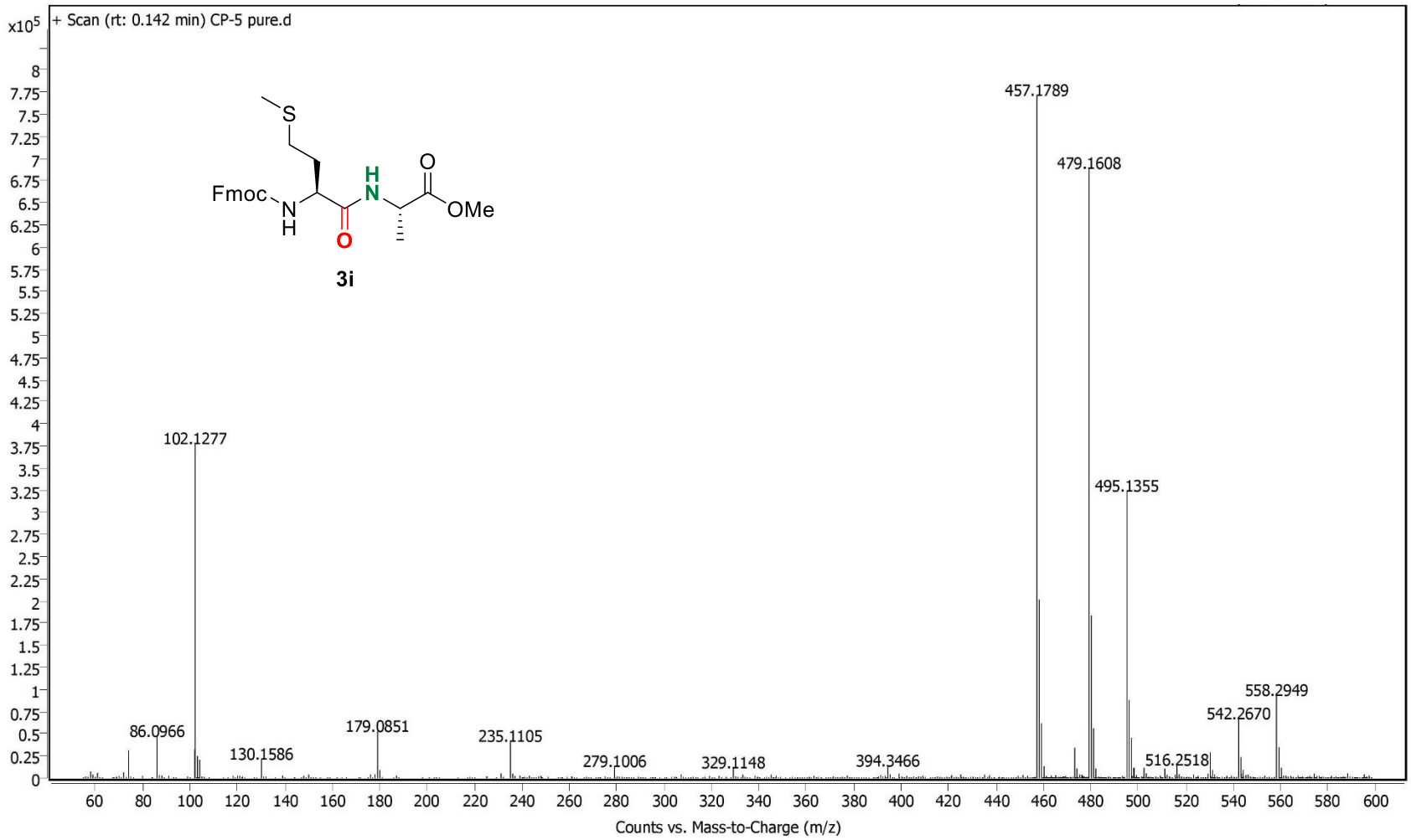


Figure S40. HRMS Spectrum of **3i**

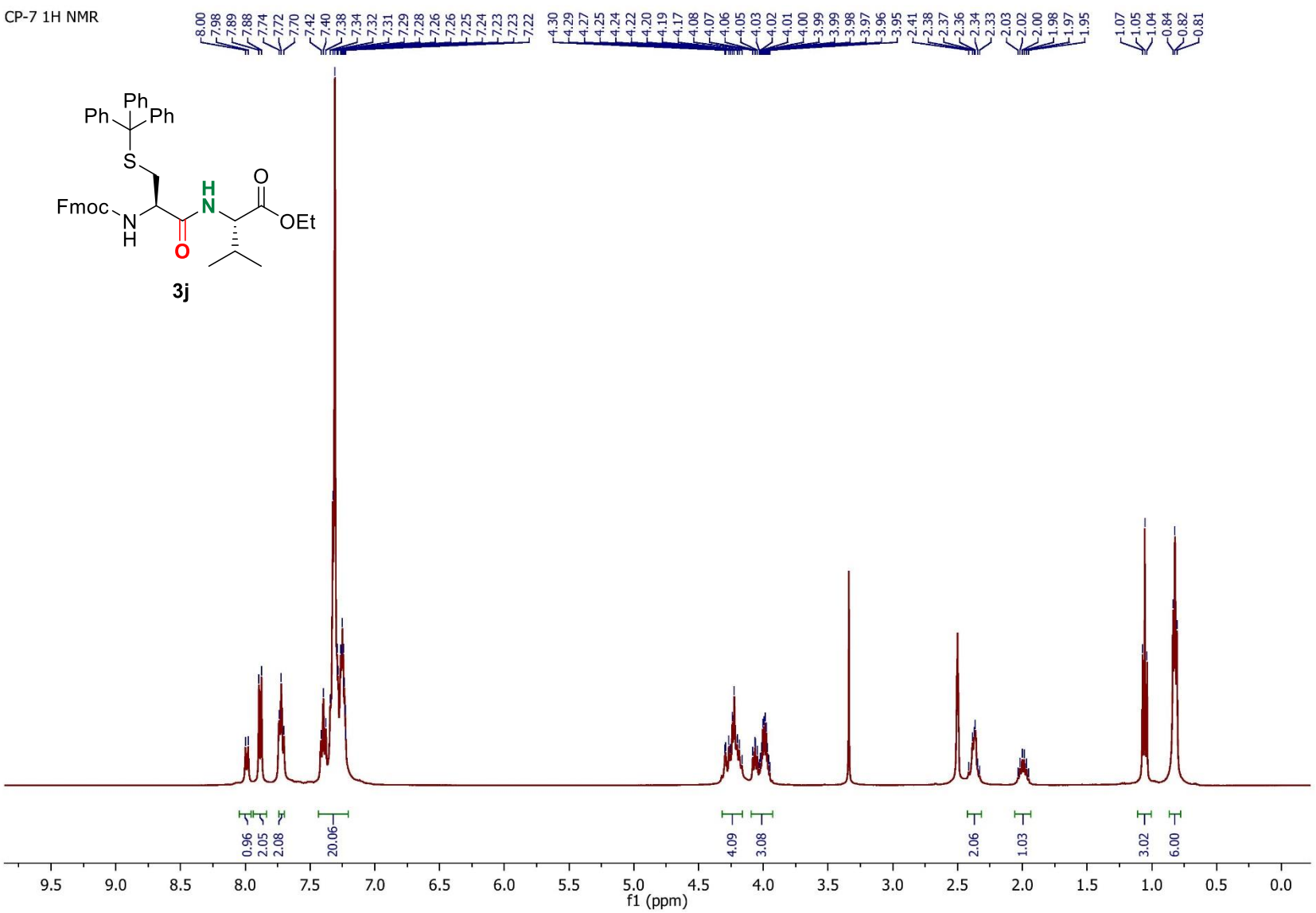


Figure S41. ^{1}H NMR Spectrum of **3j (400MHz, DMSO-d$_6$)**

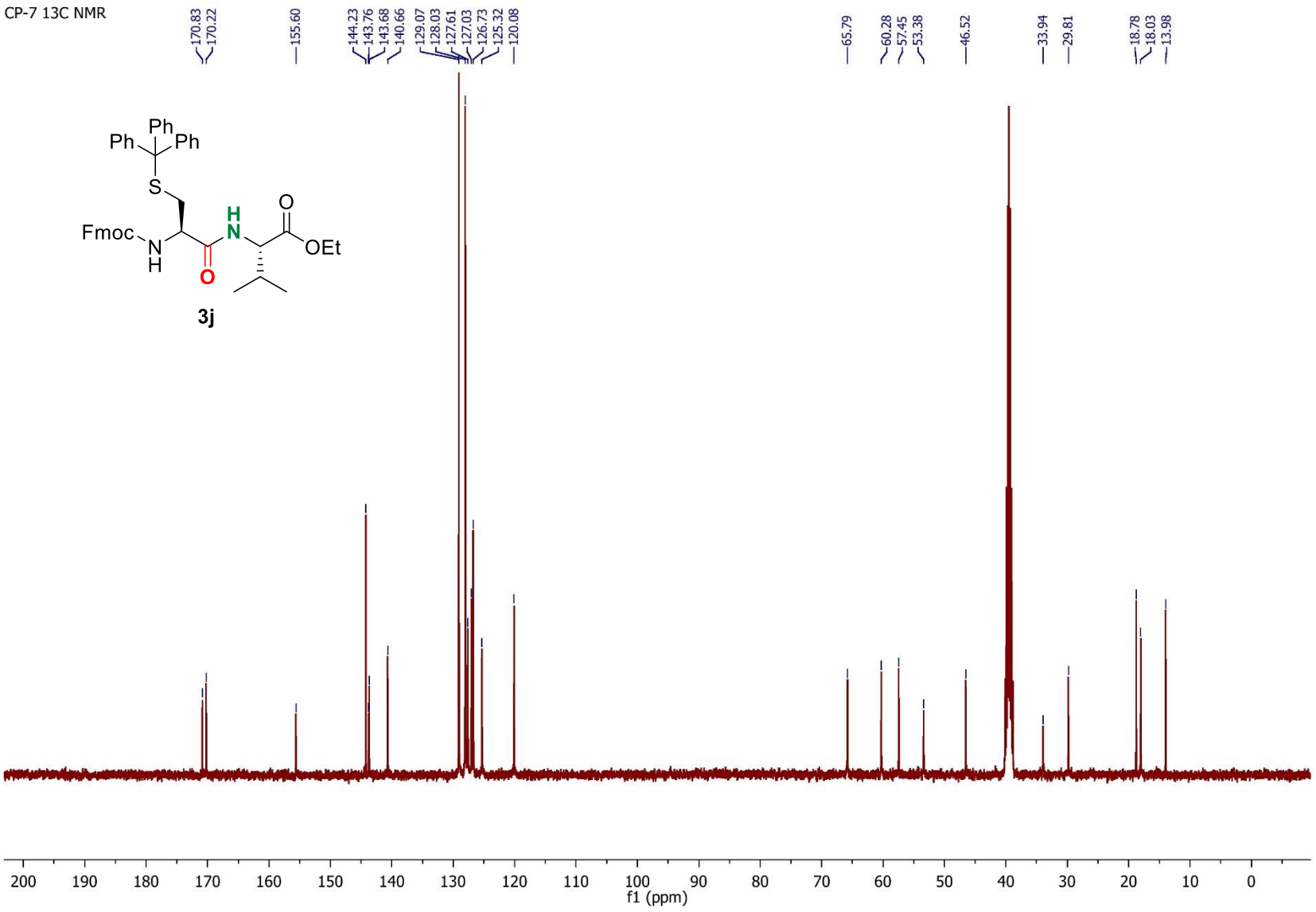


Figure S42. ^{13}C NMR Spectrum of **3j (101MHz, DMSO-d$_6$)**

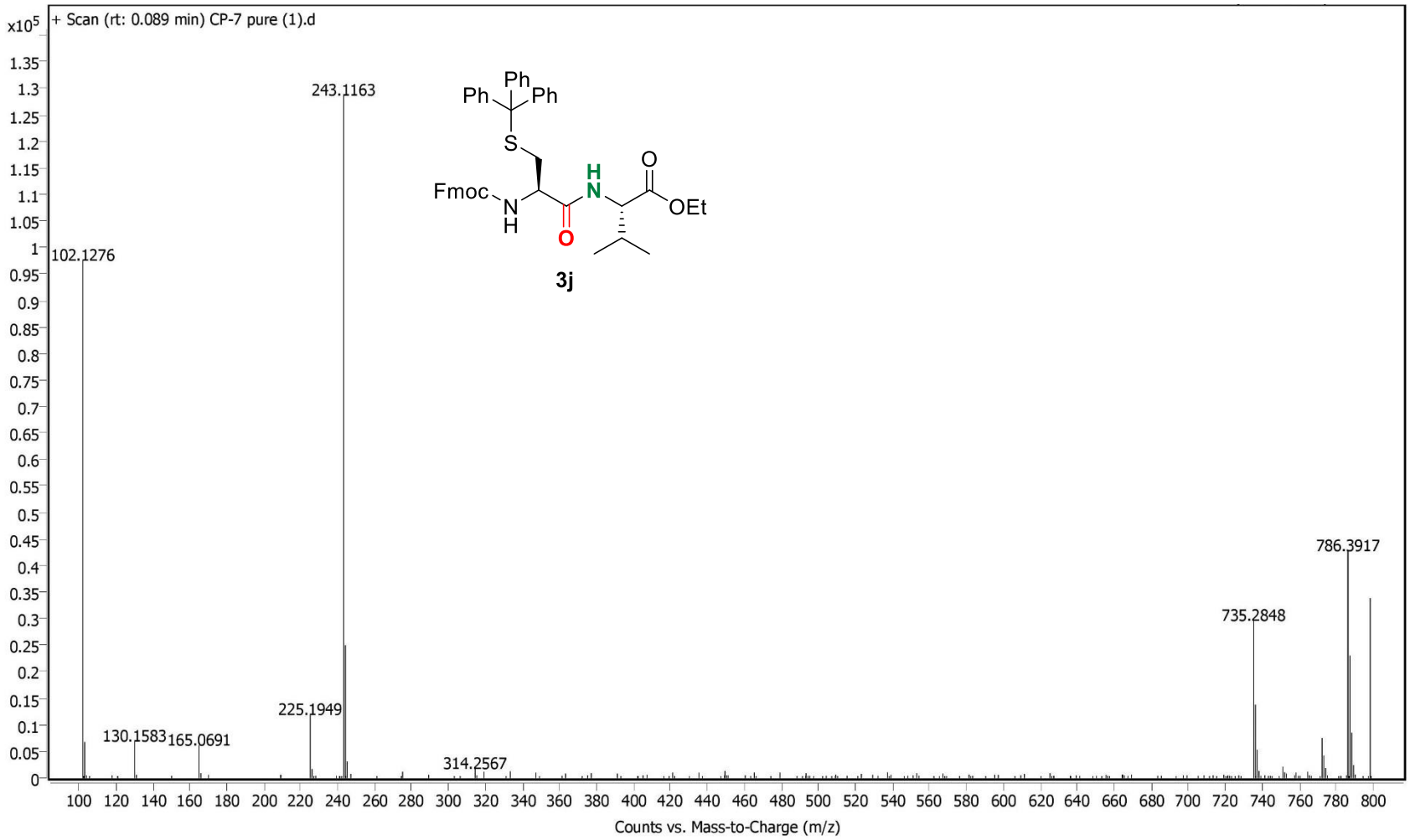


Figure S43. HRMS Spectrum of **3j**

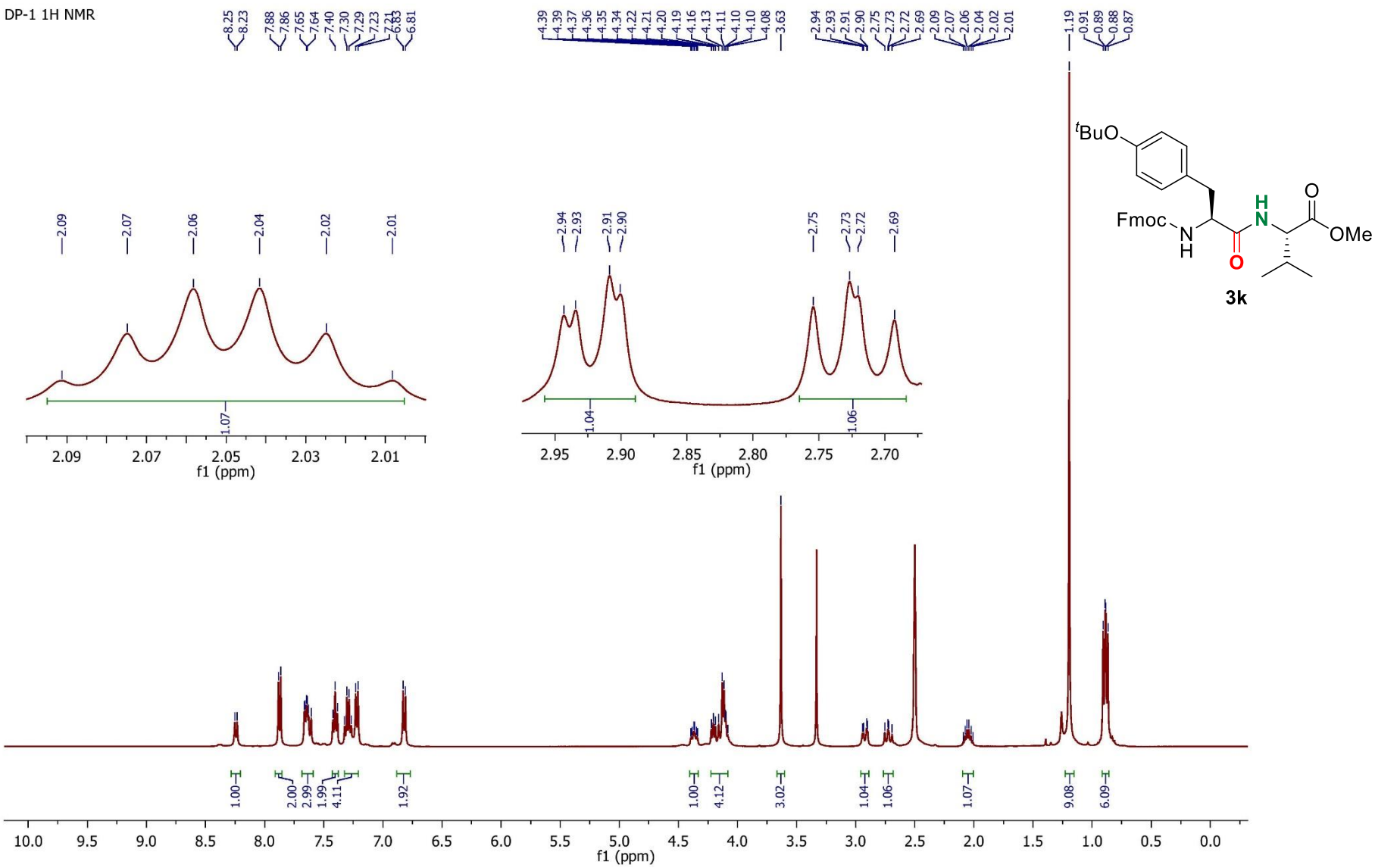


Figure S44. ^{1}H NMR Spectrum of **3k (400MHz, DMSO-d$_6$)**

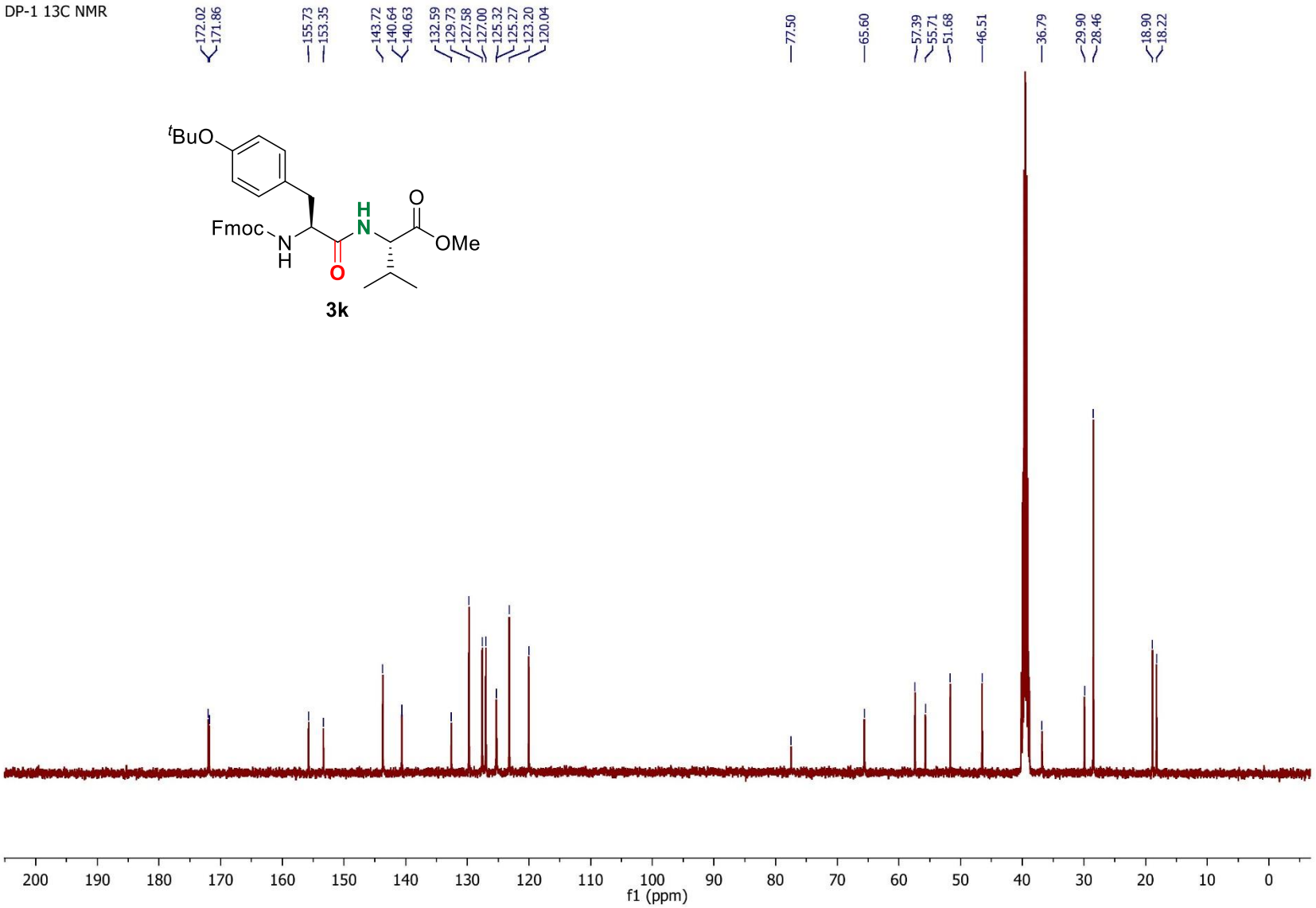


Figure S45. ^{13}C NMR Spectrum of **3k (101MHz, DMSO-d$_6$)**

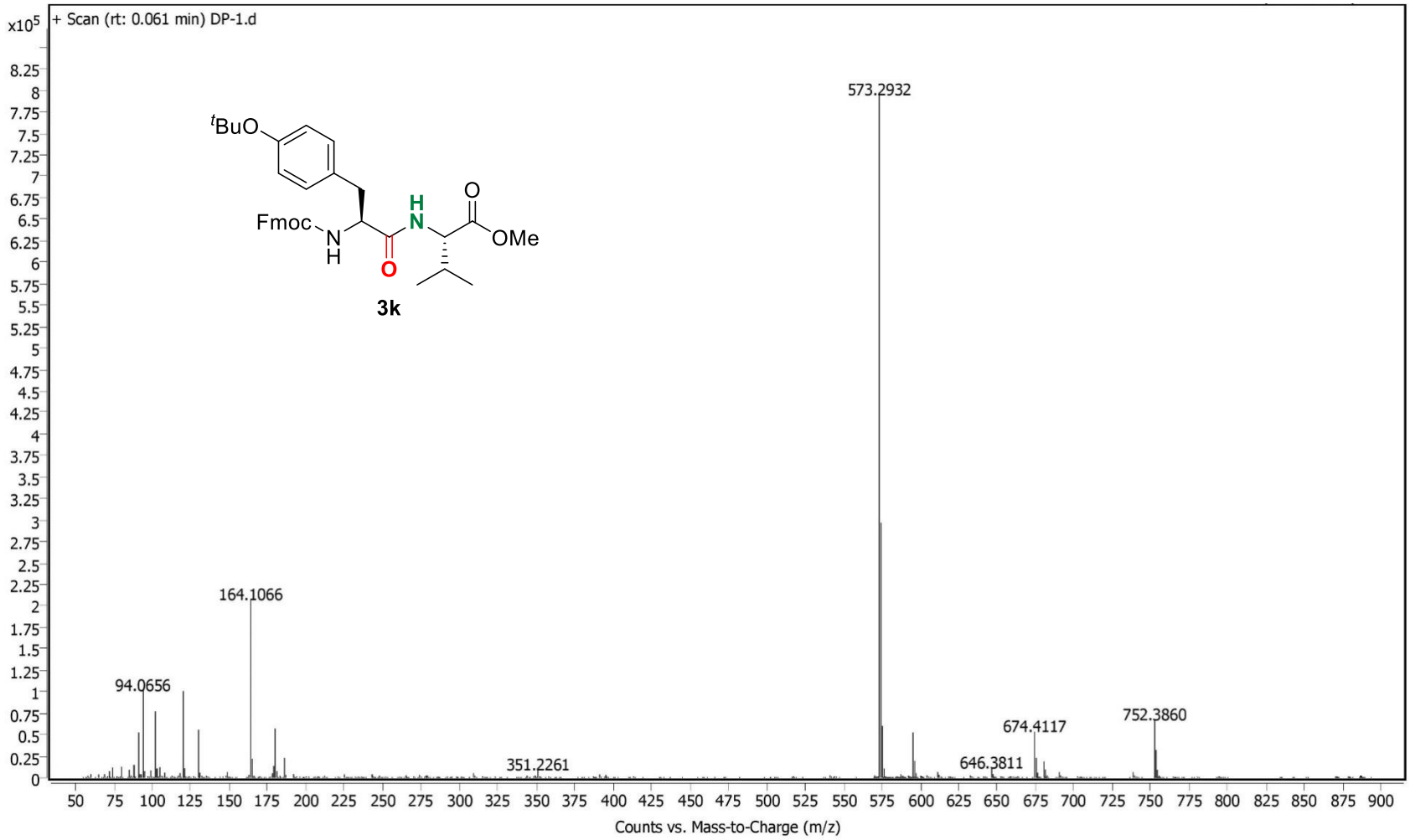


Figure S46. HRMS Spectrum of **3k**

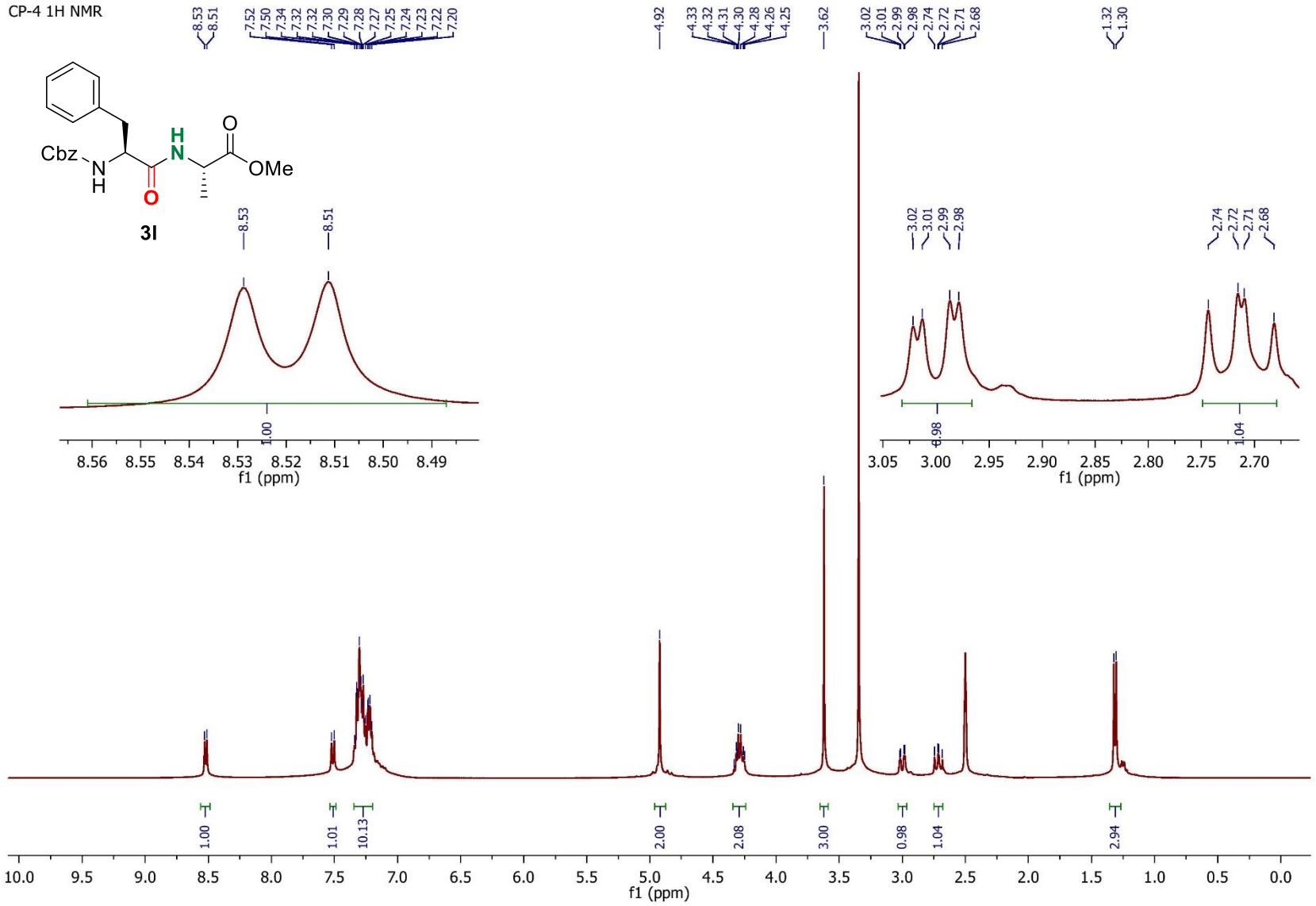


Figure S47. ^{1}H NMR Spectrum of **3l (400MHz, DMSO-d$_6$)**

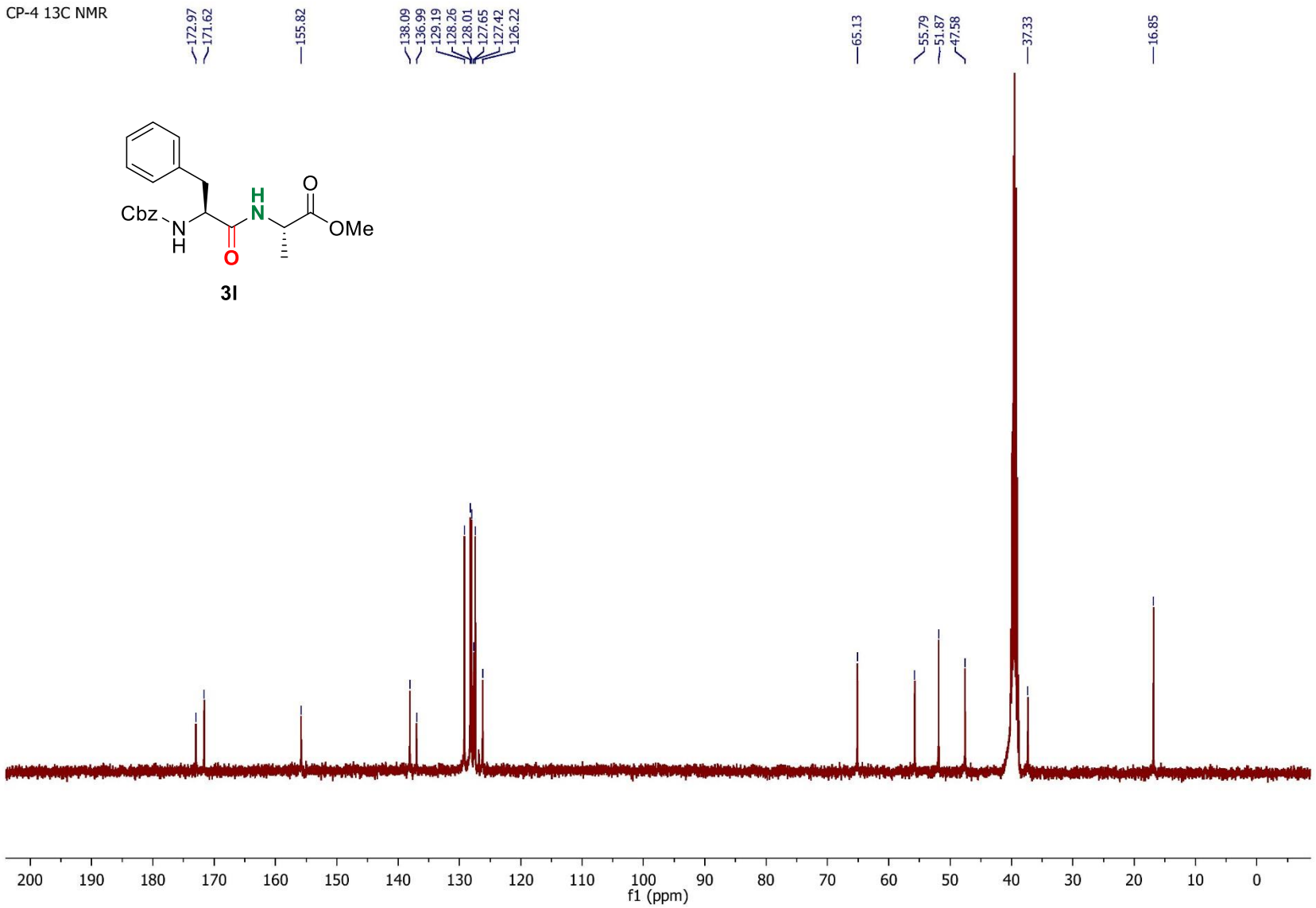


Figure S48. ^{13}C NMR Spectrum of **3l (101MHz, DMSO-d$_6$)**

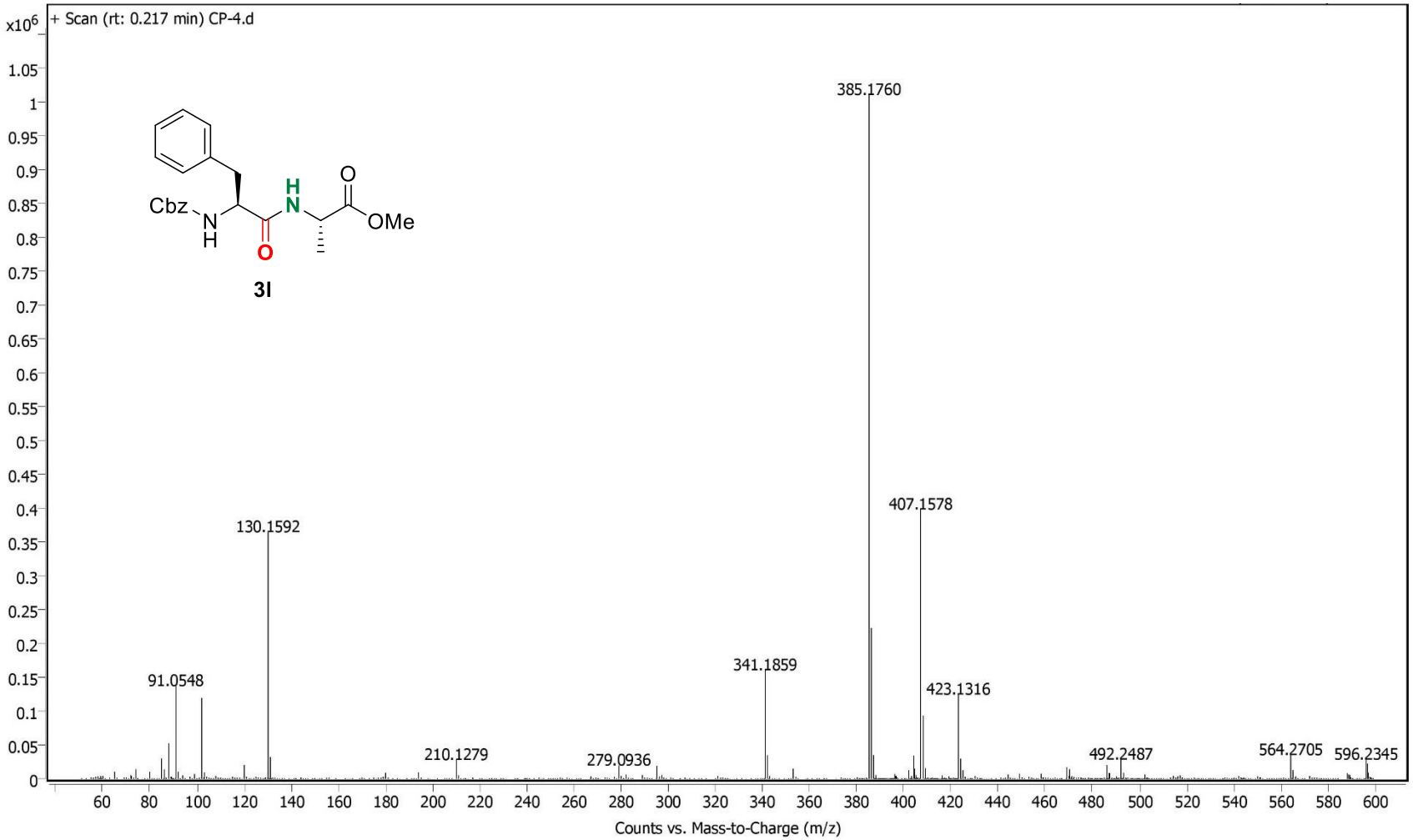


Figure S49. HRMS Spectrum of **3l**

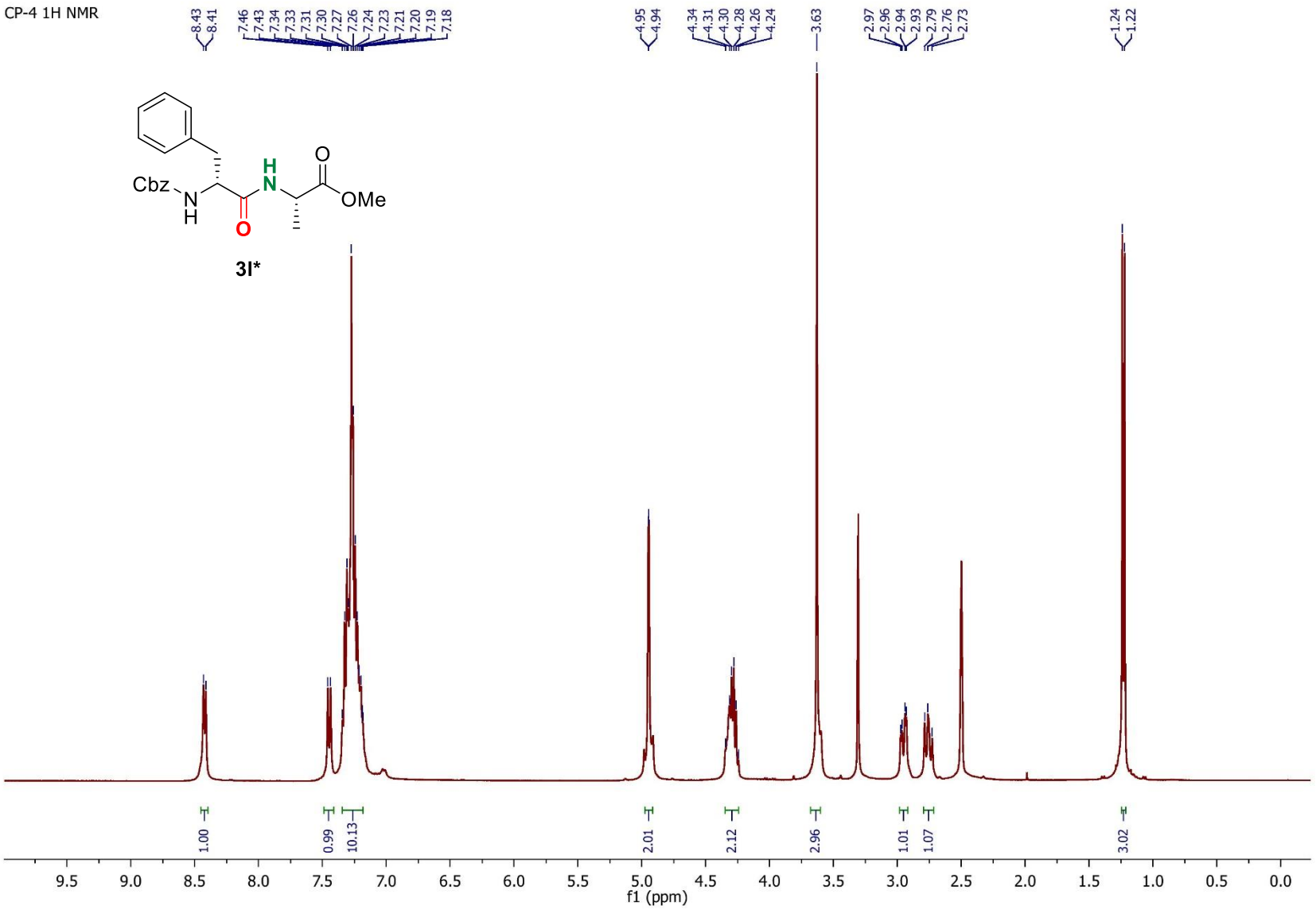


Figure S50. ^{1}H NMR Spectrum of **3l* (400MHz, DMSO-d$_6$)**

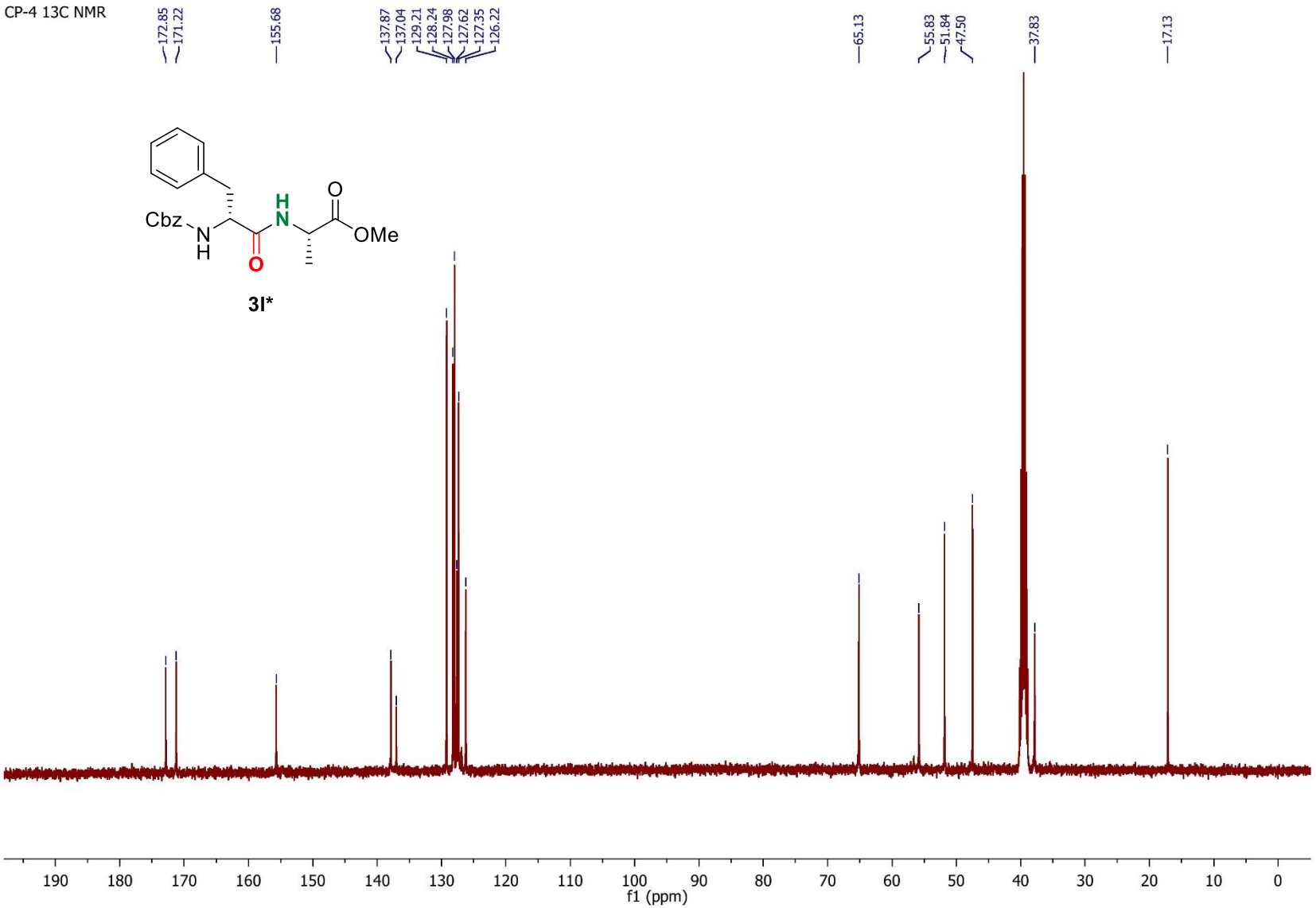


Figure S51. ^{13}C NMR Spectrum of **3l* (101MHz, DMSO-d$_6$)**

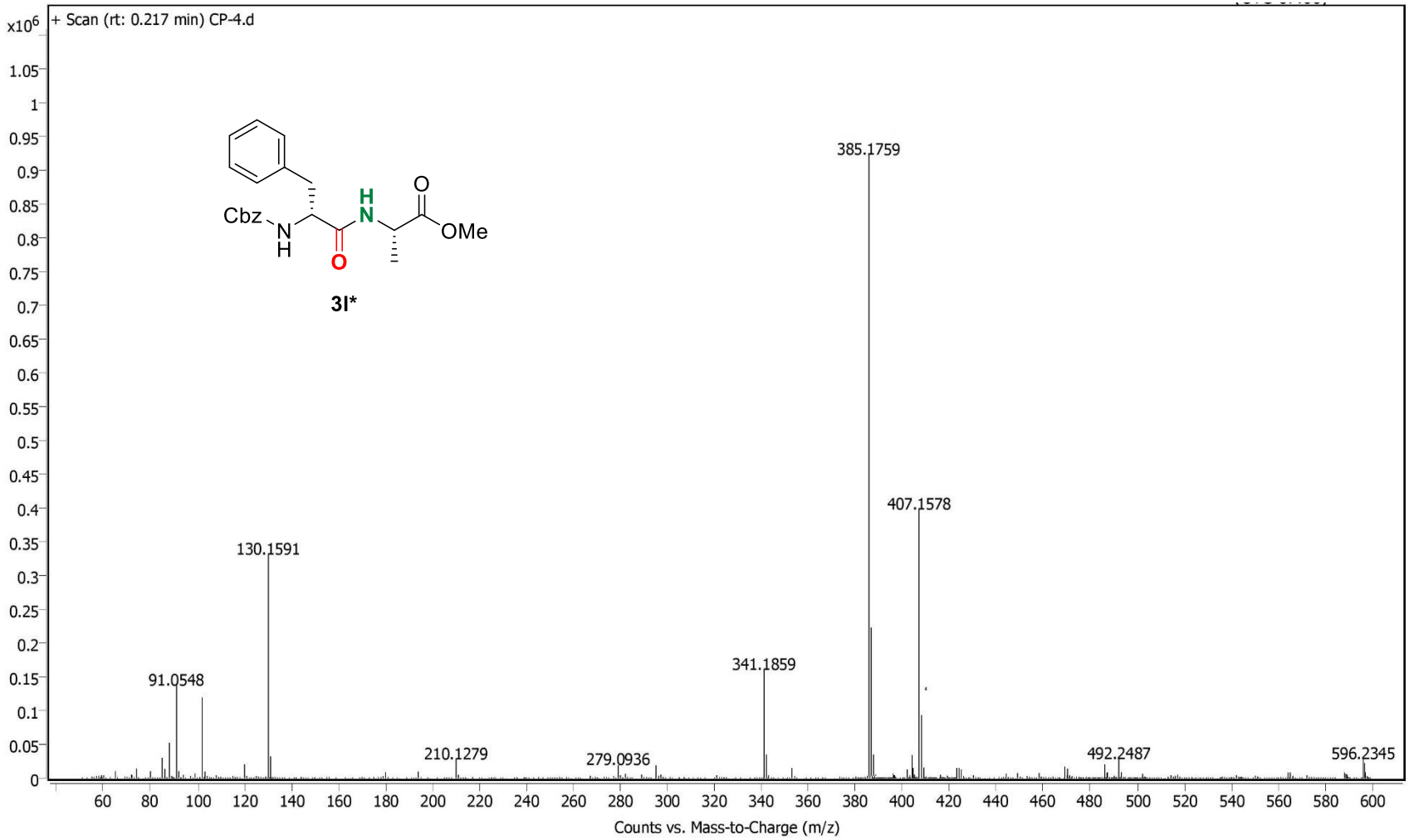


Figure S52. HRMS Spectrum of **3l***

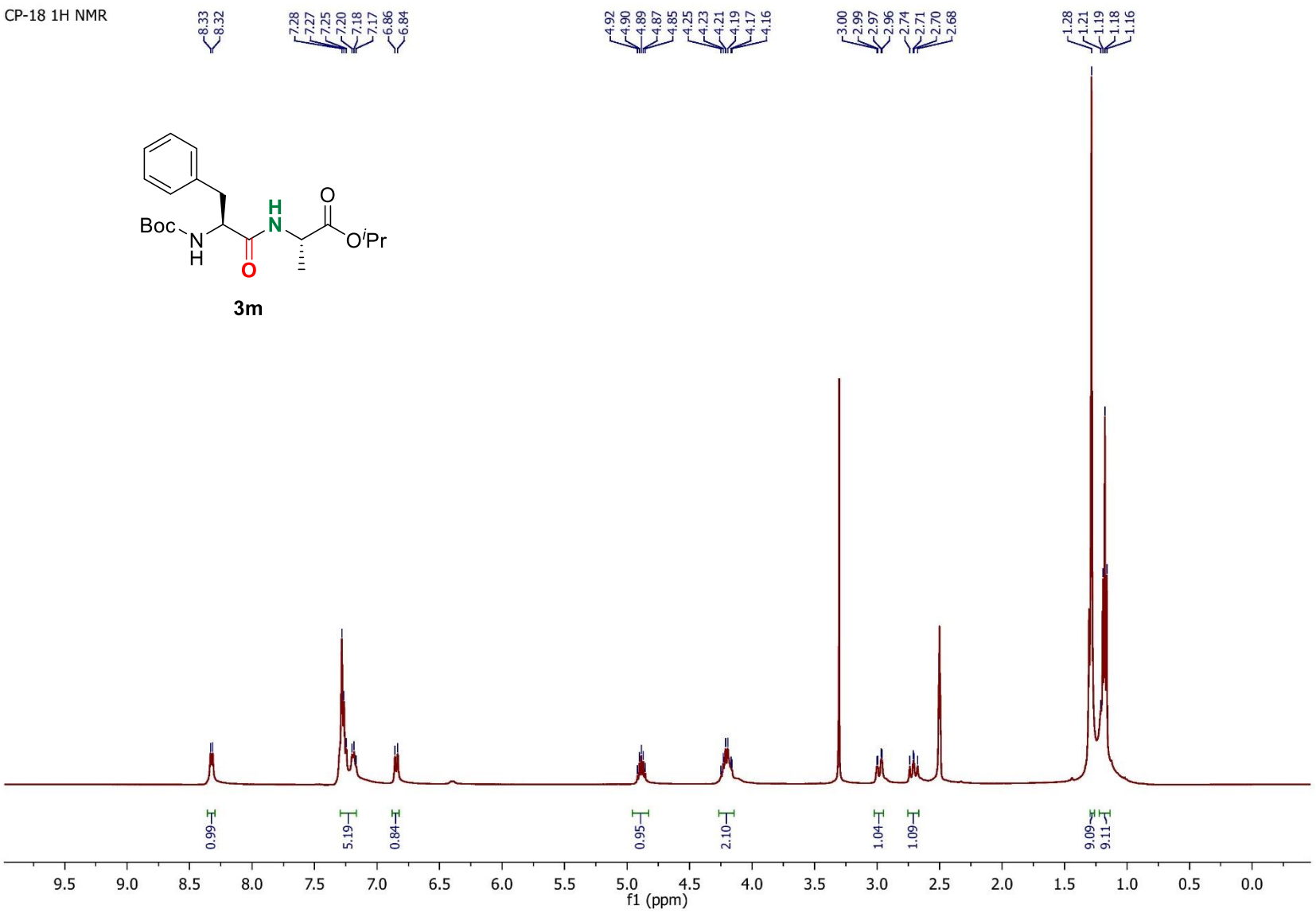


Figure S53. ^{1}H NMR Spectrum of **3m (400MHz, DMSO-d$_6$)**

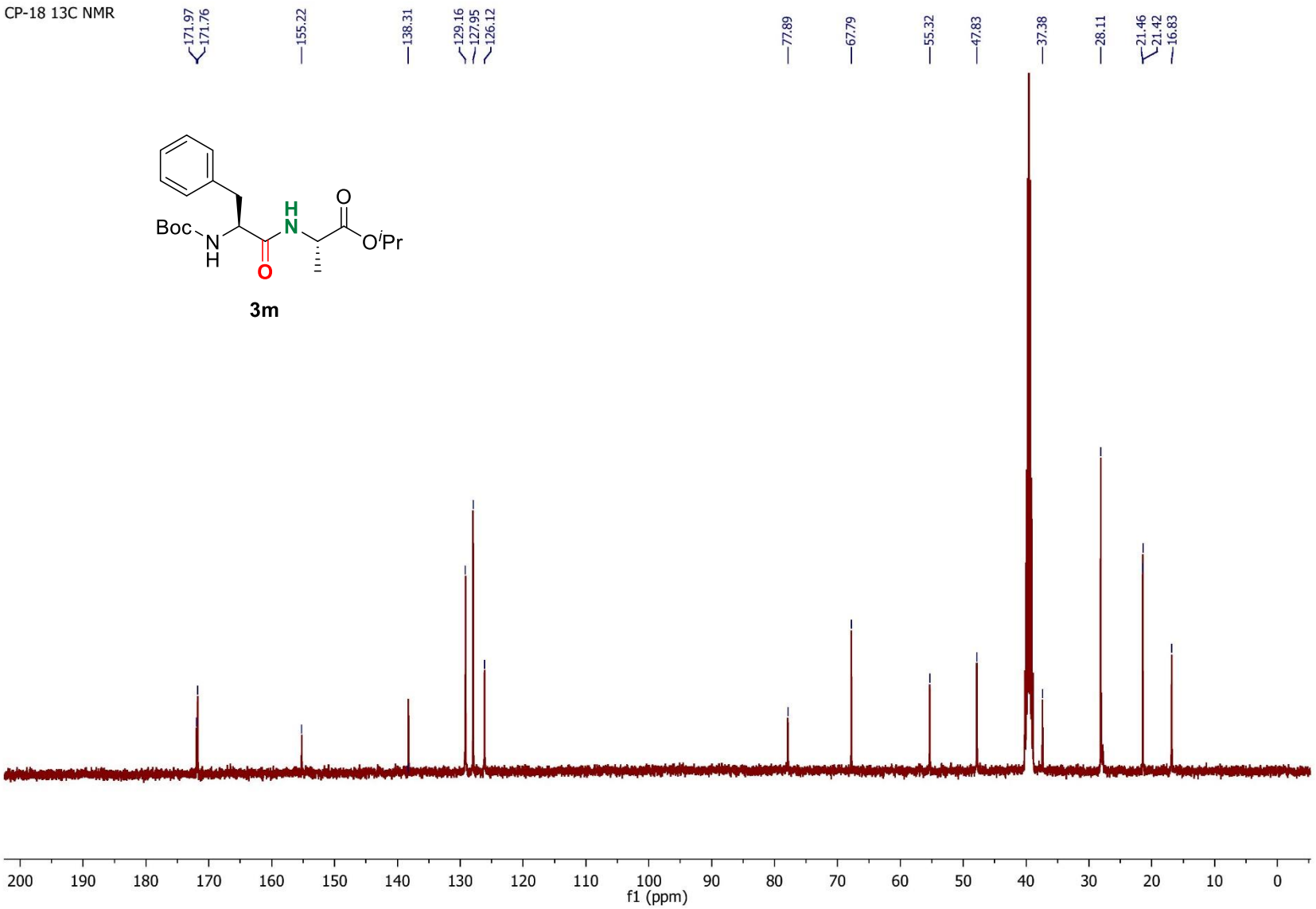


Figure S54. ^{13}C NMR Spectrum of **3m (101MHz, DMSO-d$_6$)**

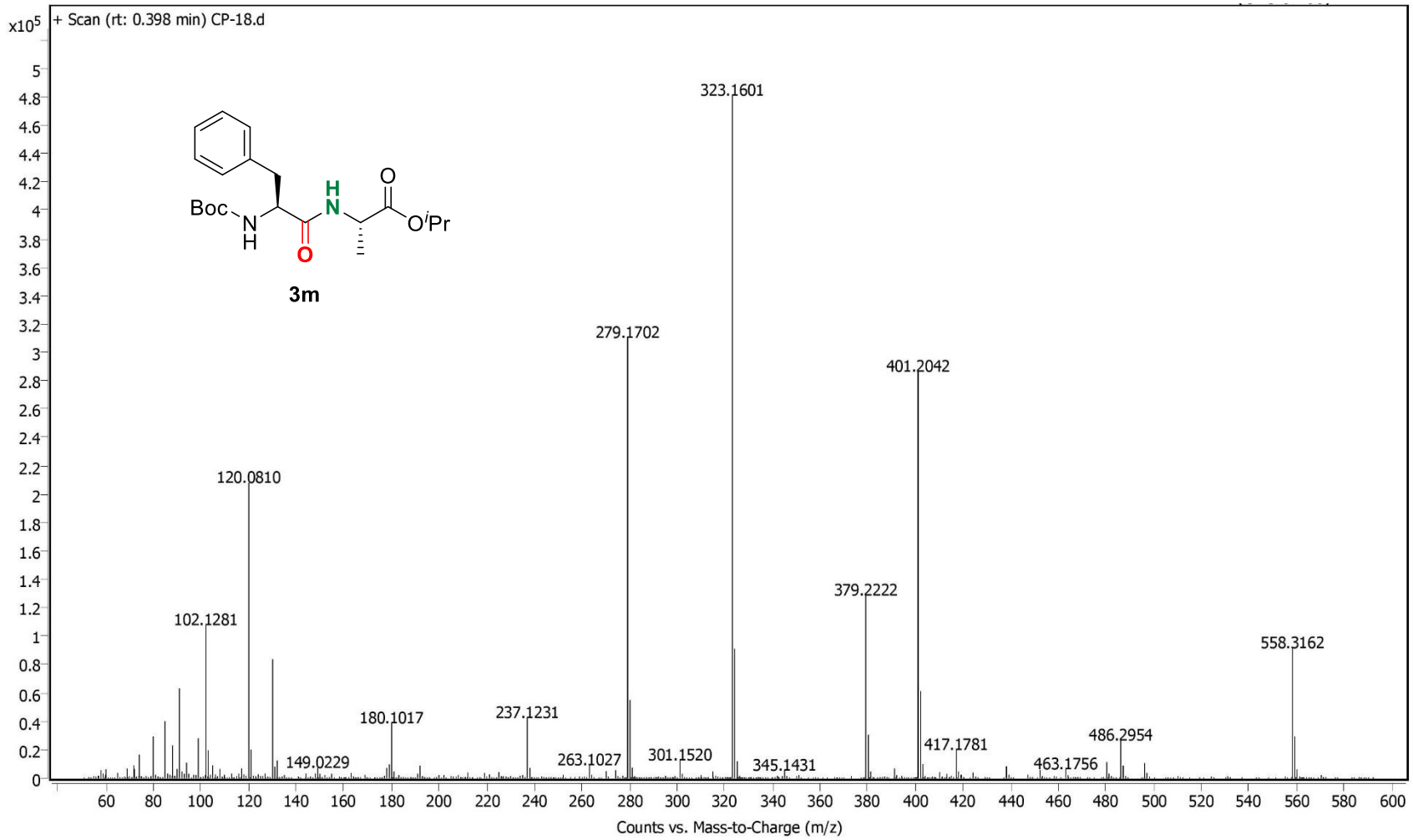


Figure S55. HRMS Spectrum of **3m**

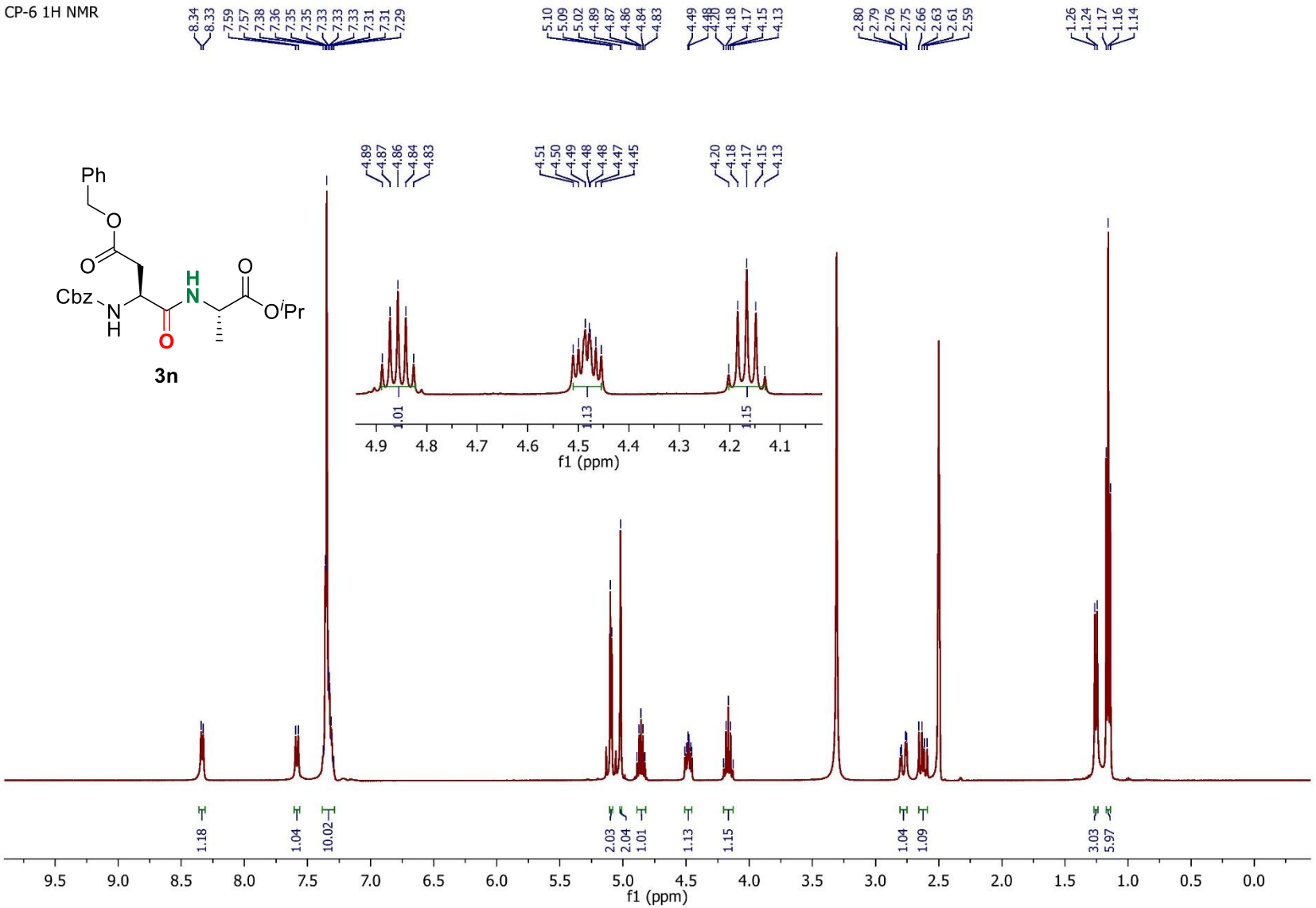


Figure S56. ^{1}H NMR Spectrum of **3n (400MHz, DMSO-d$_6$)**

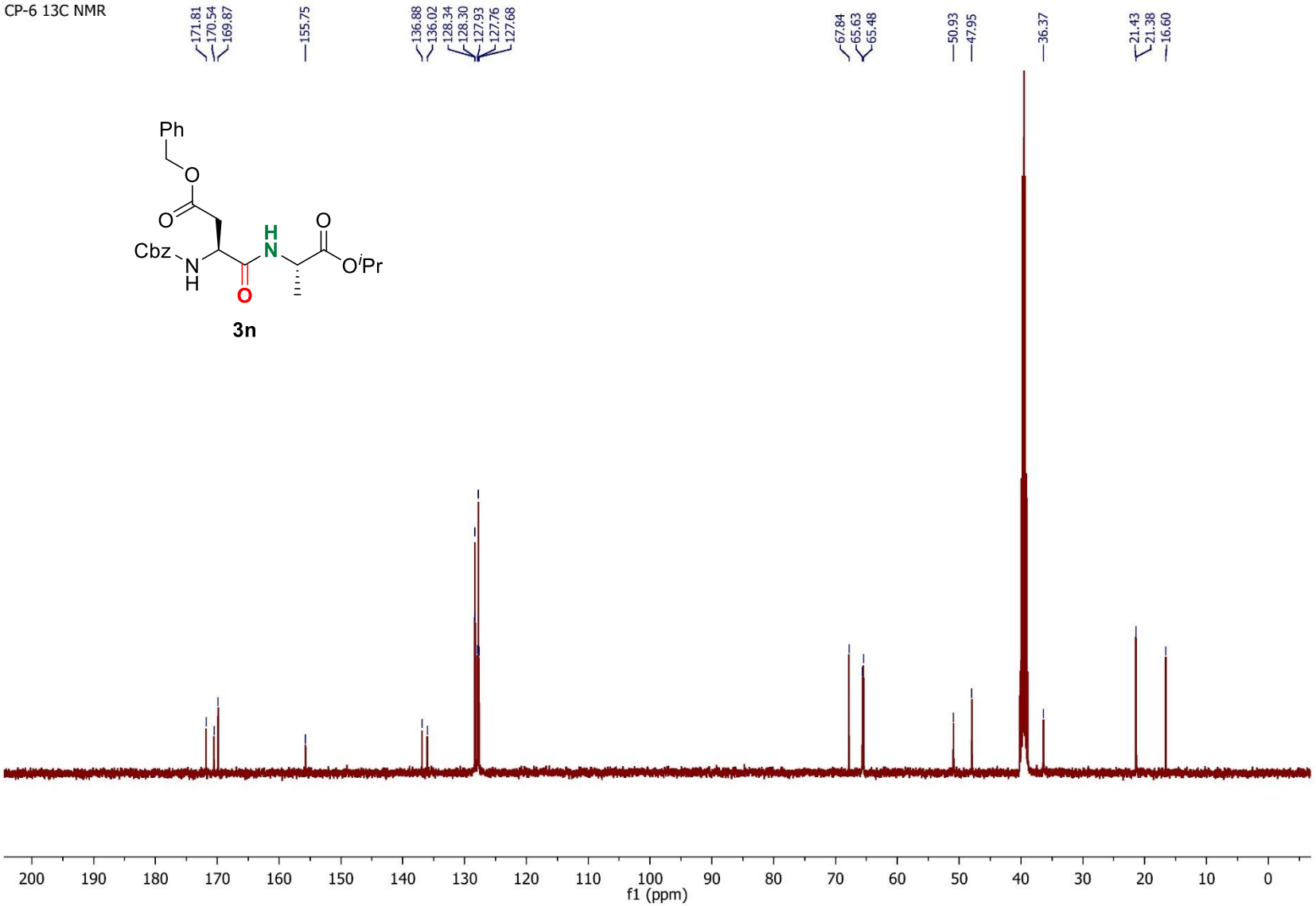


Figure S57. ^{13}C NMR Spectrum of **3n (101MHz, DMSO-d$_6$)**

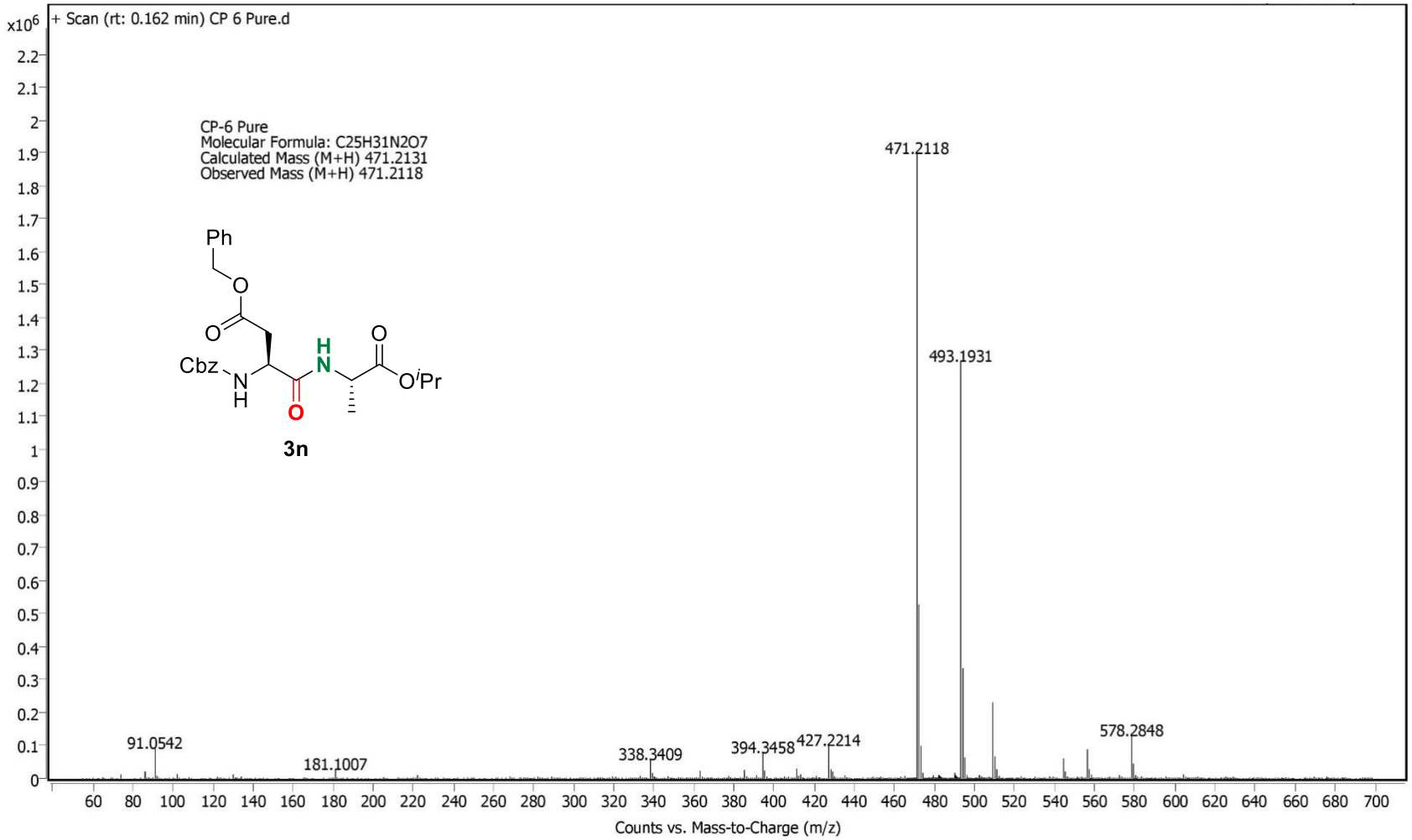


Figure S58. HRMS Spectrum of **3n**

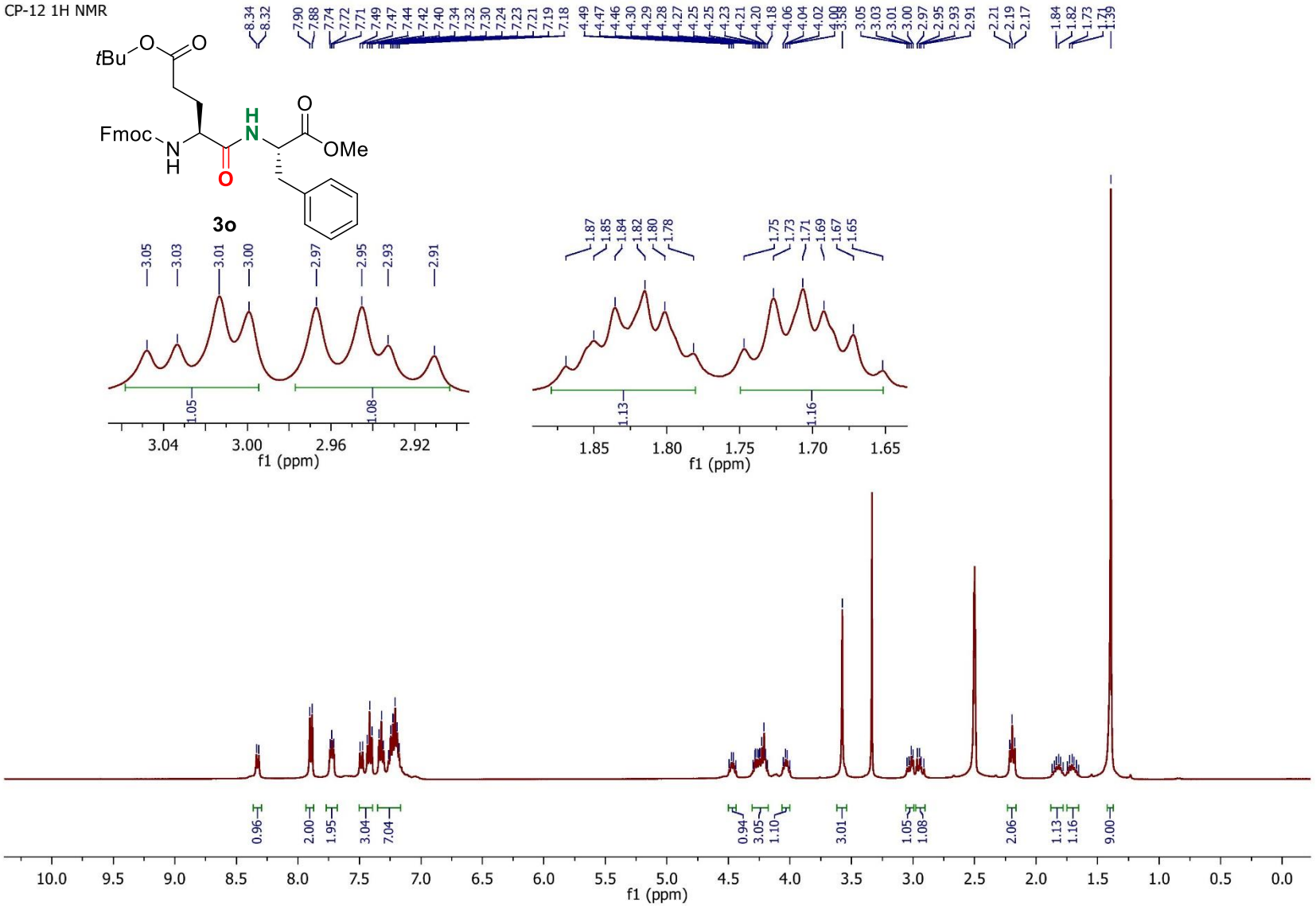


Figure S59. ^{1}H NMR Spectrum of **3o (400MHz, DMSO-d$_6$)**

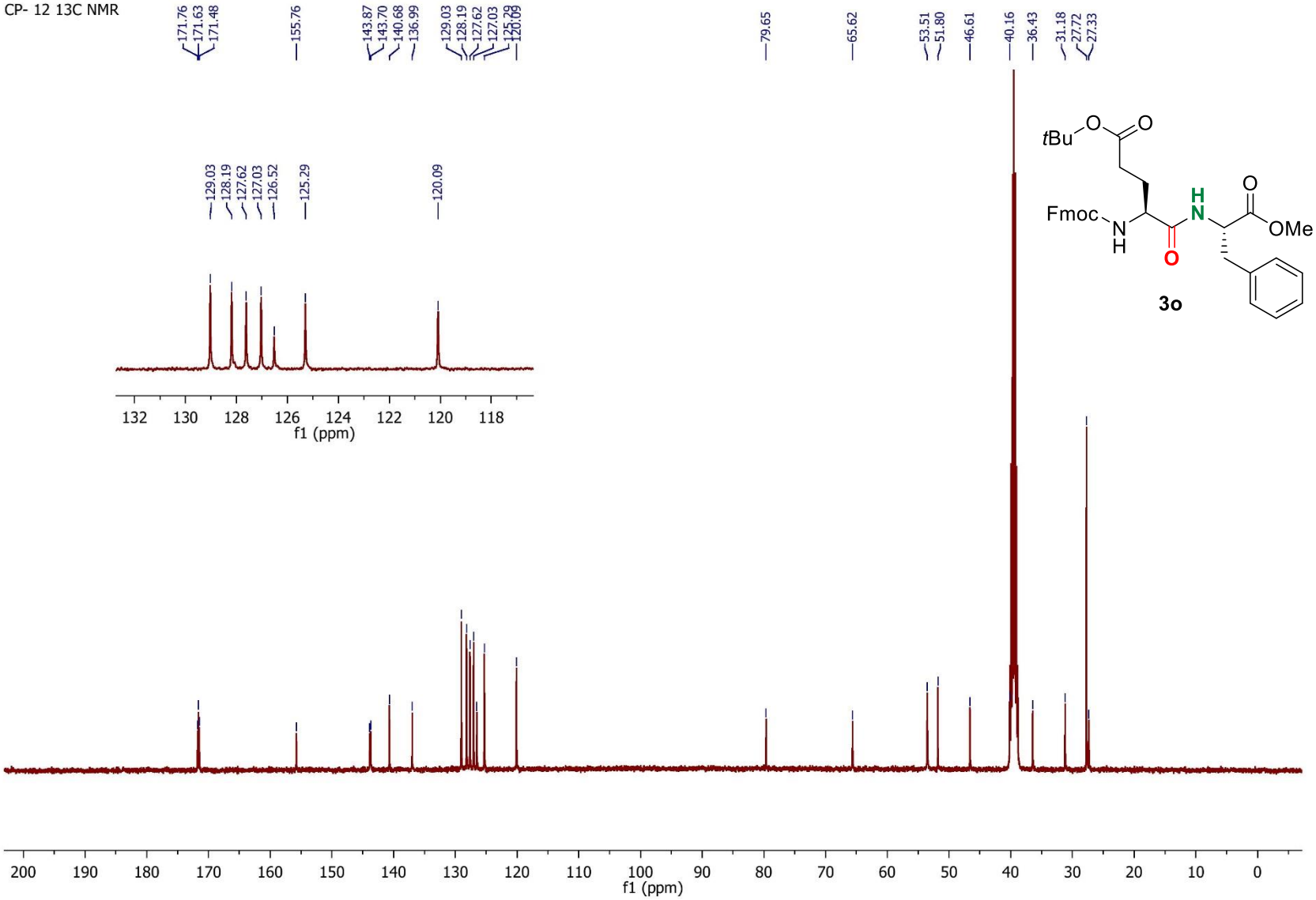


Figure S60. ^{13}C NMR Spectrum of **3o (101MHz, DMSO-d$_6$)**

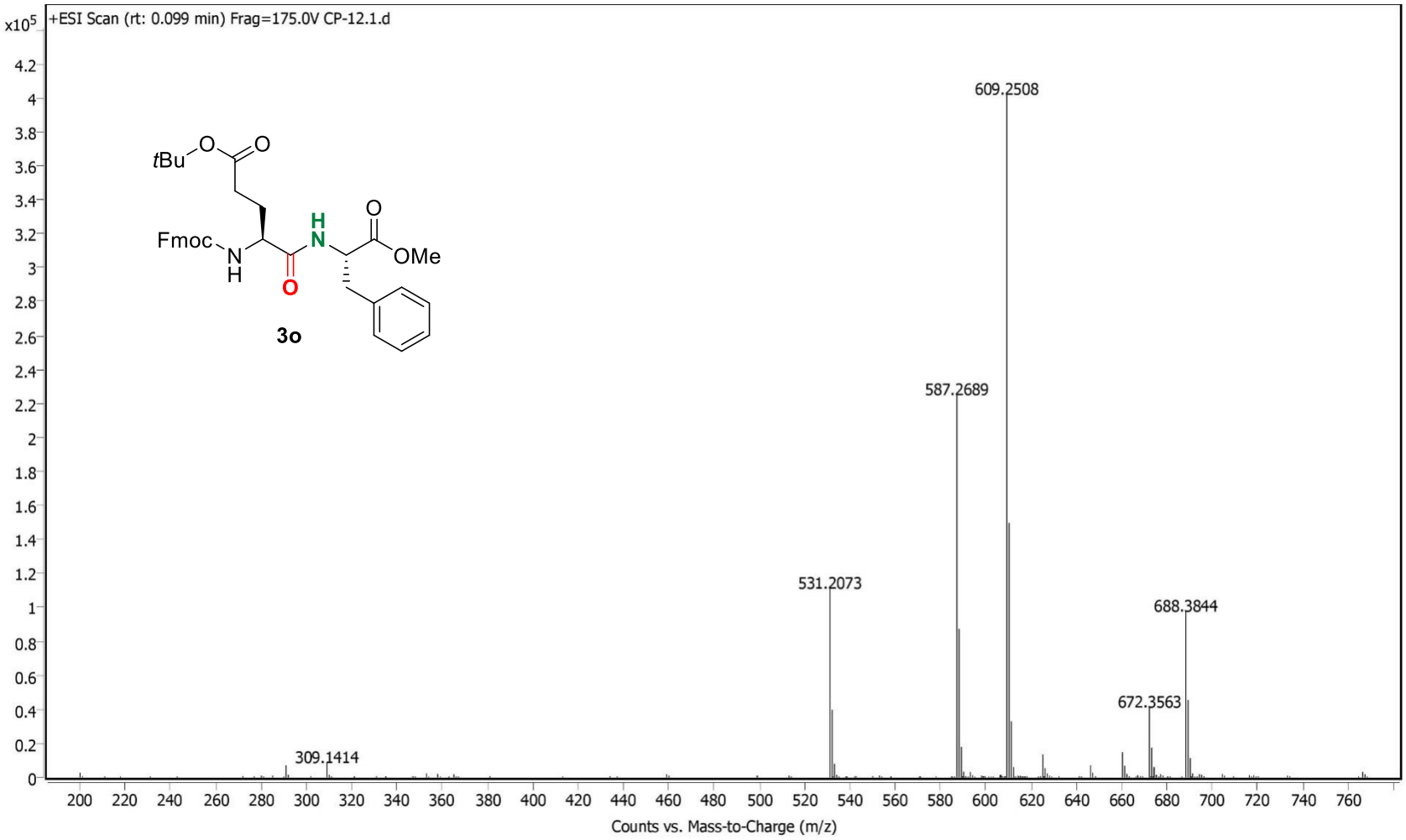


Figure S61. HRMS Spectrum of **3o**

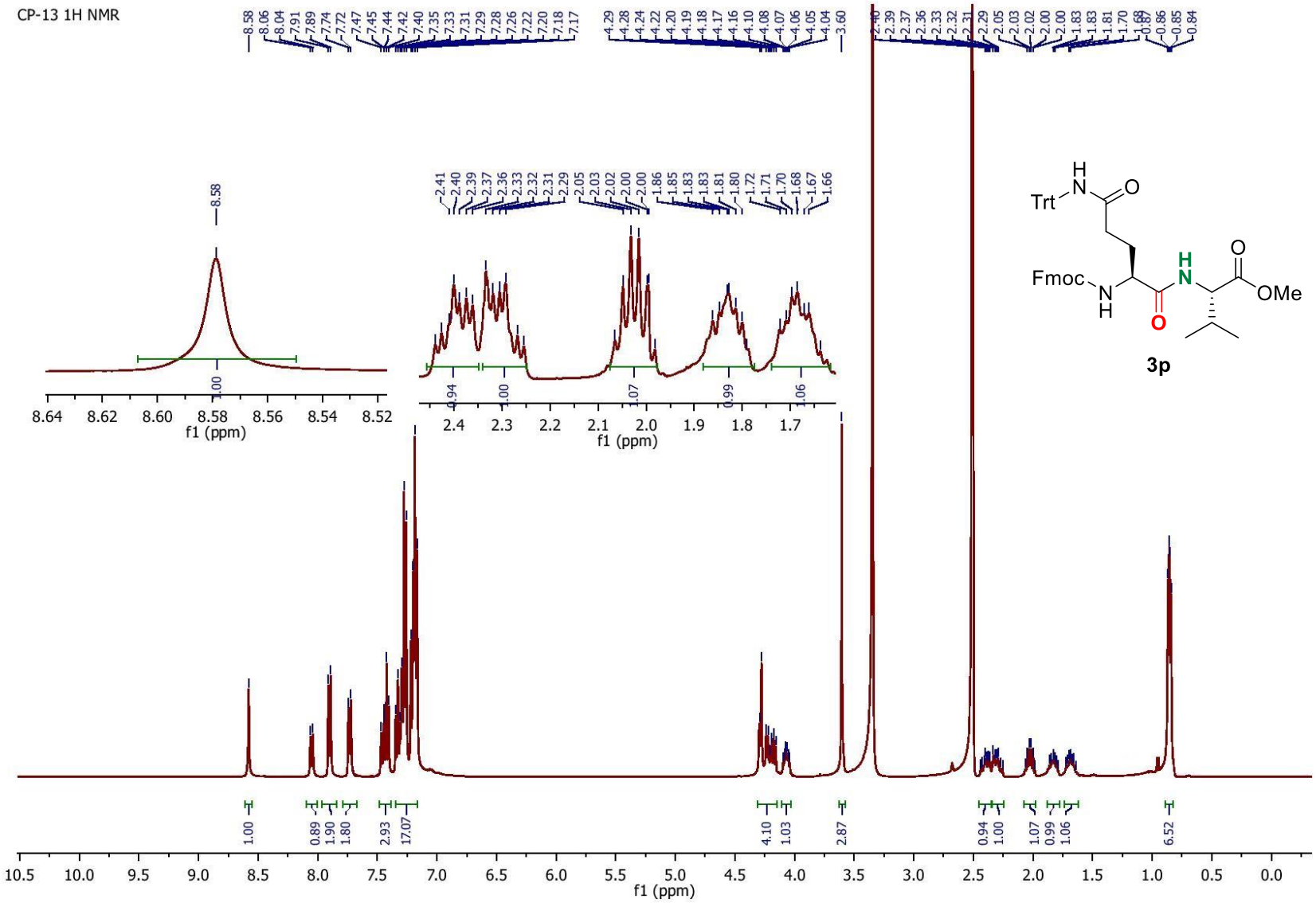


Figure S62. ^{1}H NMR Spectrum of **3p (400MHz, DMSO-d$_6$)**

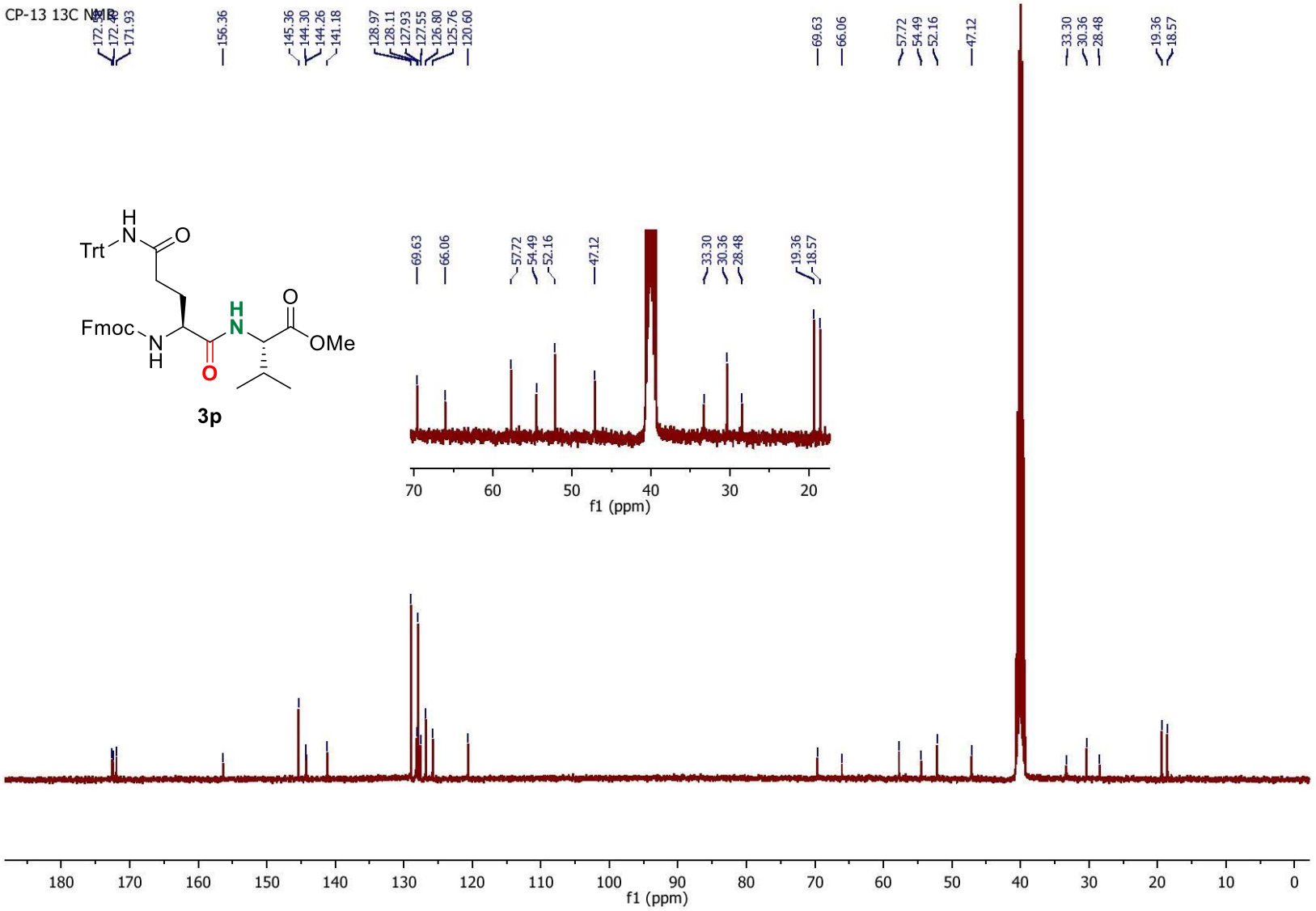


Figure S63. ^{13}C NMR Spectrum of **3p (101MHz, DMSO-d$_6$)**

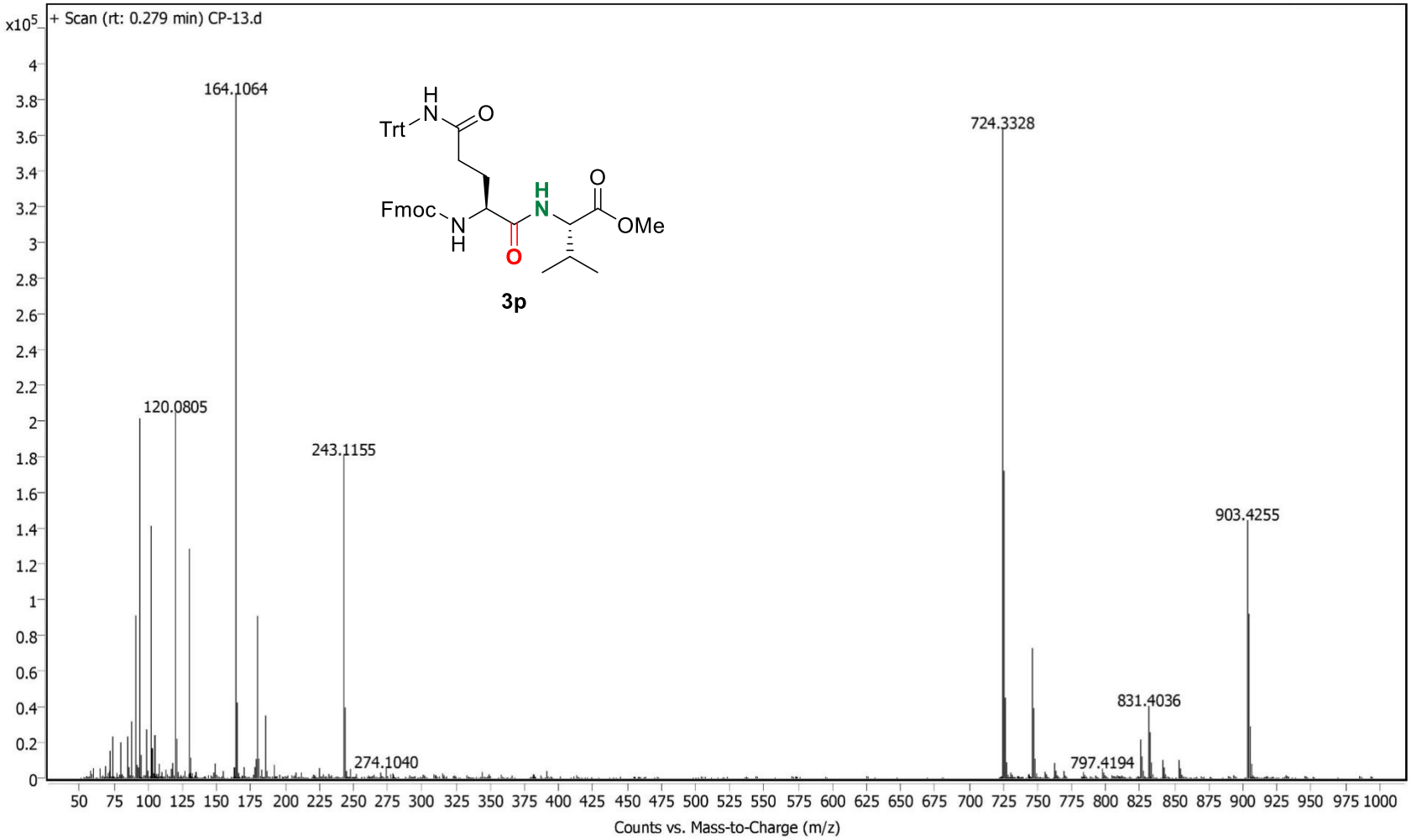


Figure S64. HRMS Spectrum of **3p**

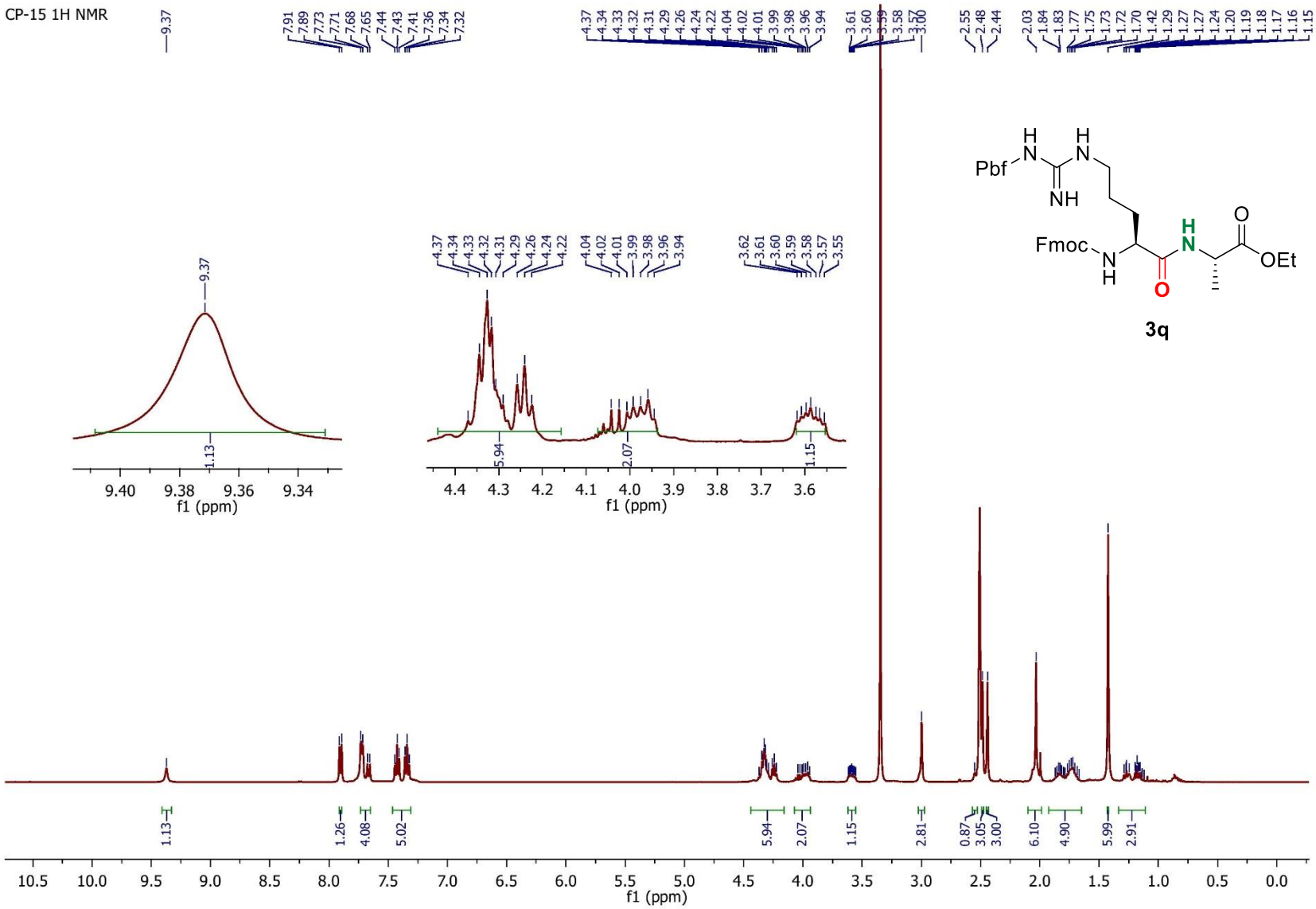


Figure S65. ^{1}H NMR Spectrum of **3q (400MHz, DMSO-d$_6$)**

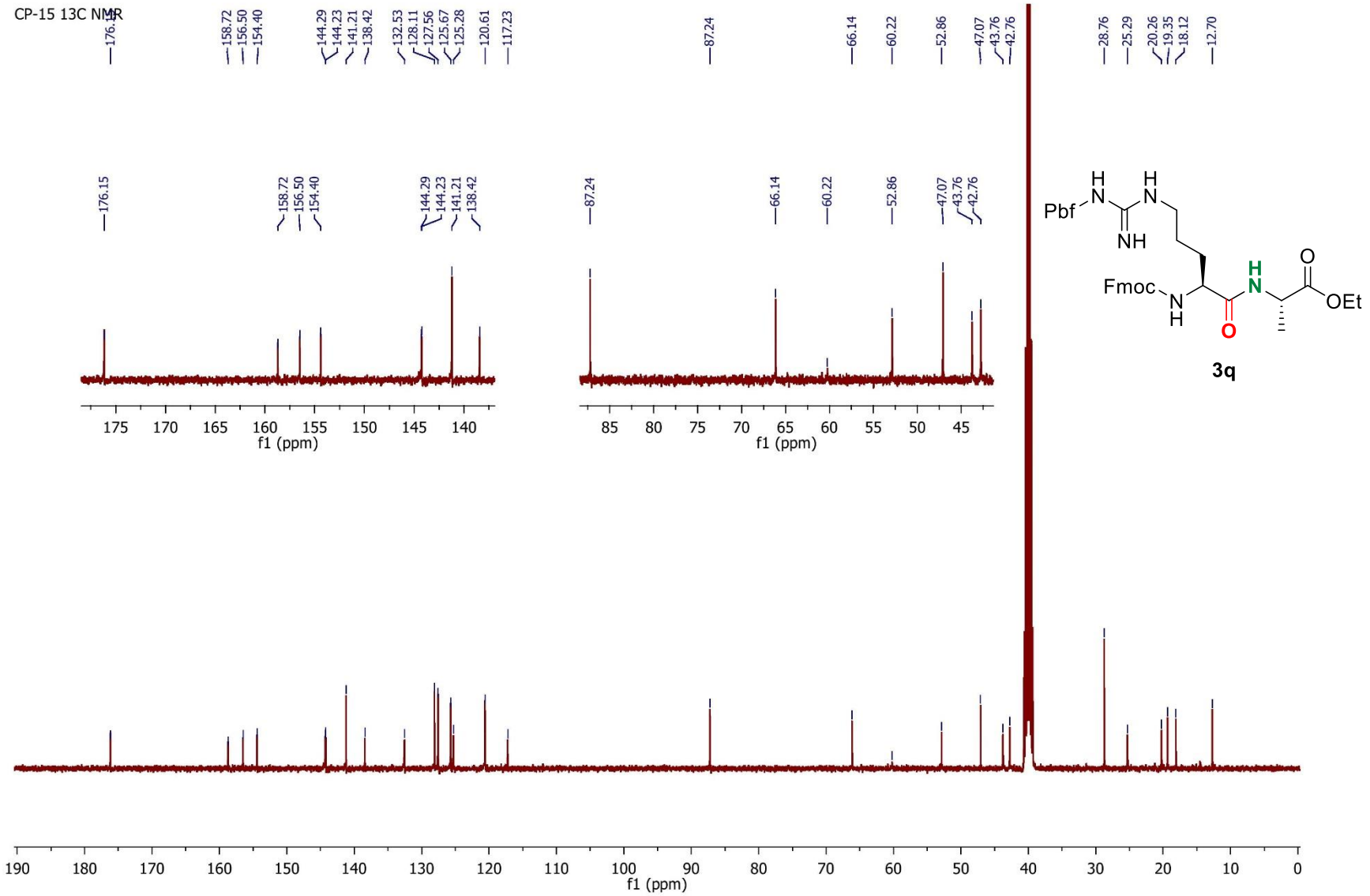


Figure S66. ^{13}C NMR Spectrum of **3q (101MHz, DMSO-d$_6$)**

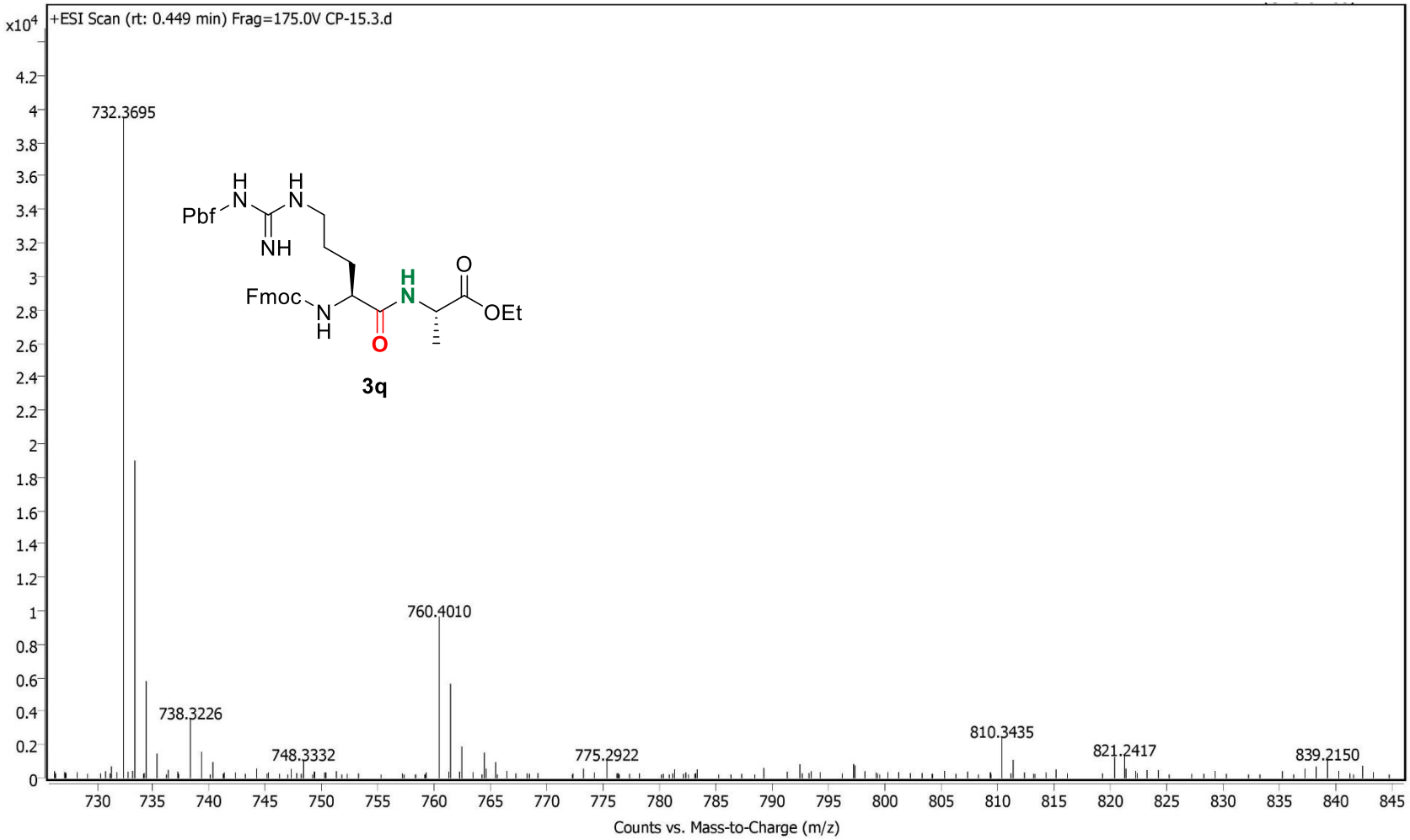


Figure S67. HRMS Spectrum of **3q**

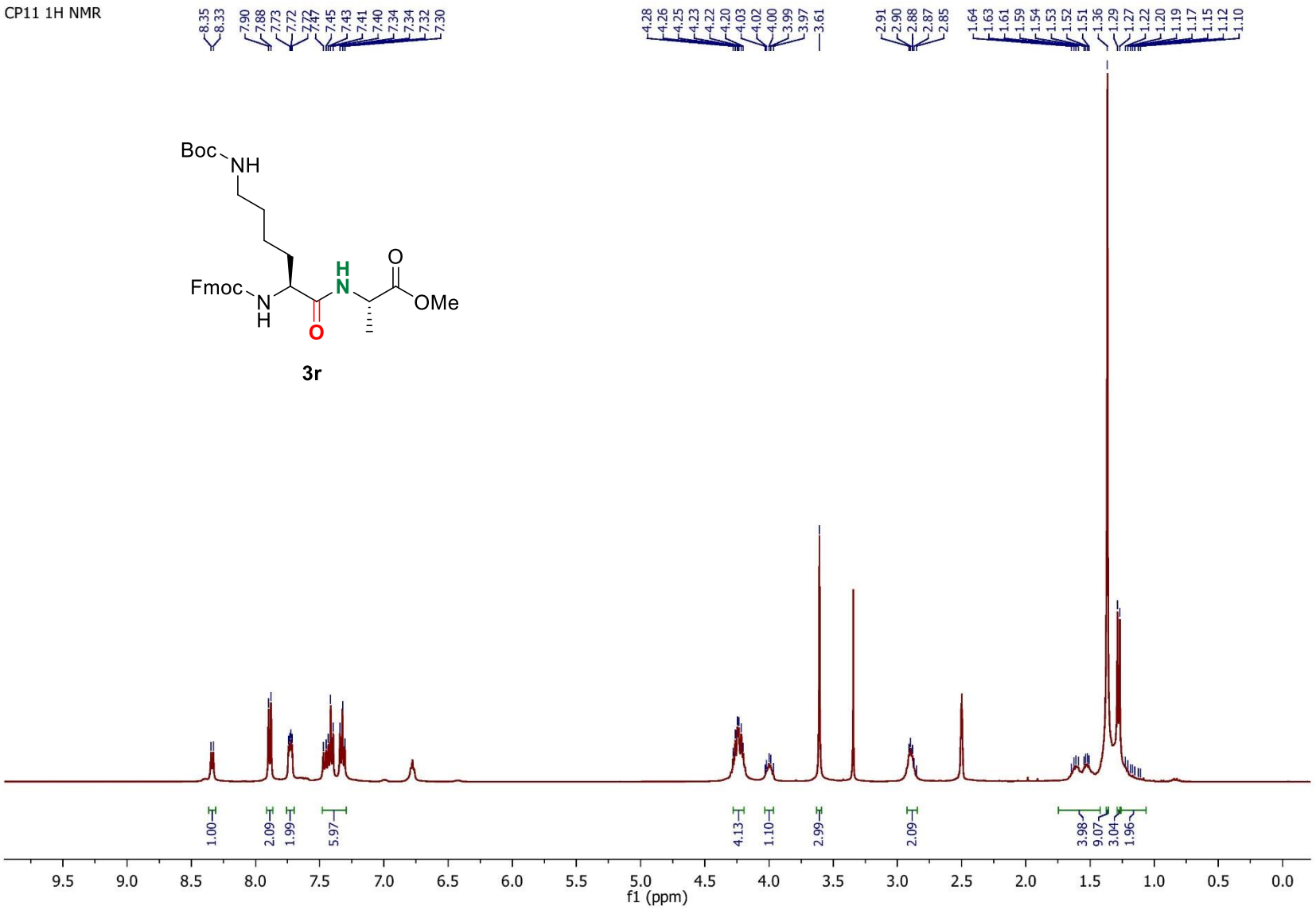


Figure S68. ^{1}H NMR Spectrum of **3r (400MHz, DMSO-d$_6$)**

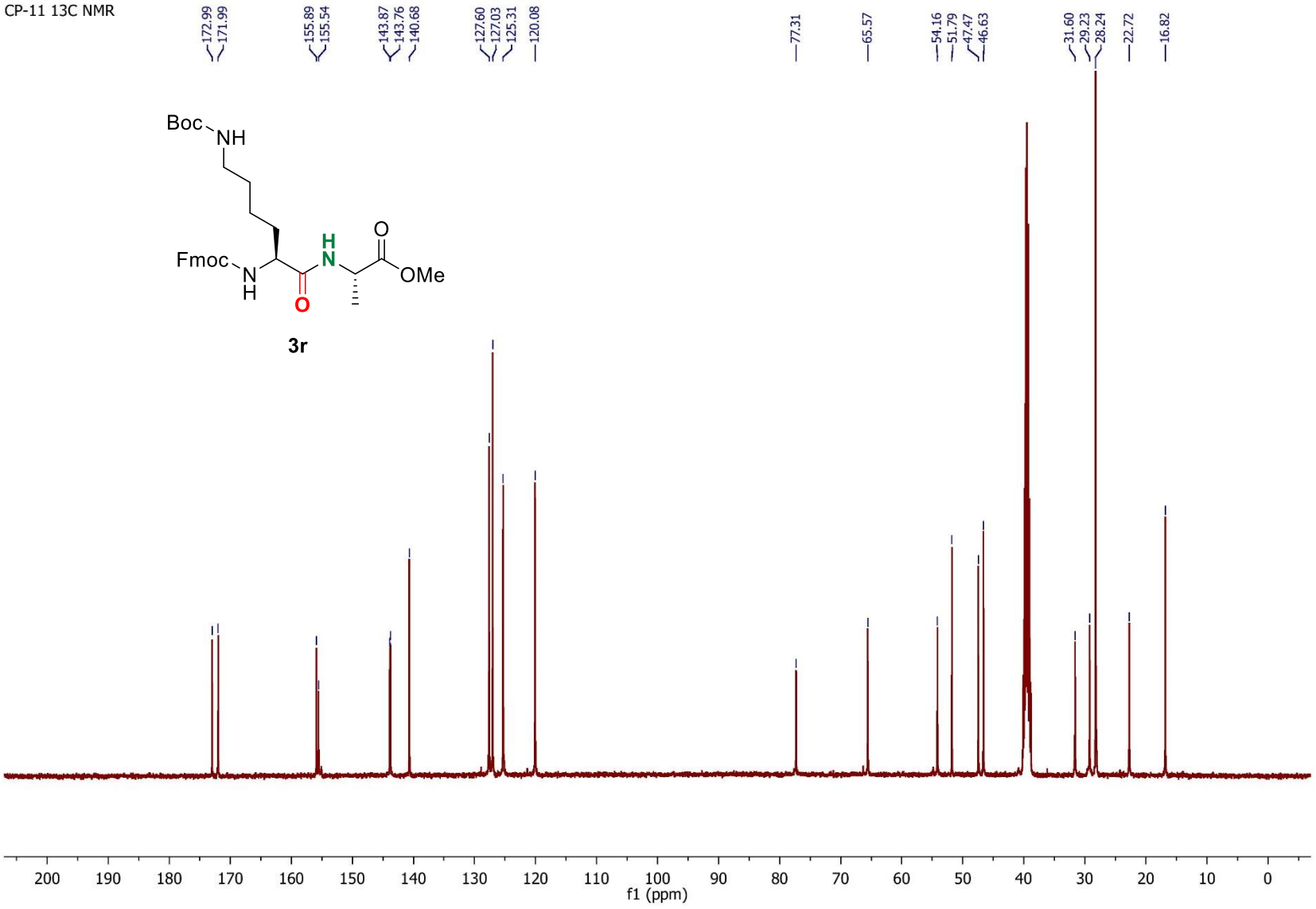


Figure S69. ^{13}C NMR Spectrum of **3r (101MHz, DMSO-d$_6$)**

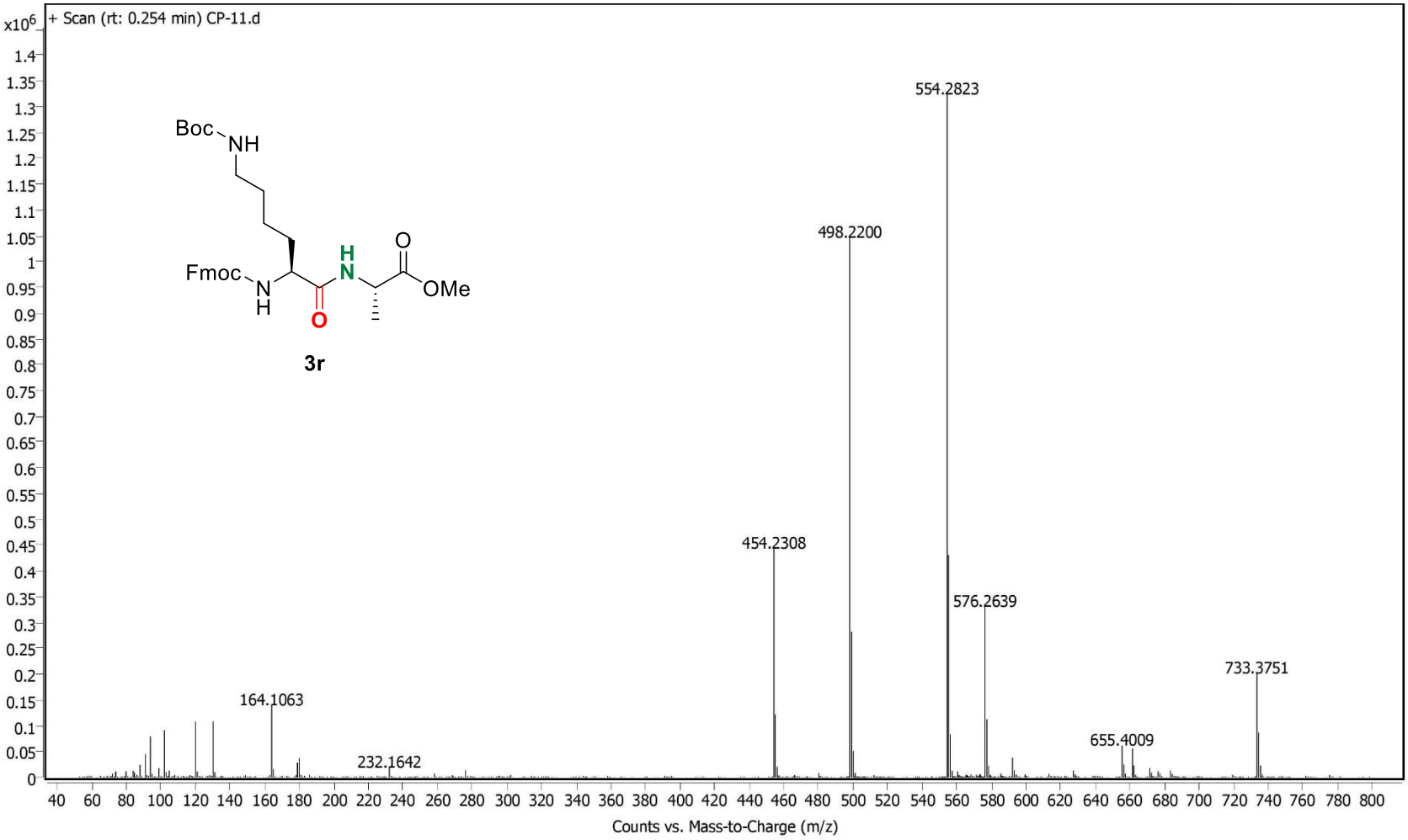


Figure S70. HRMS Spectrum of **3r**

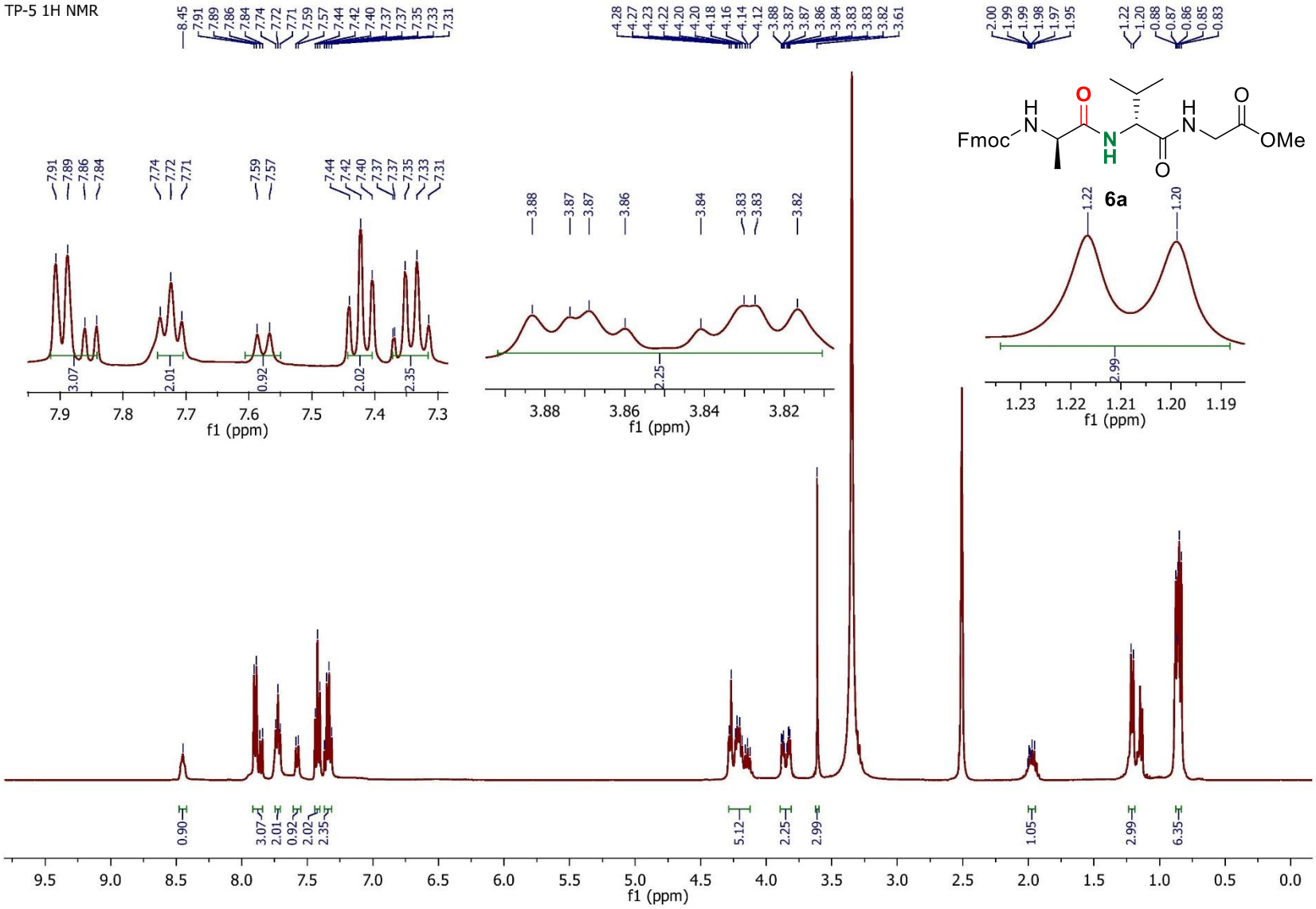


Figure S71. ^{1}H NMR Spectrum of **6a (400MHz, DMSO-d$_6$)**

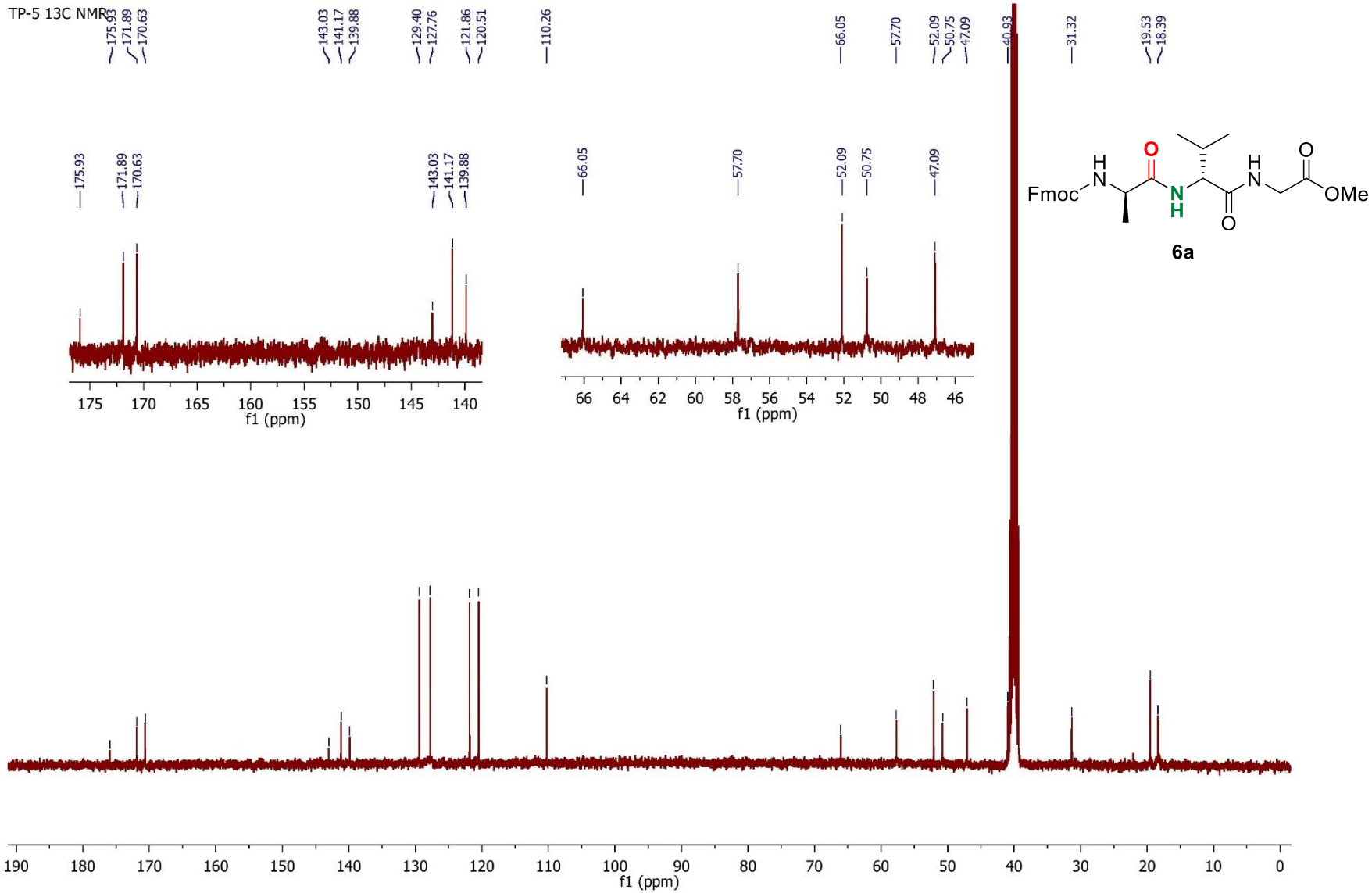


Figure S72. ^{13}C NMR Spectrum of **(101MHz, DMSO-d$_6$)**

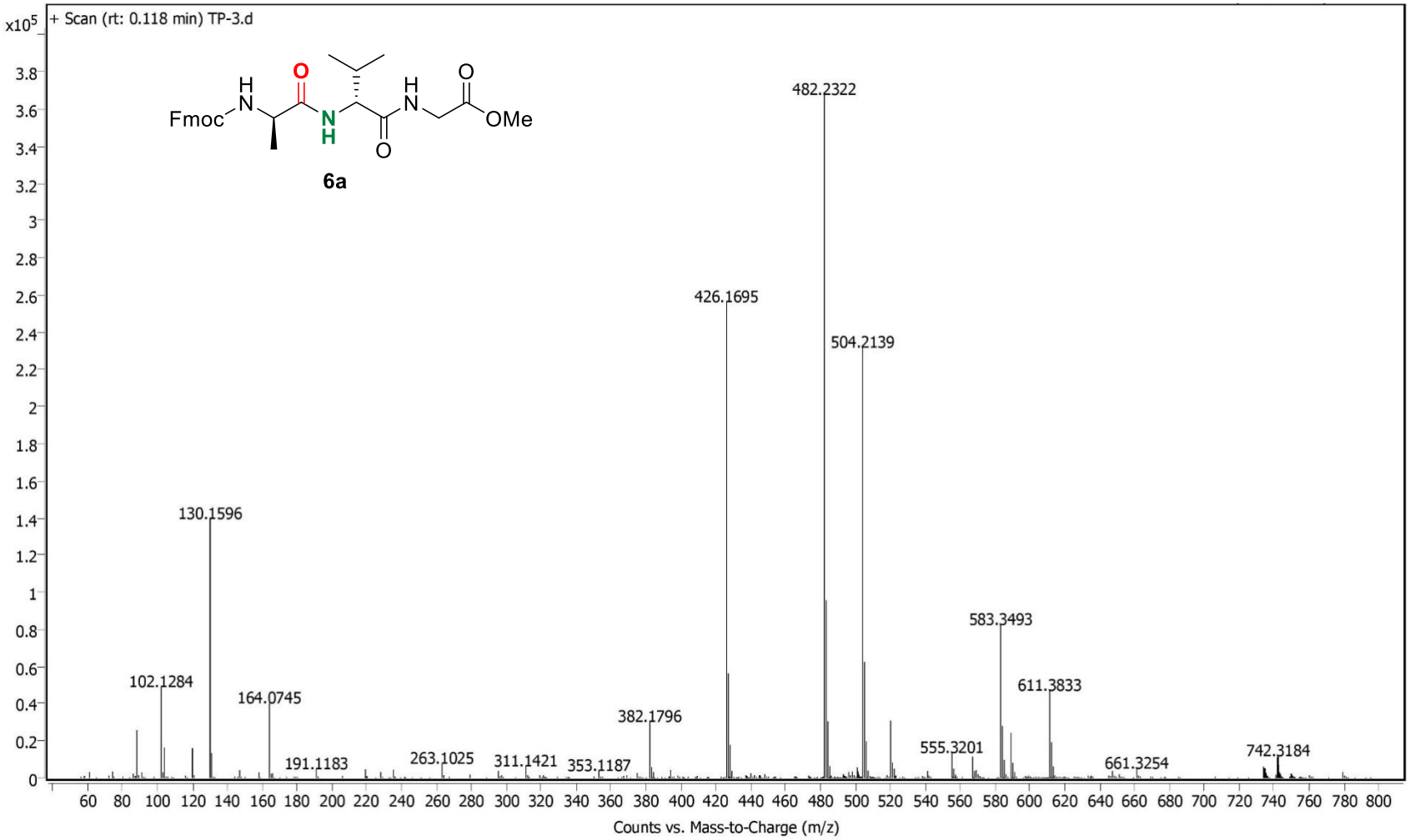


Figure S73. HRMS Spectrum of **6a**

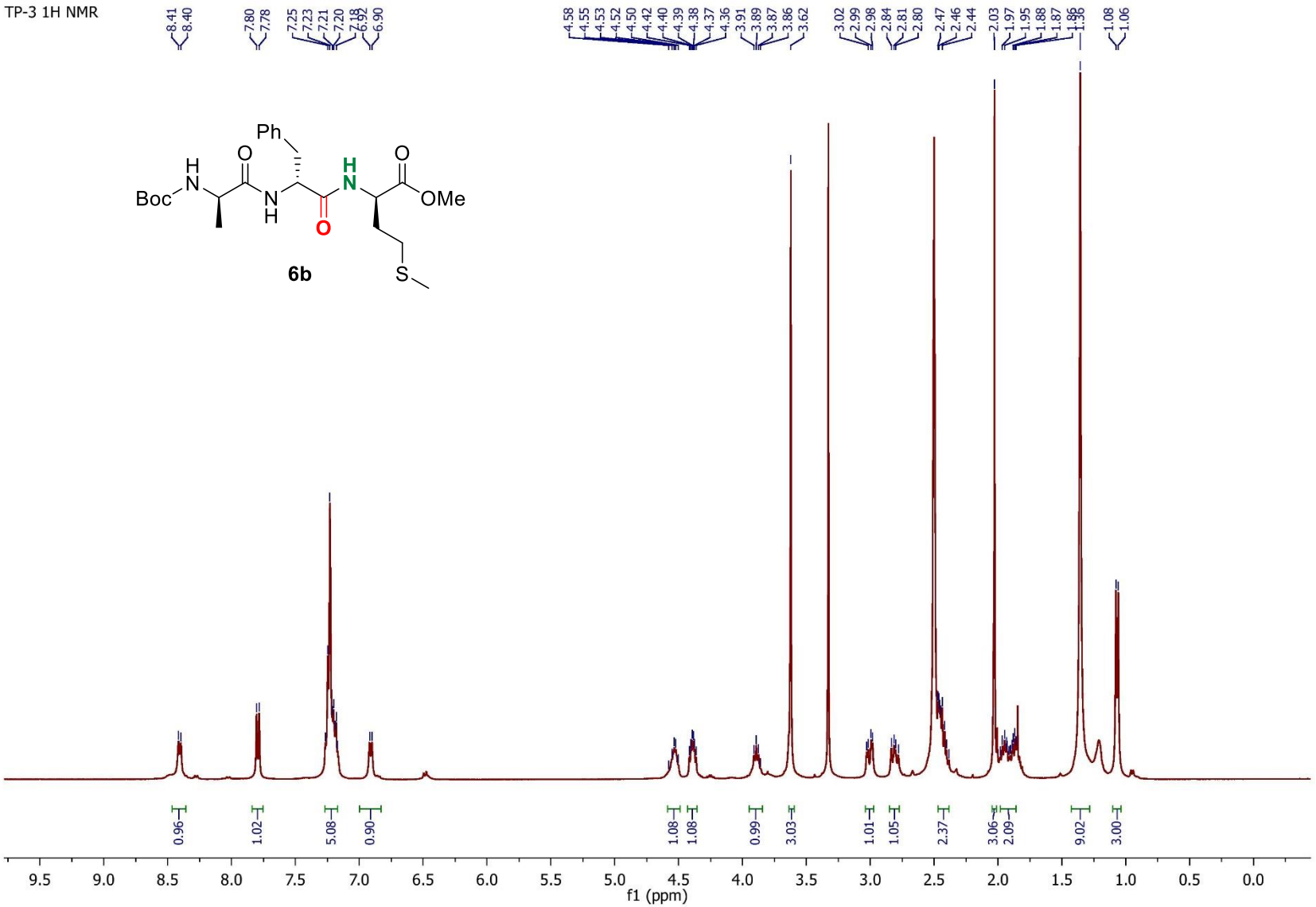


Figure S74. ^{1}H NMR Spectrum of **6b (400MHz, DMSO-d$_6$)**

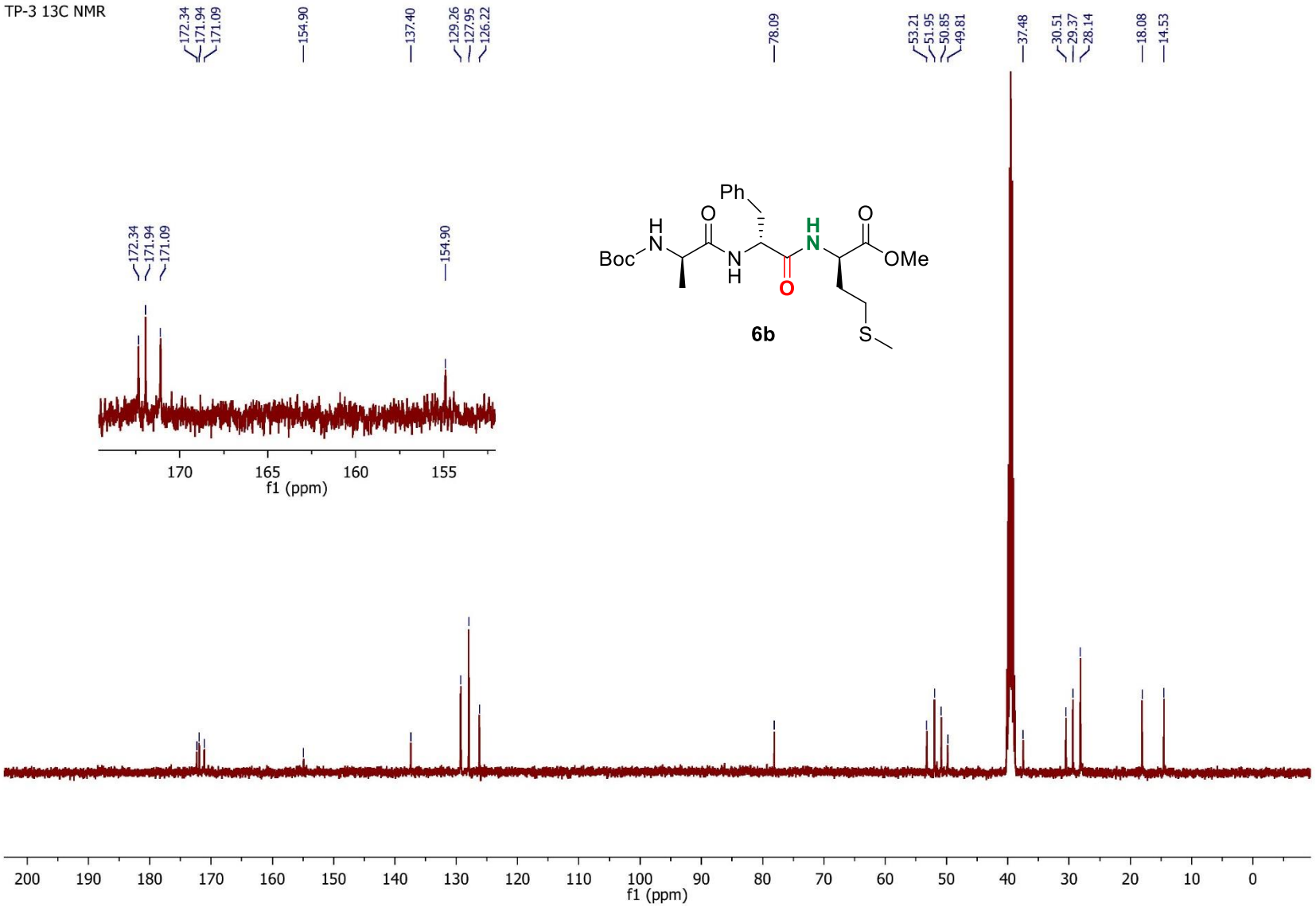


Figure S75. ^{13}C NMR Spectrum of **6b(101MHz, DMSO-d$_6$)**

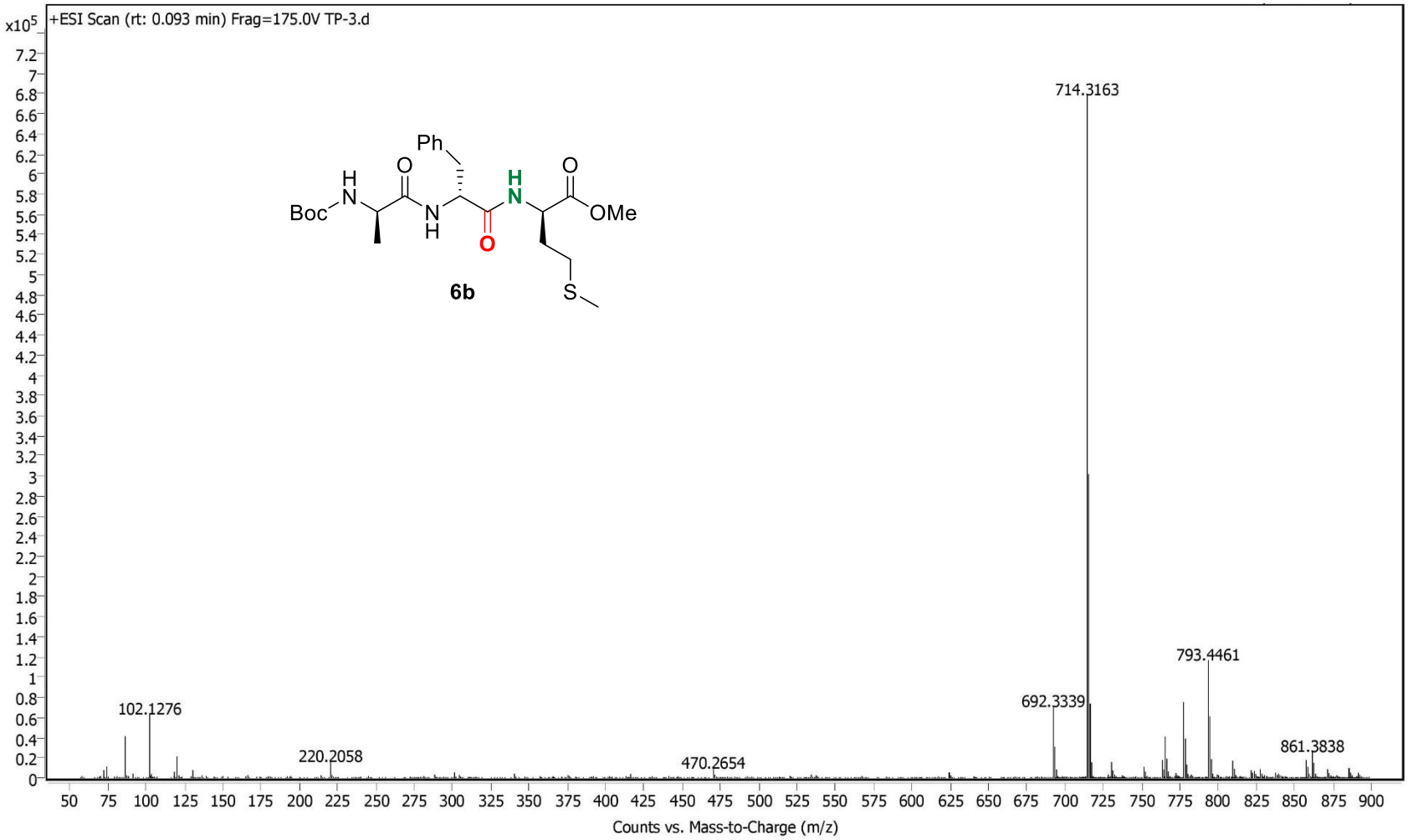


Figure S76. HRMS Spectrum of **6b**

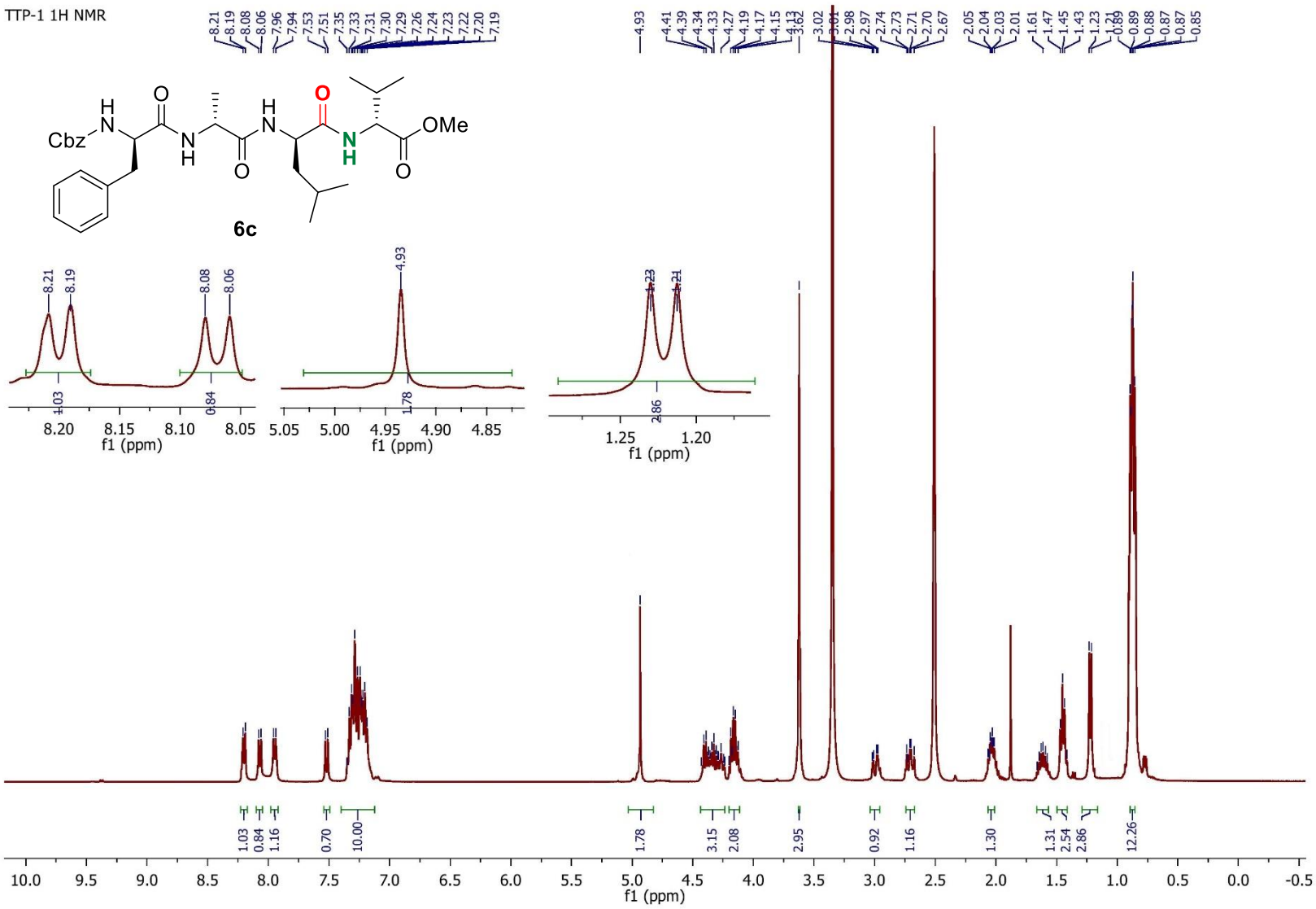


Figure S77. ^{1}H NMR Spectrum of **6c (400MHz, DMSO-d$_6$)**

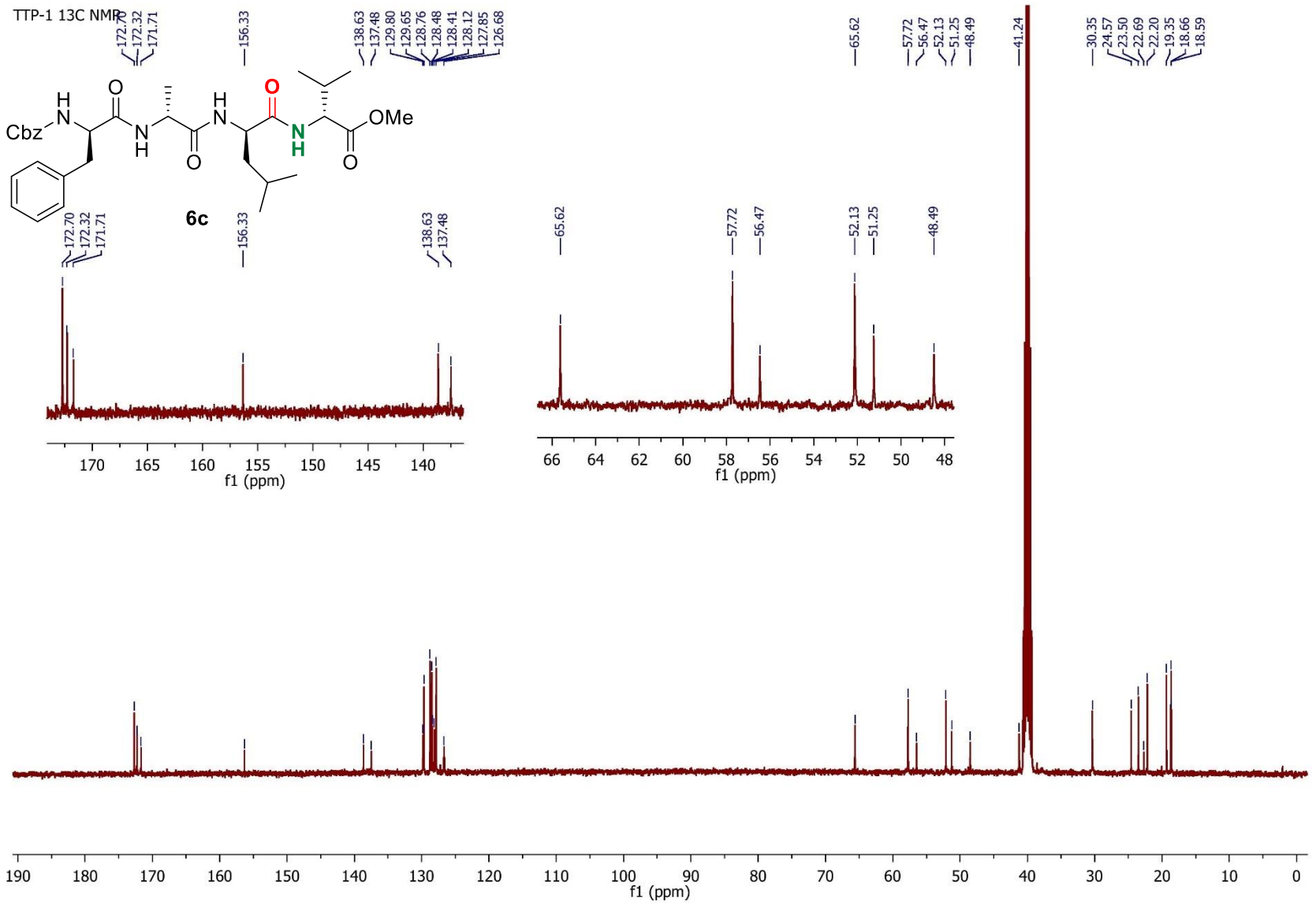


Figure S78. ^{13}C NMR Spectrum of **6c (101MHz, DMSO-d$_6$)**

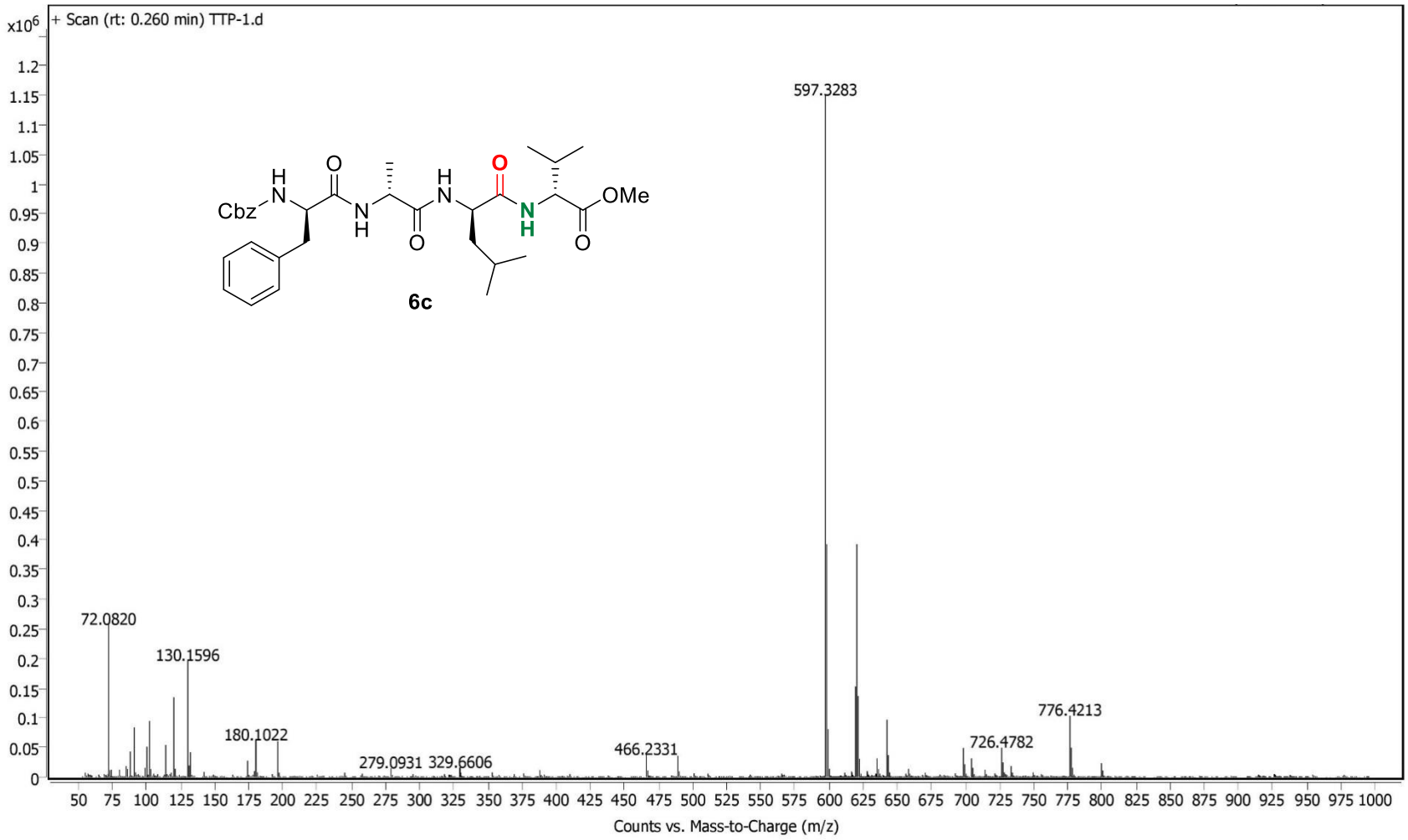


Figure S79. HRMS Spectrum of **6c**

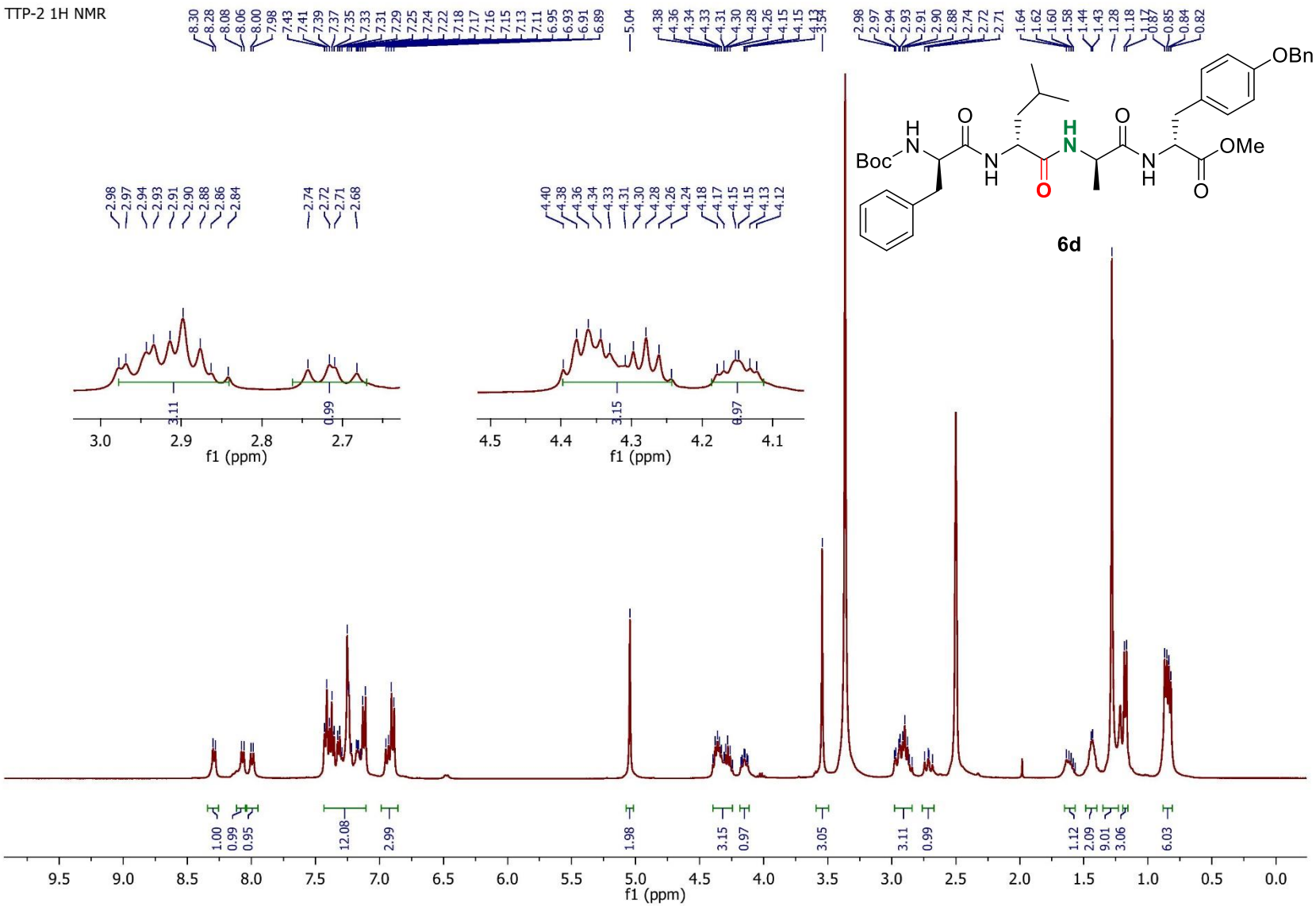


Figure S80. ^{1}H NMR Spectrum of **6d (400MHz, DMSO-d$_6$)**

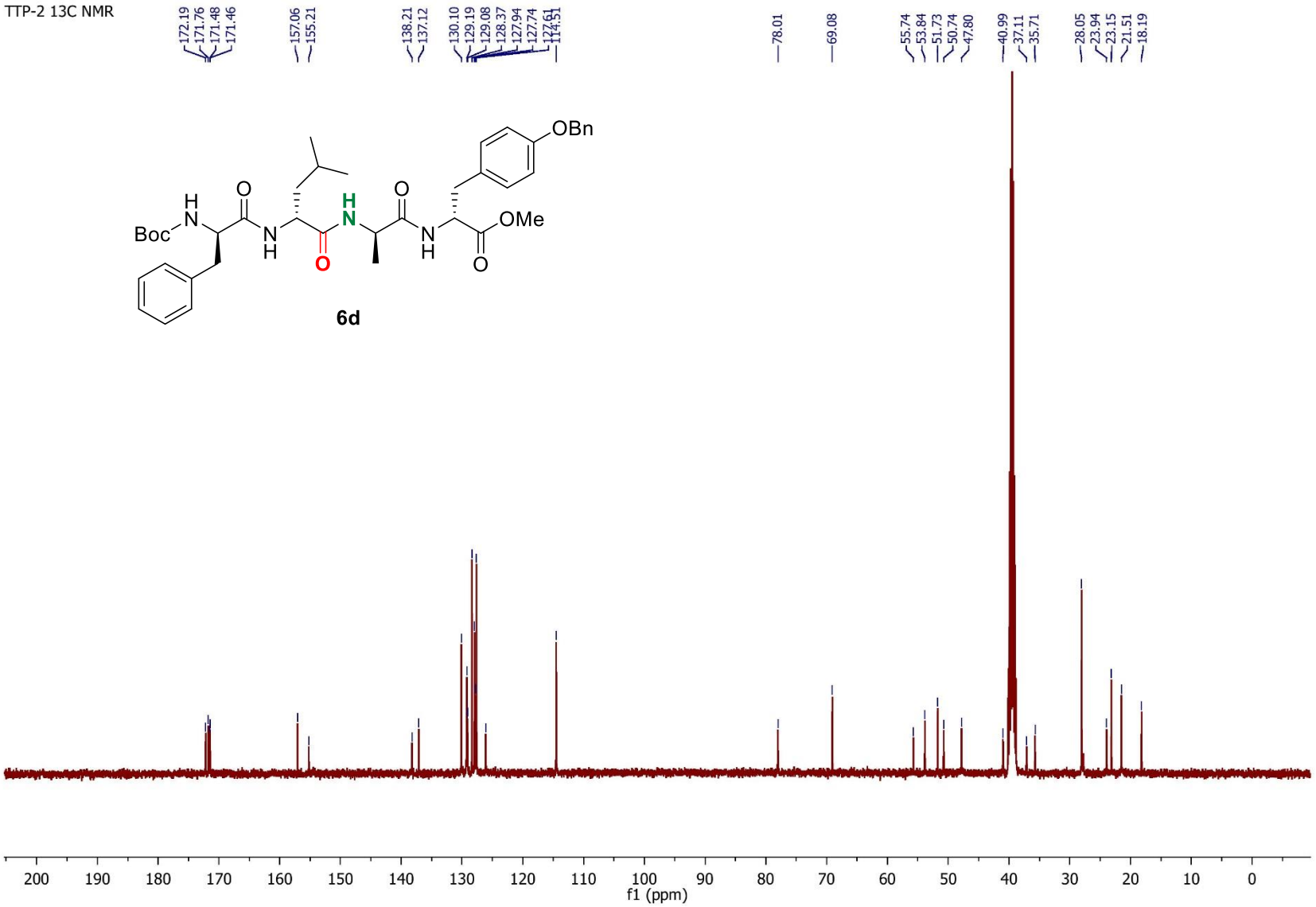


Figure S81. ^{13}C NMR Spectrum of **6d (101MHz, DMSO-d$_6$)**

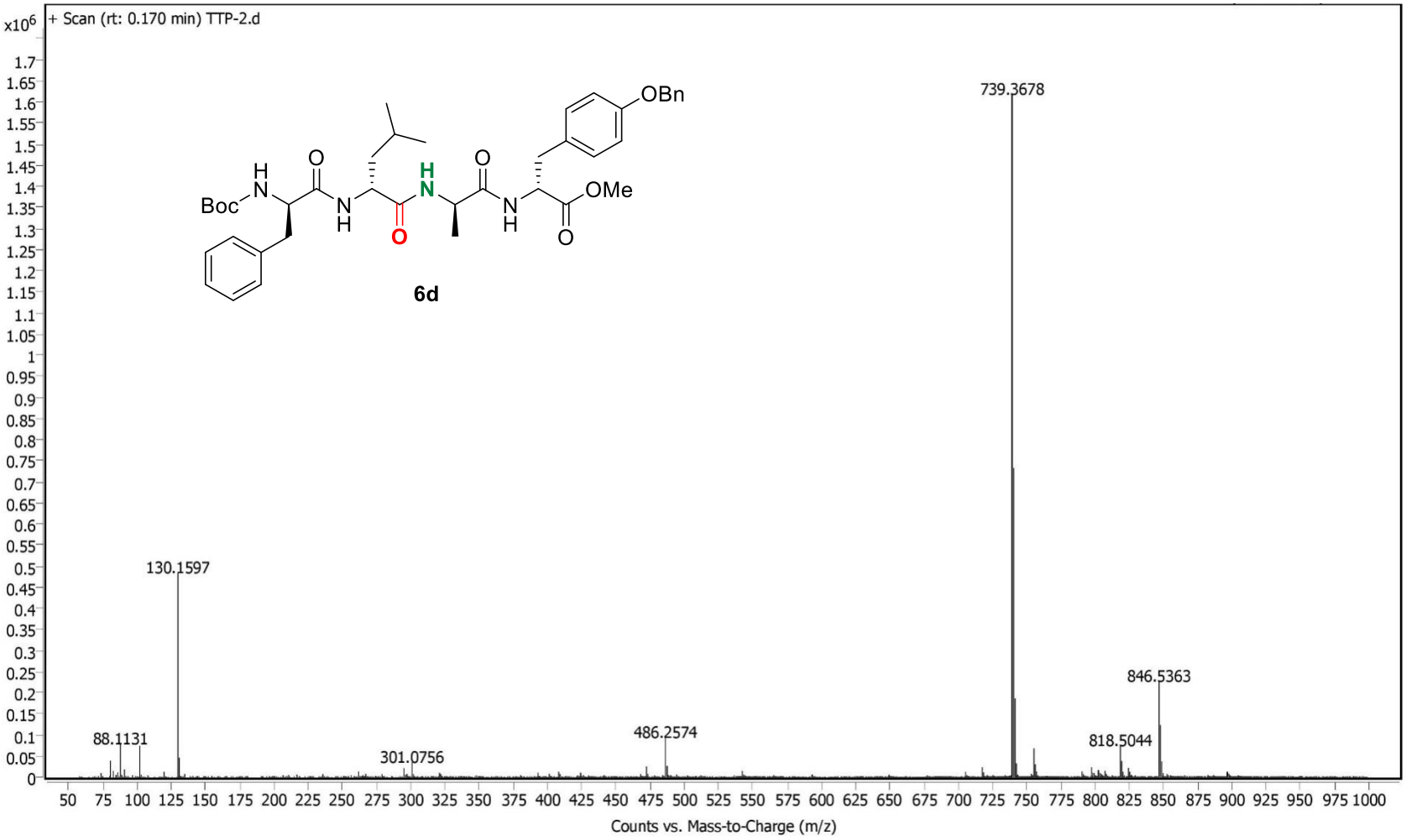


Figure S82. HRMS Spectrum of **6d**

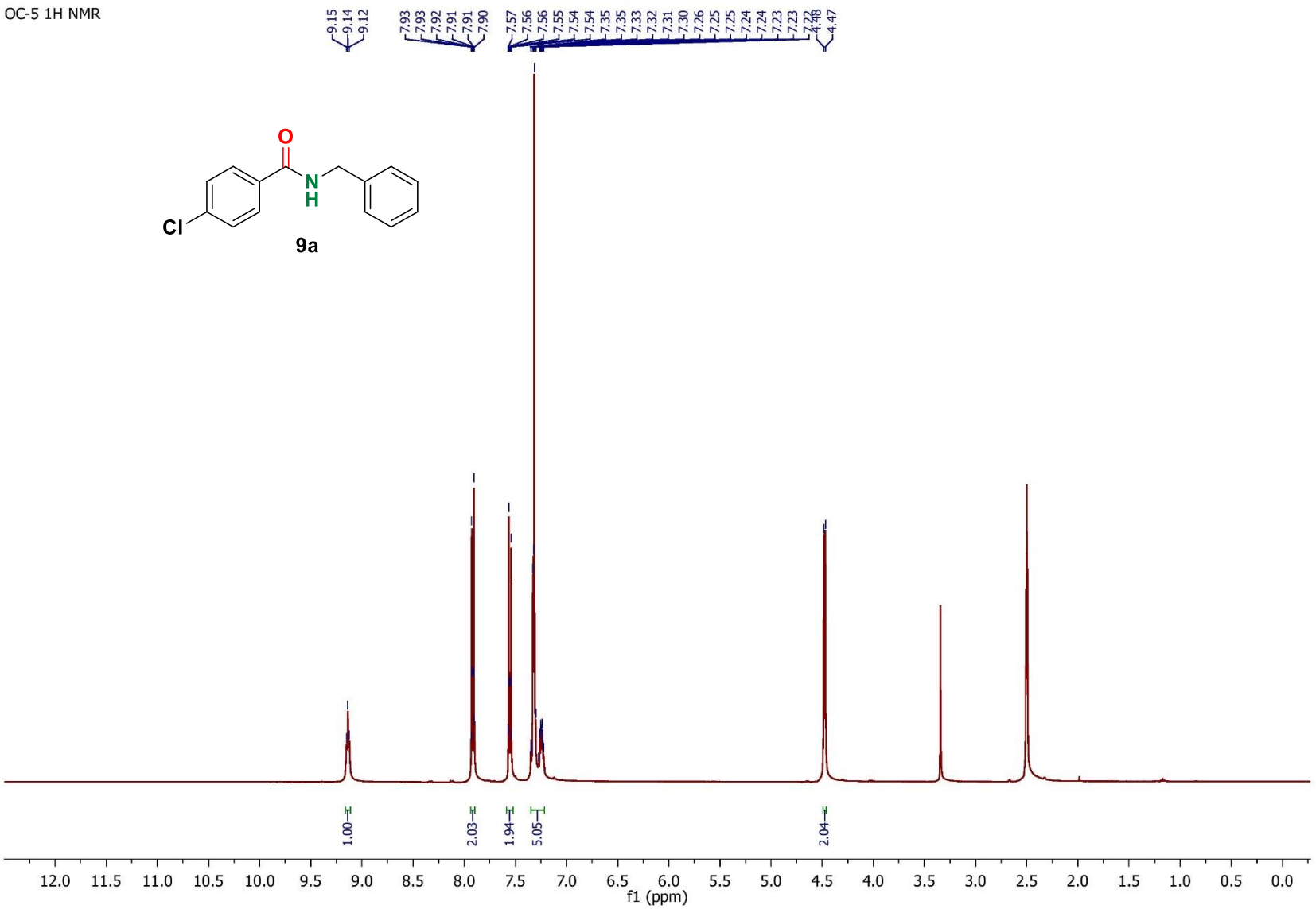


Figure S83. ^{1}H NMR Spectrum of **9a (400MHz, DMSO-d$_6$)**

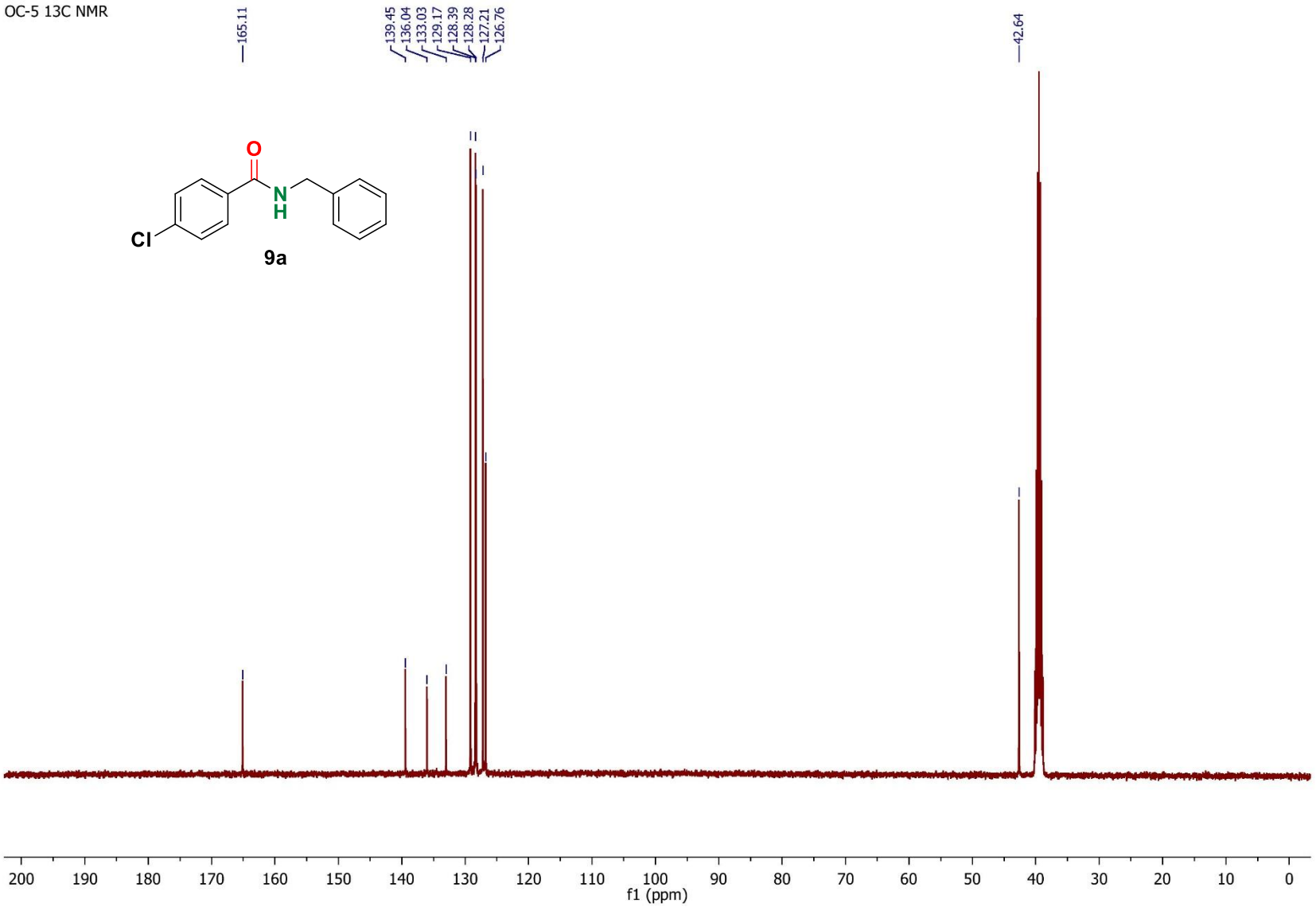


Figure S84. ^{13}C NMR Spectrum of **9a (101MHz, DMSO-d$_6$)**

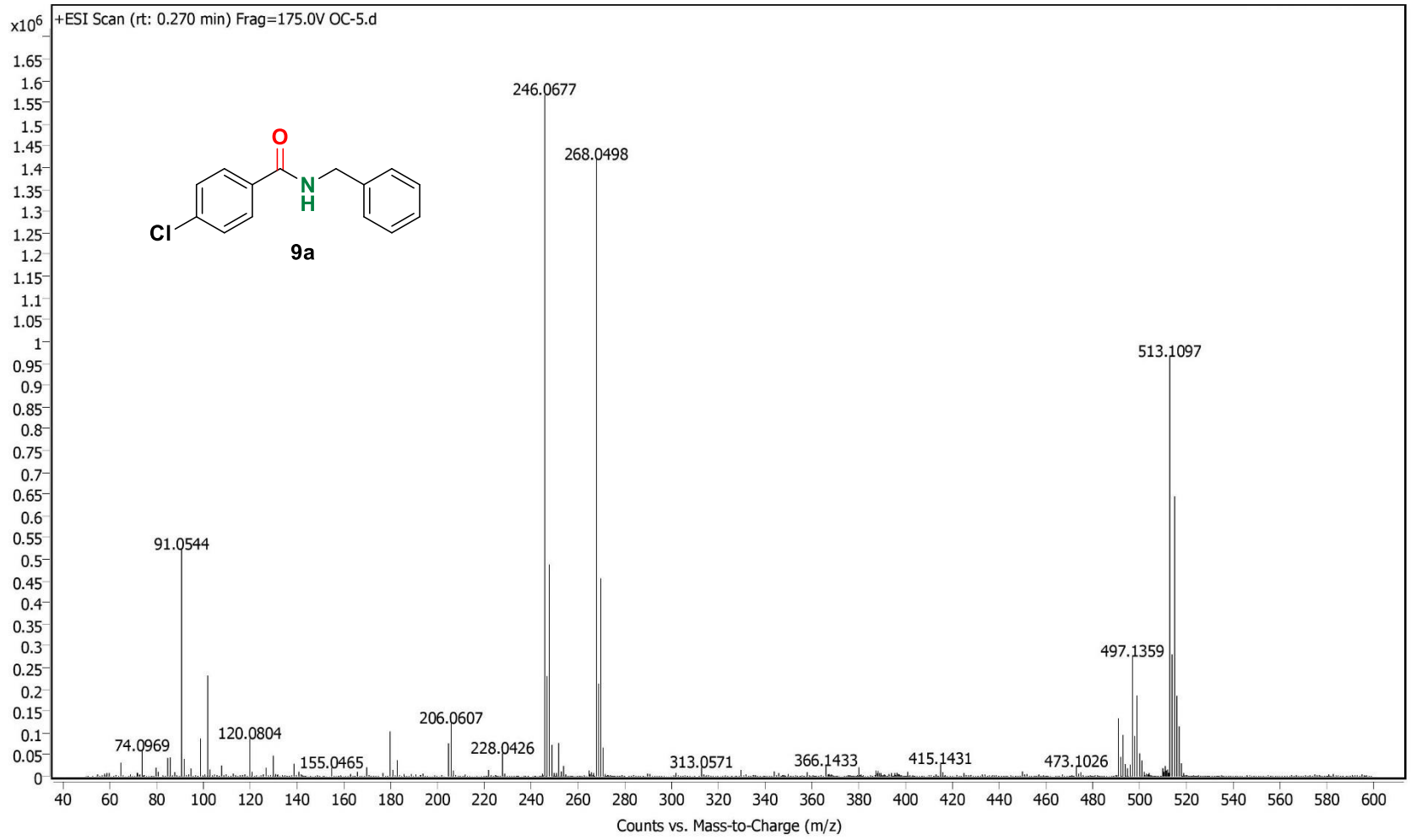


Figure S85. HRMS Spectrum of **9a**

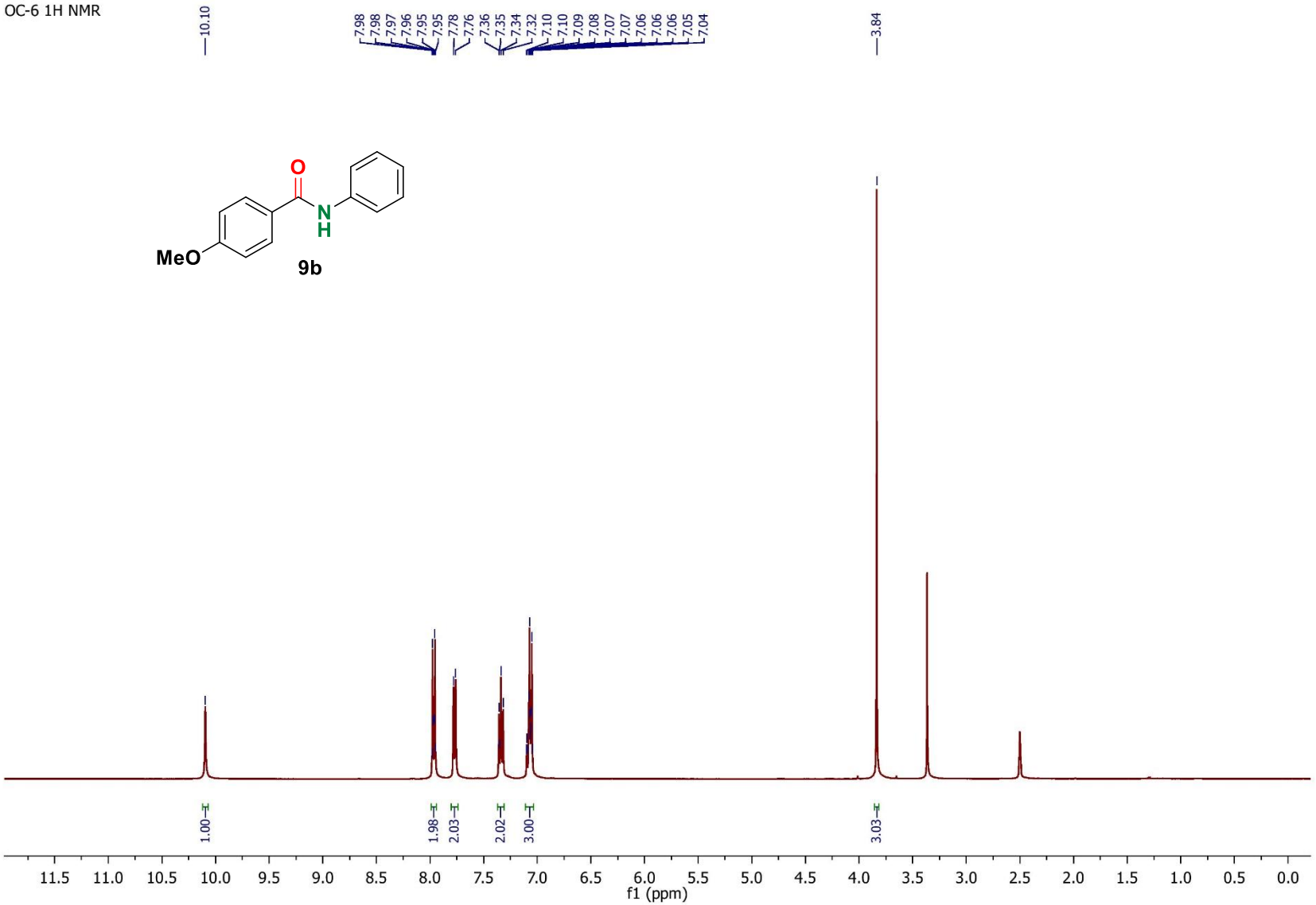


Figure S86. ^{1}H NMR Spectrum of **9b (400MHz, DMSO-d$_6$)**

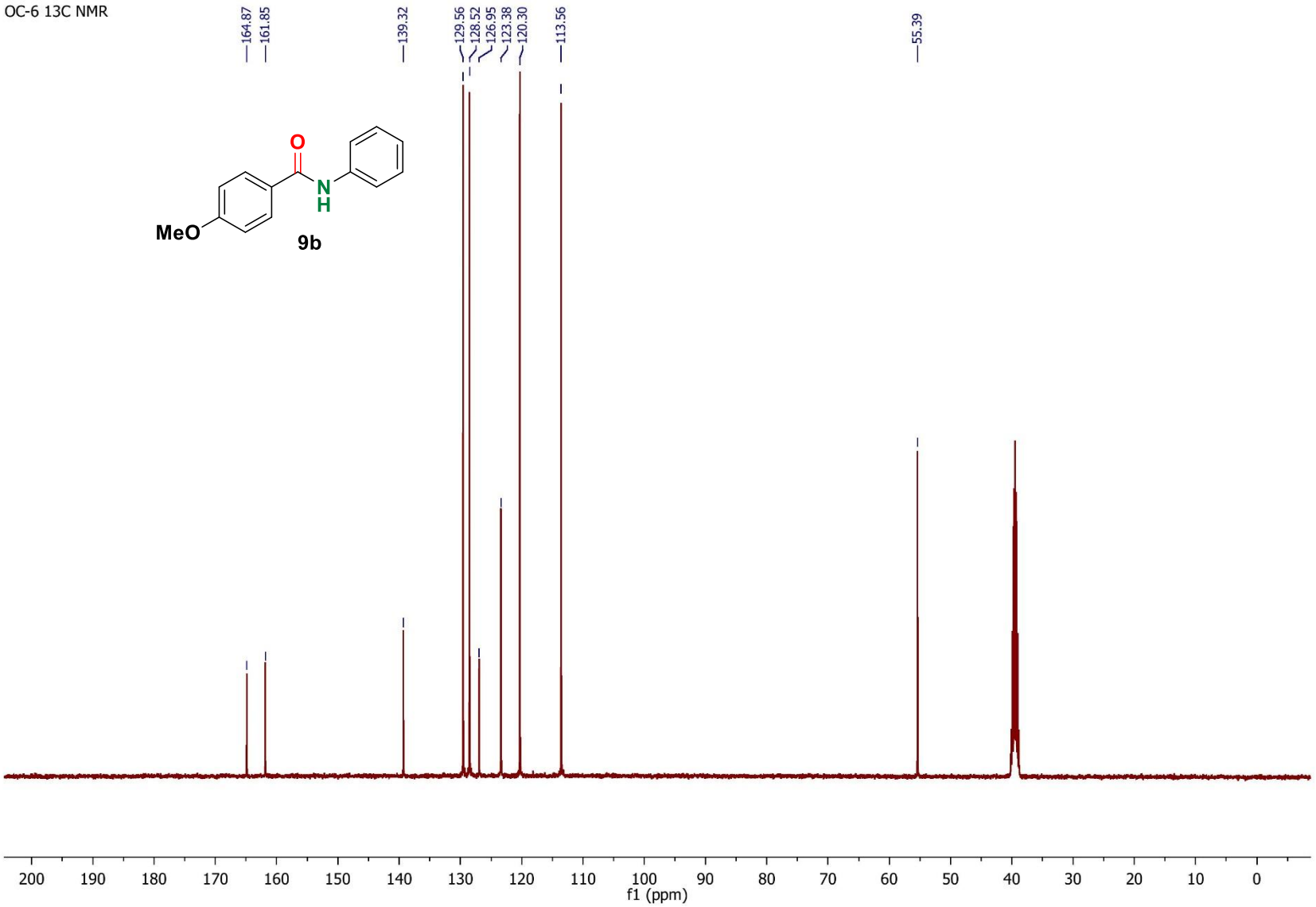


Figure S87. ^{13}C NMR Spectrum of **9b (101MHz, DMSO-d$_6$)**

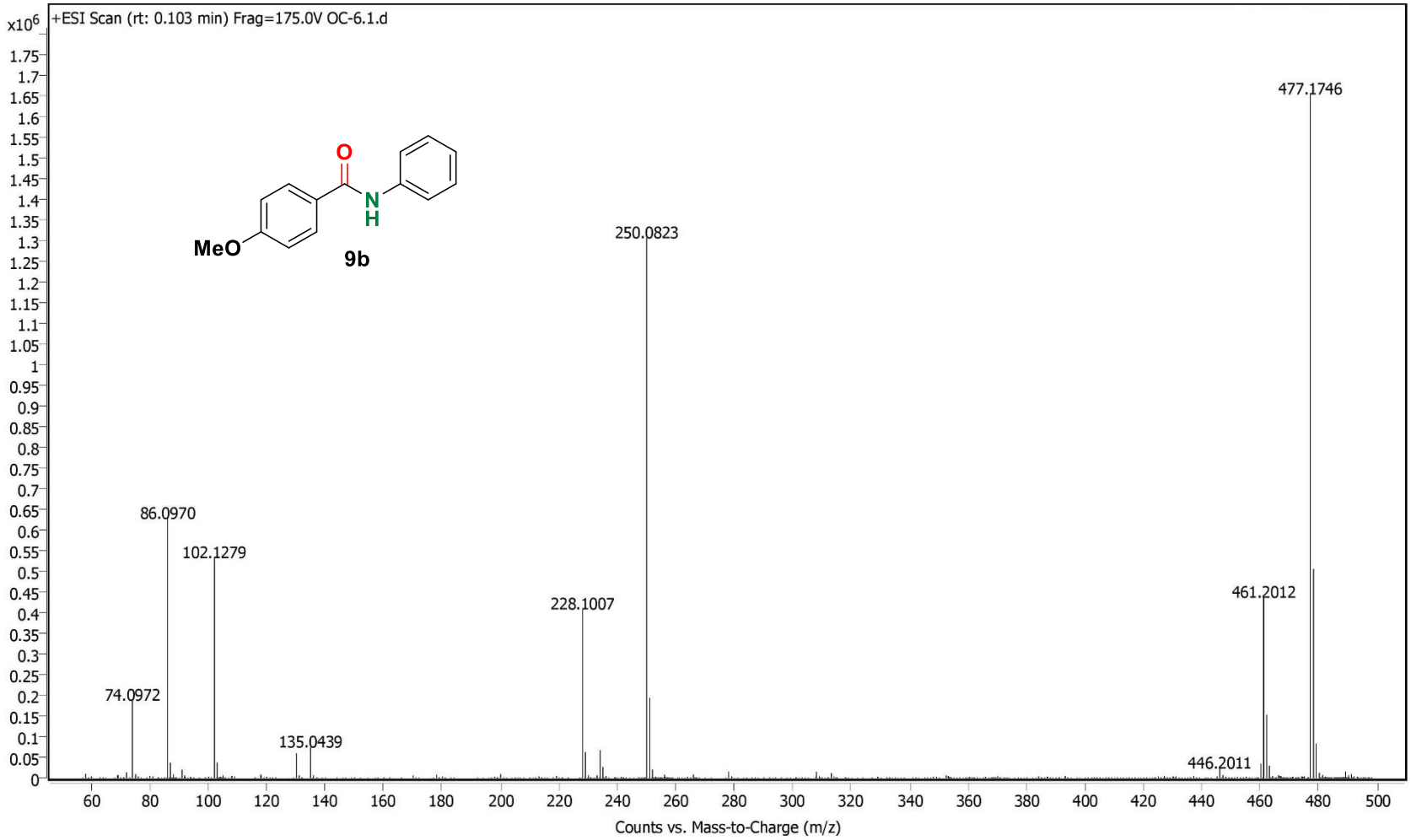


Figure S88. HRMS Spectrum of **9b**

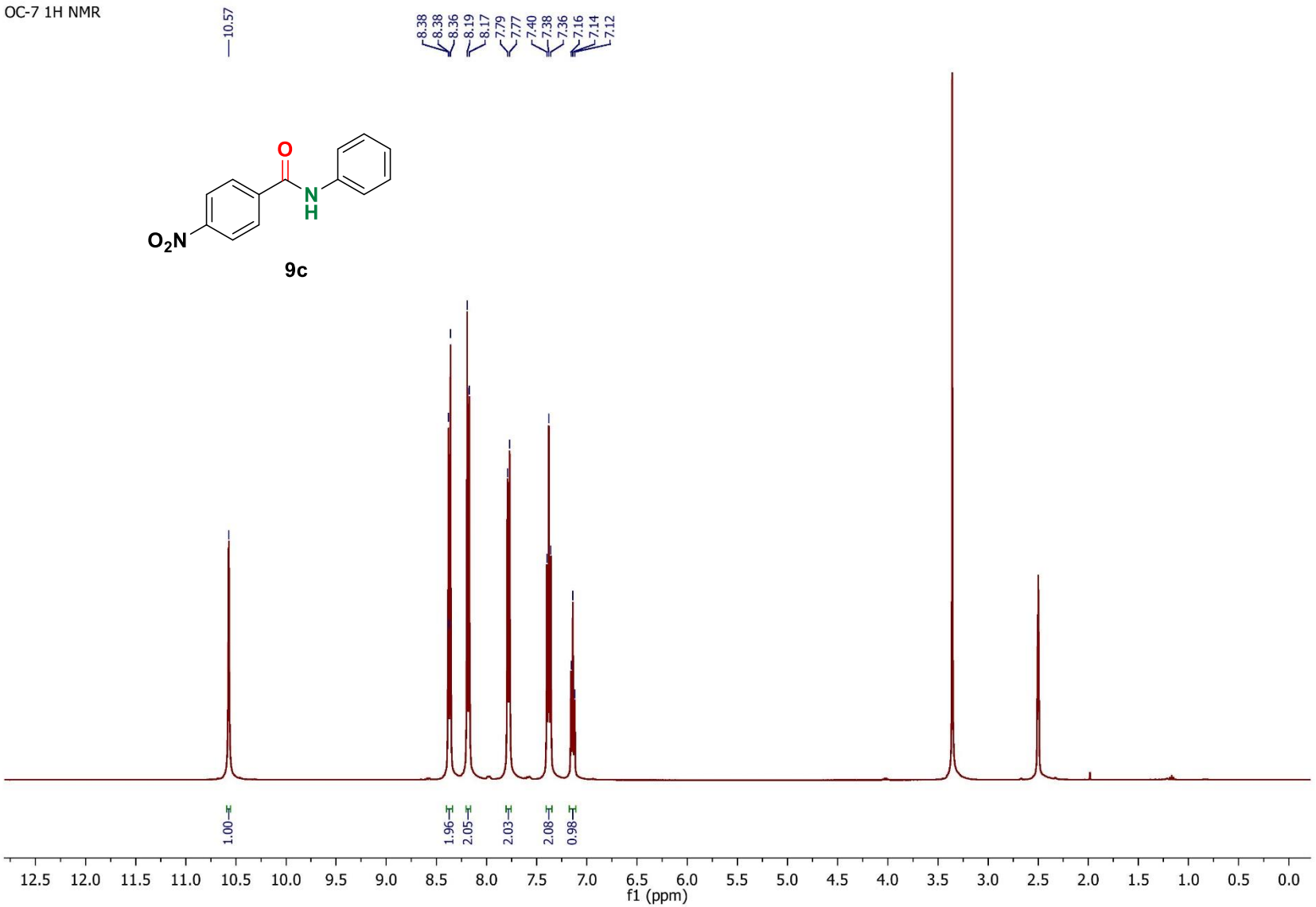


Figure S89. ^{1}H NMR Spectrum of **9c (400MHz, DMSO-d$_6$)**

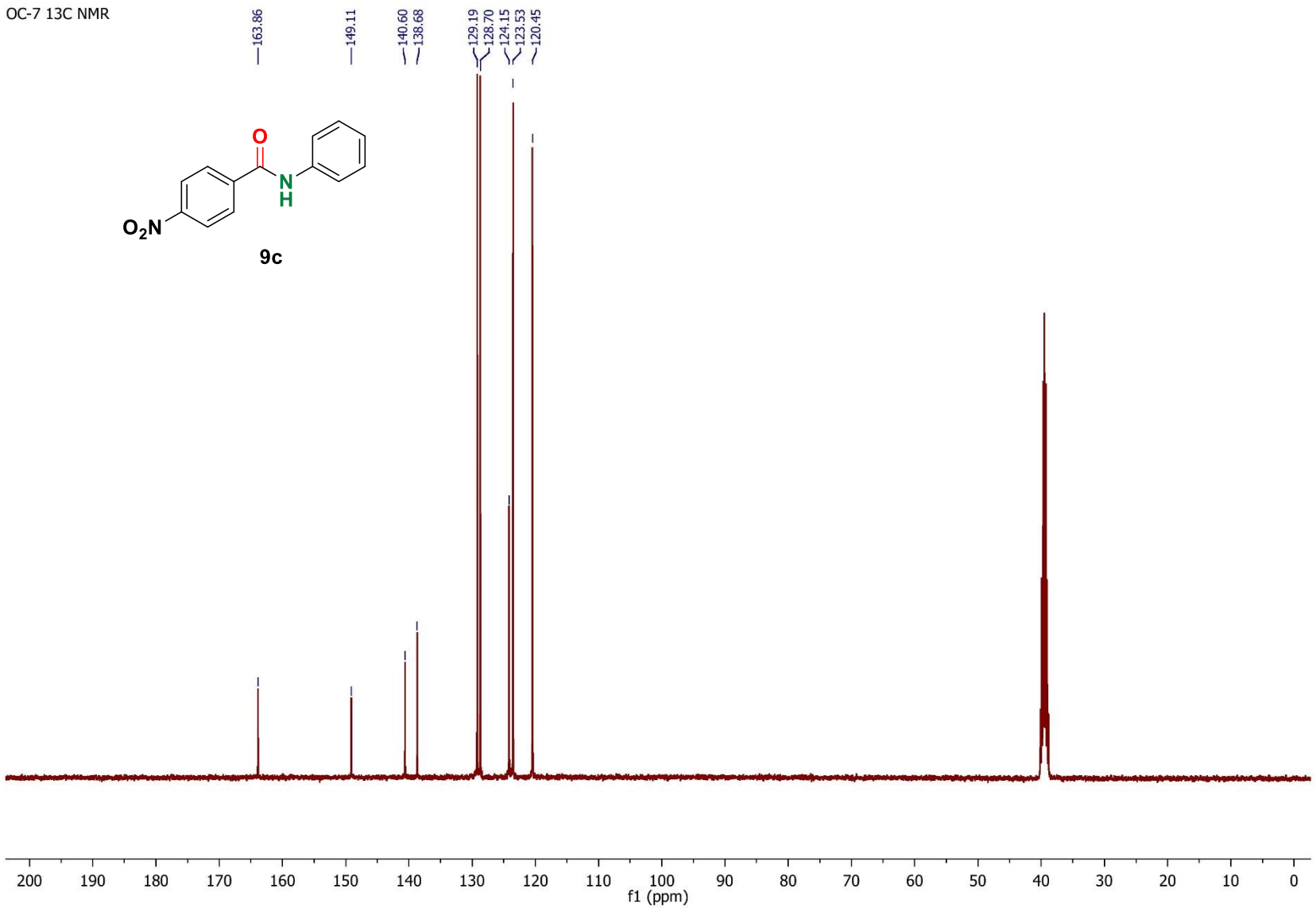


Figure S90. ^{13}C NMR Spectrum of **9c (101MHz, DMSO-d$_6$)**

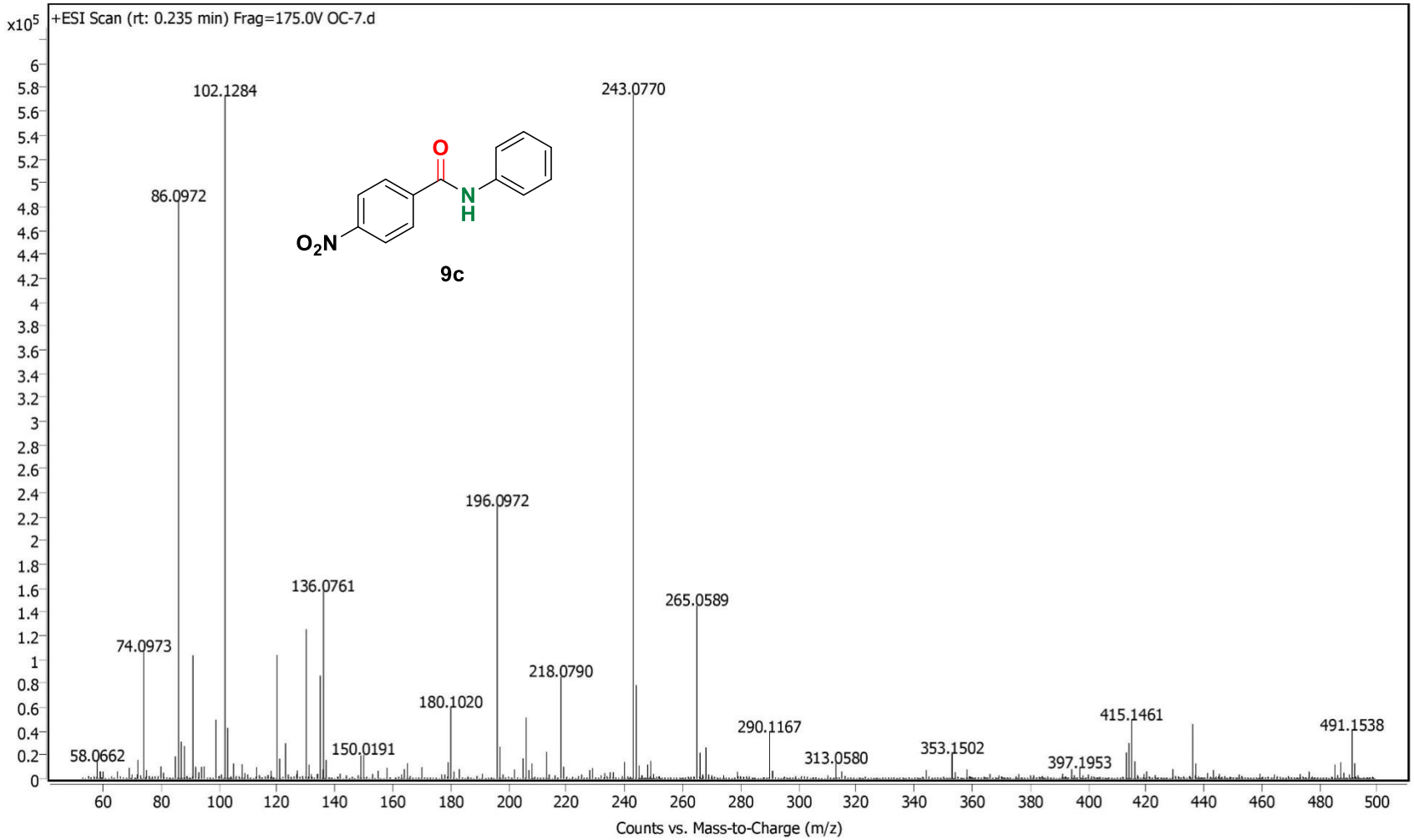


Figure S91. HRMS Spectrum of **9c**

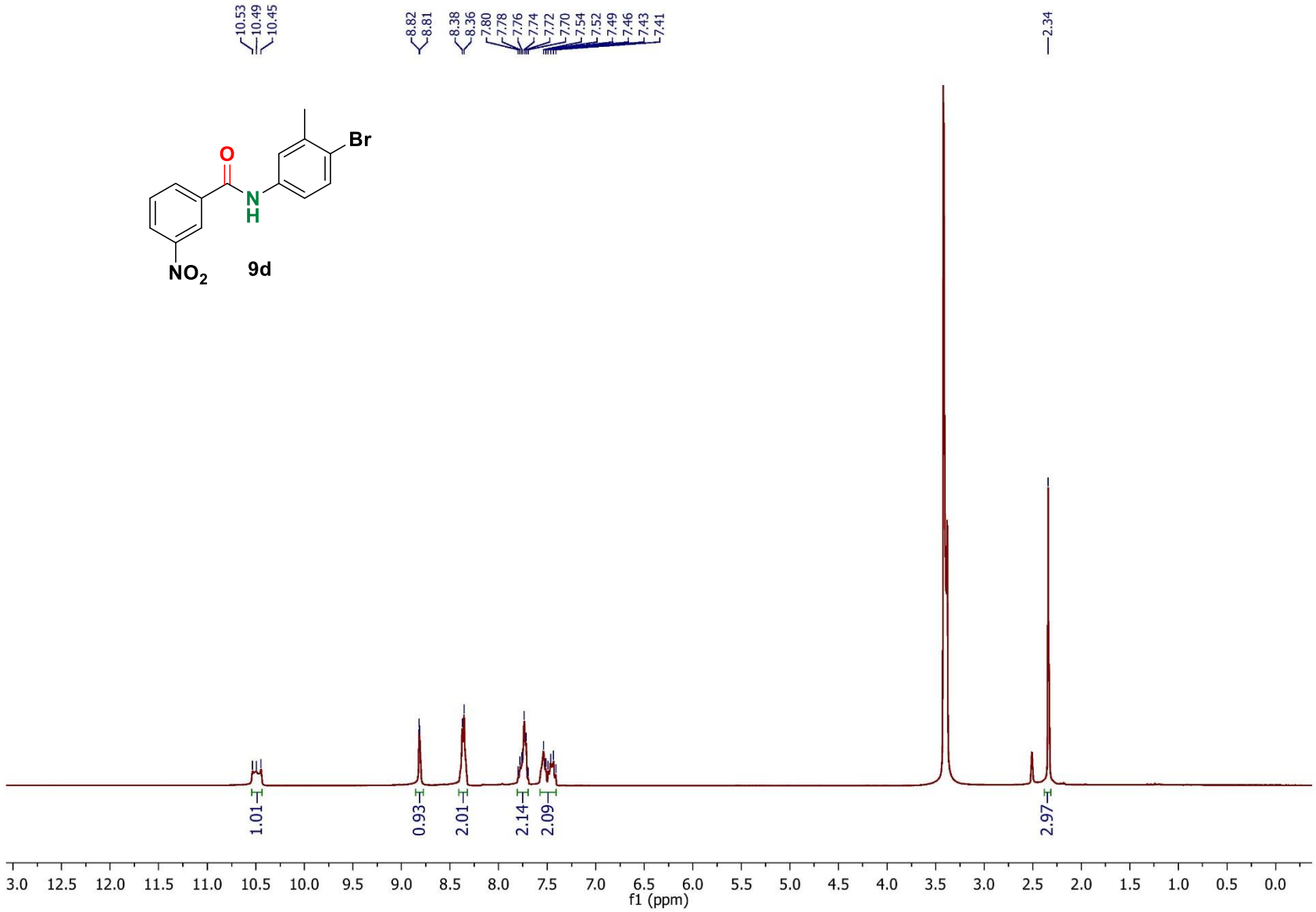


Figure S92. ^{1}H NMR Spectrum of **9d (400MHz, DMSO-d$_6$)**

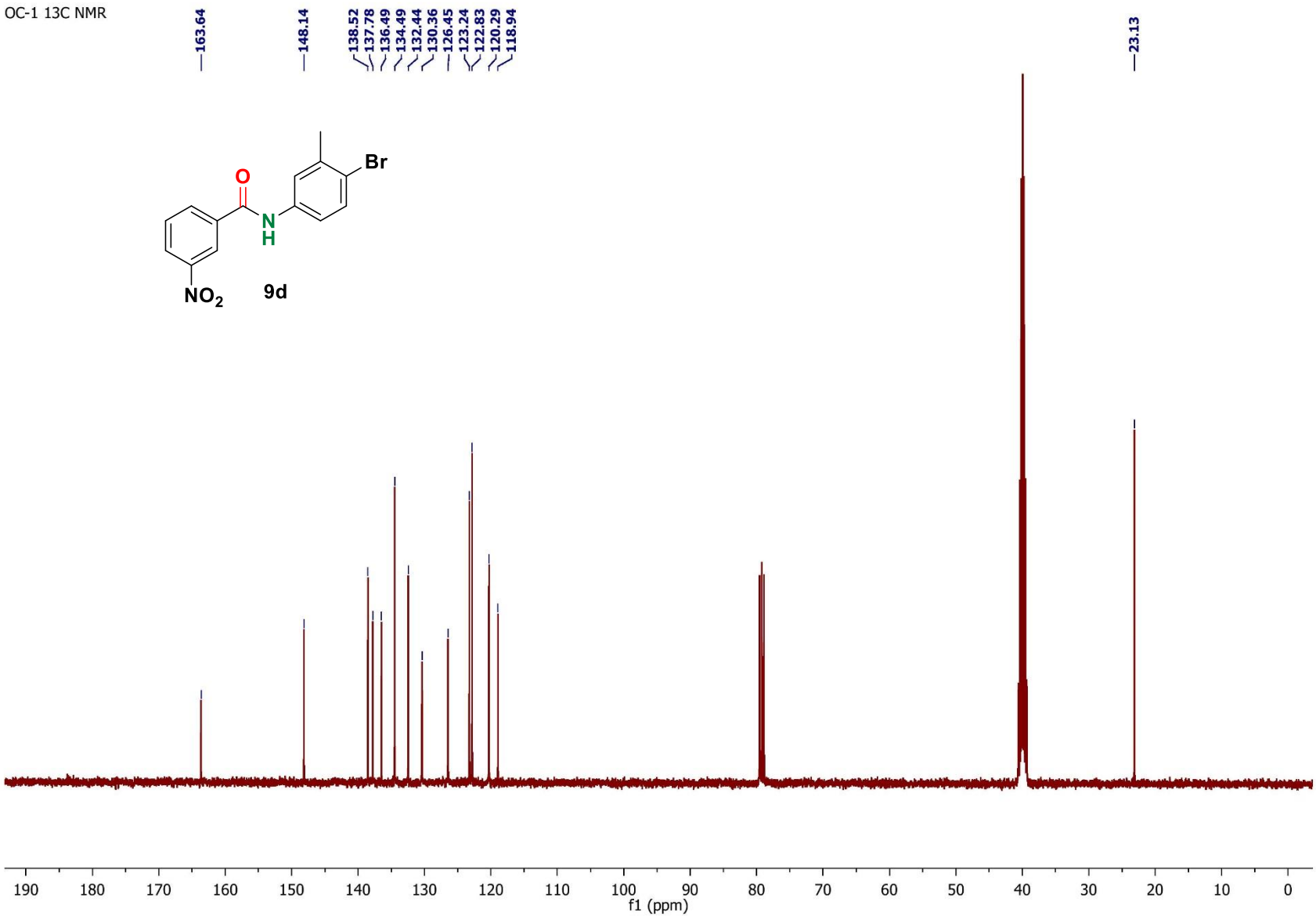


Figure S93. ^{13}C NMR Spectrum of **9d (101MHz, DMSO-d$_6$)**

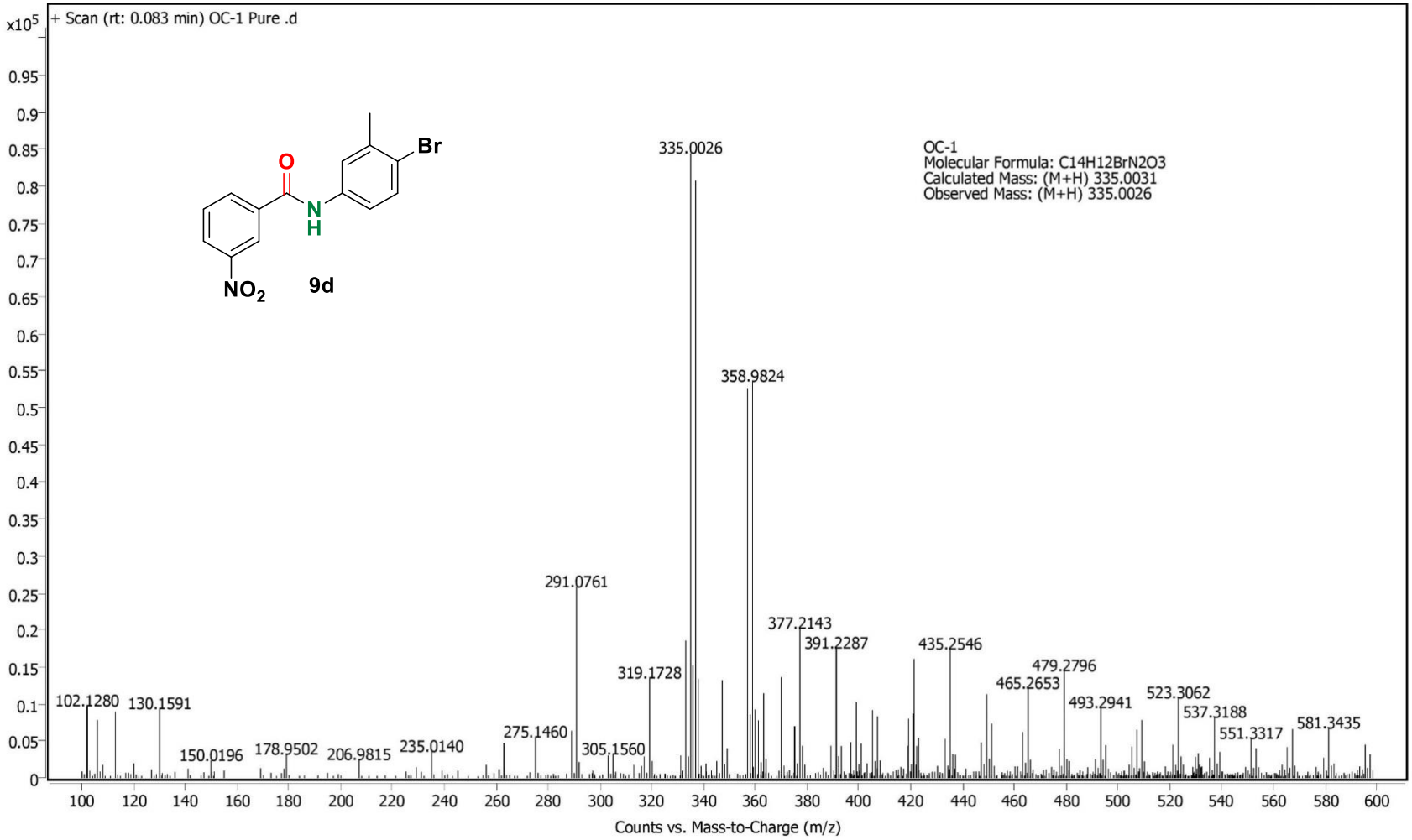


Figure S94. HRMS Spectrum of **9d**

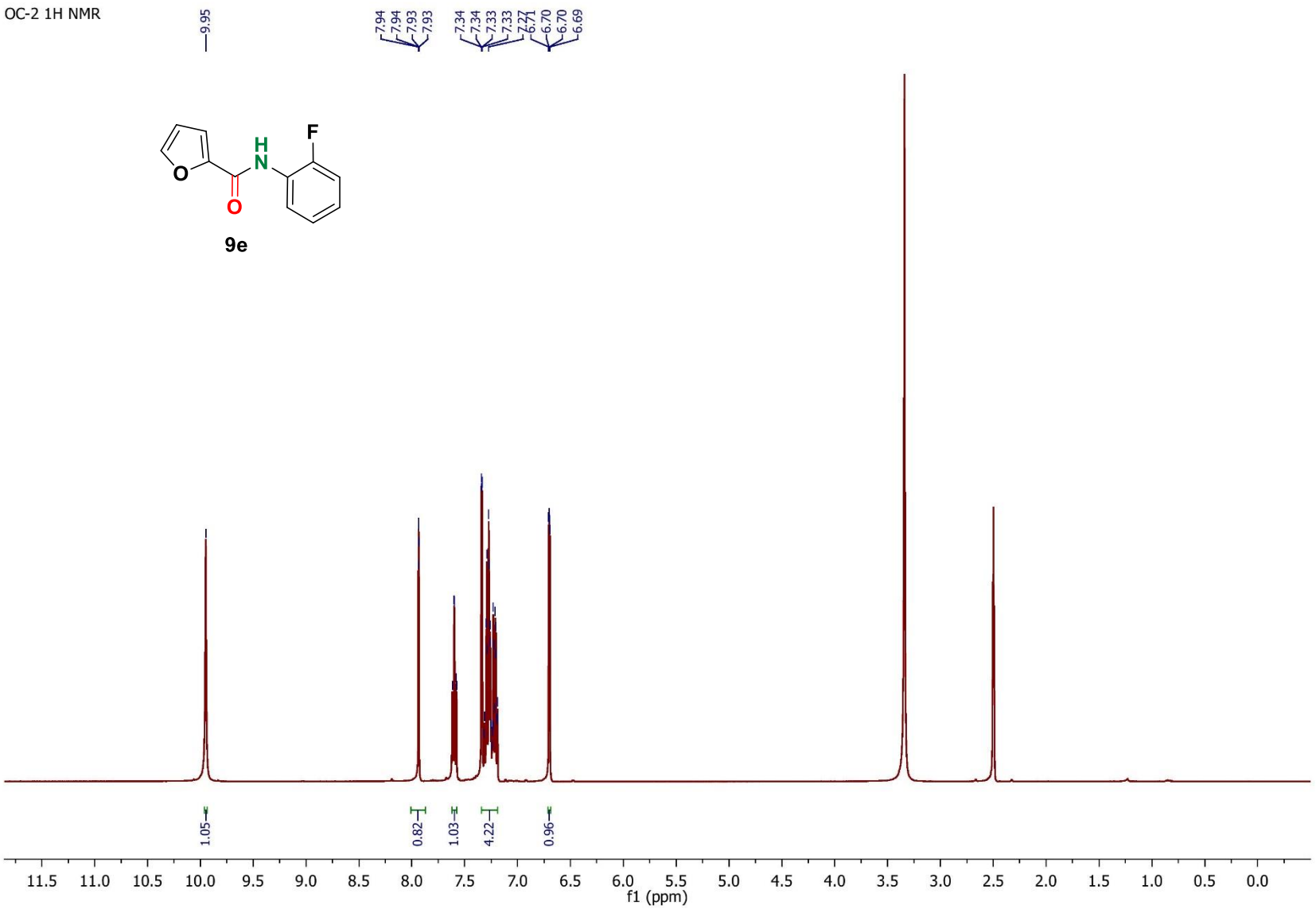


Figure S95. ^{1}H NMR Spectrum of **9e (400MHz, DMSO-d$_6$)**

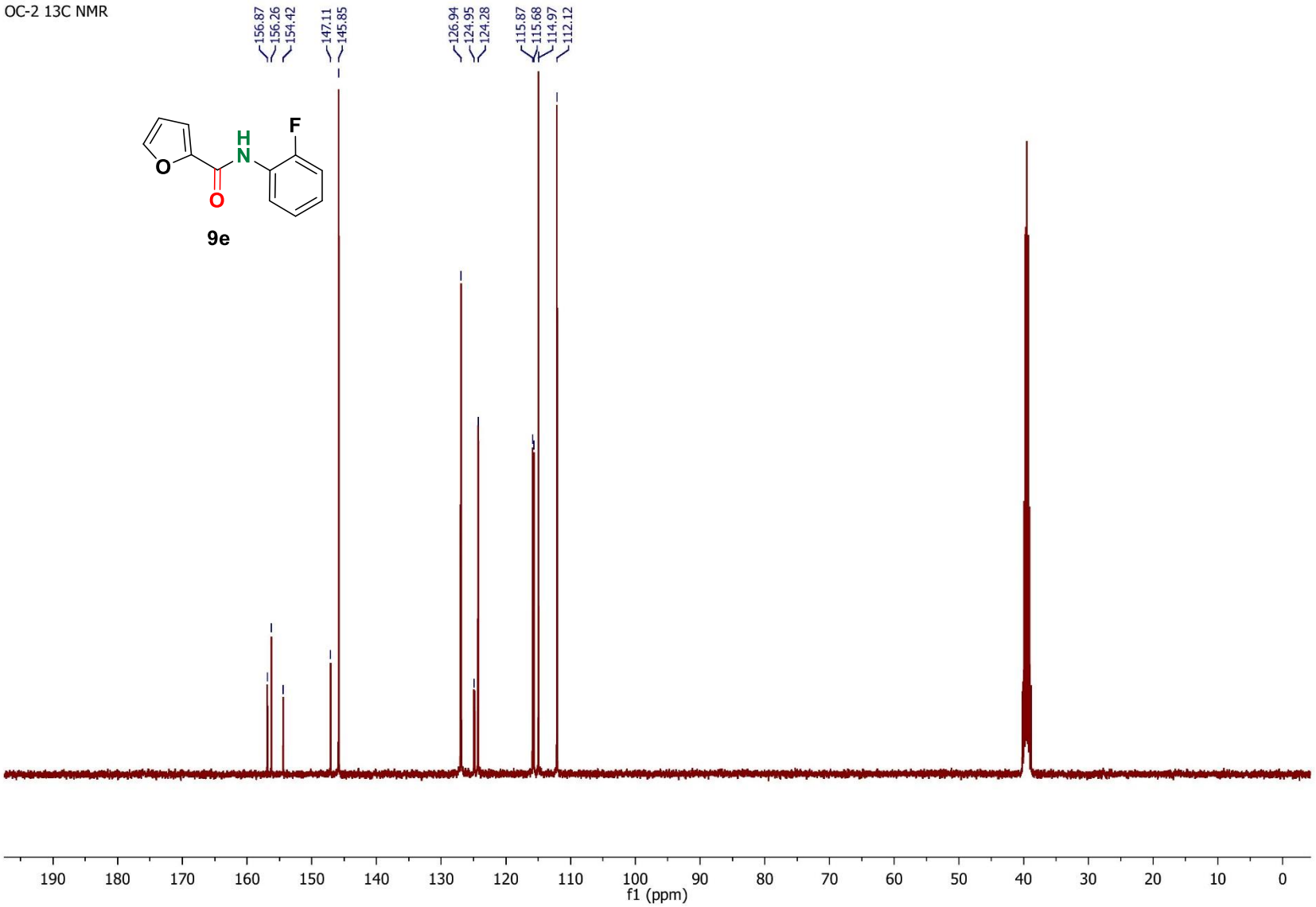


Figure S96. ^{13}C NMR Spectrum of **9e (101MHz, DMSO-d$_6$)**

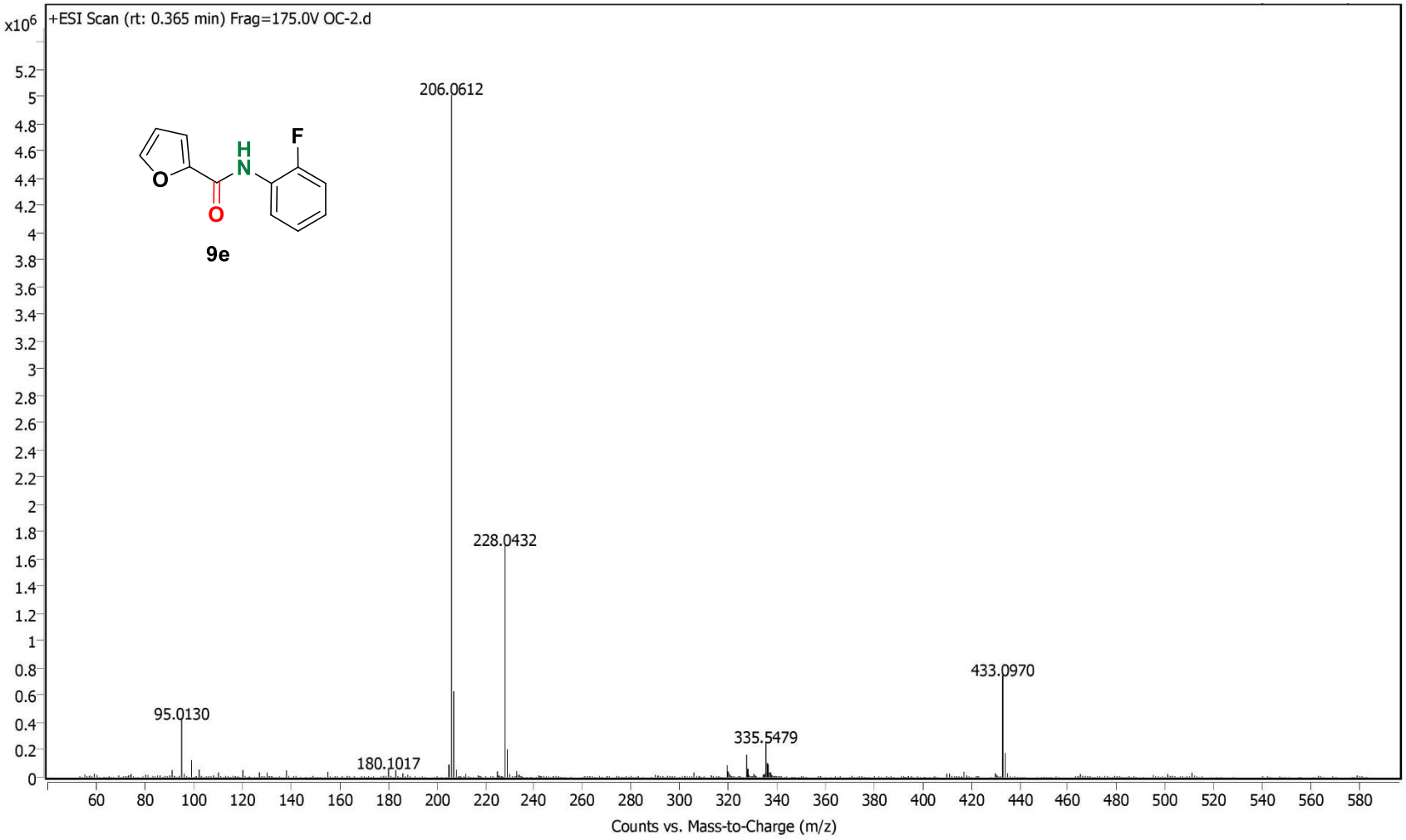


Figure S97. HRMS Spectrum of **9e**

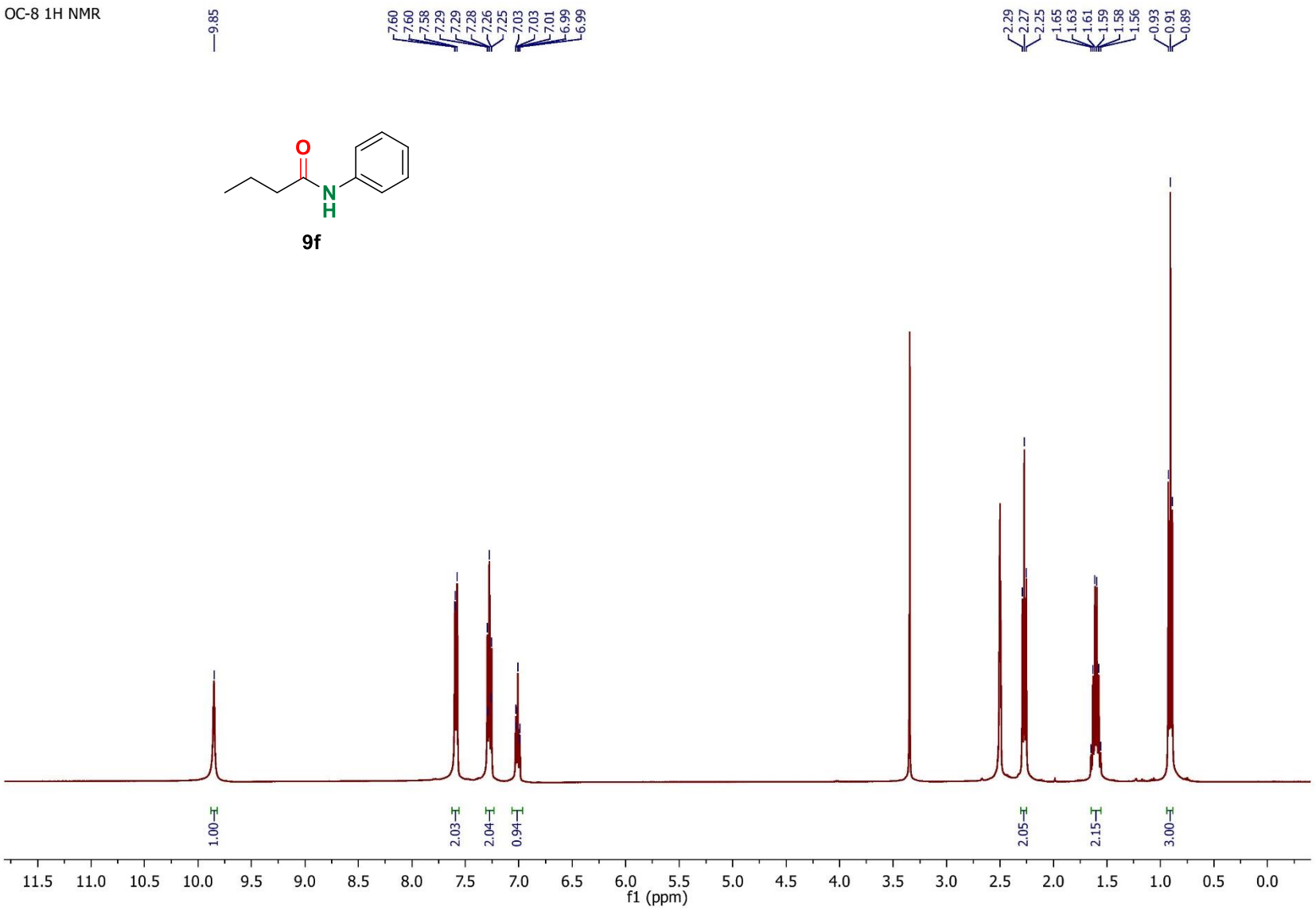


Figure S98. ^{1}H NMR Spectrum of **9f (400MHz, DMSO-d_6)**

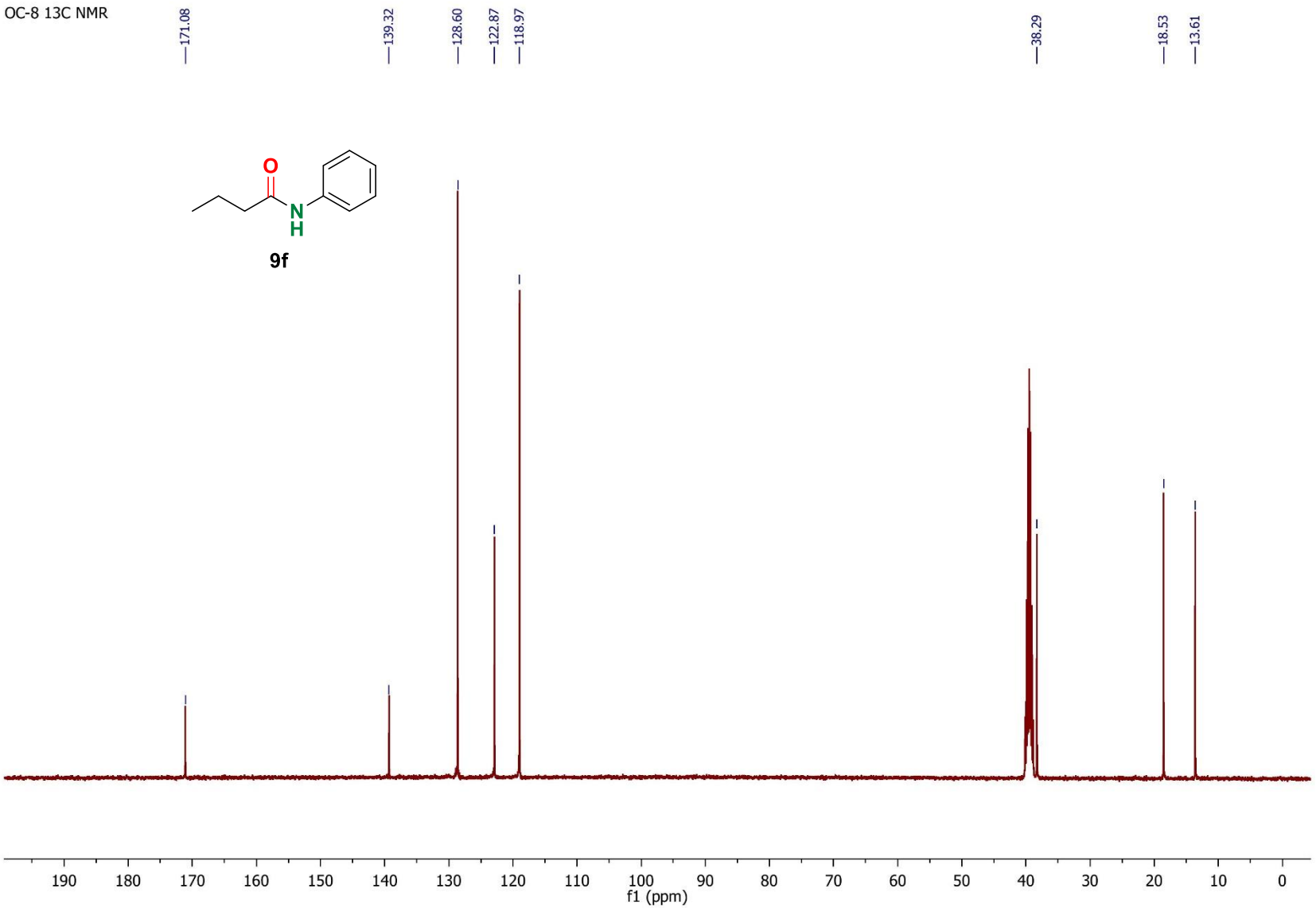


Figure S99. ^{13}C NMR Spectrum of **9f (101MHz, DMSO-d$_6$)**

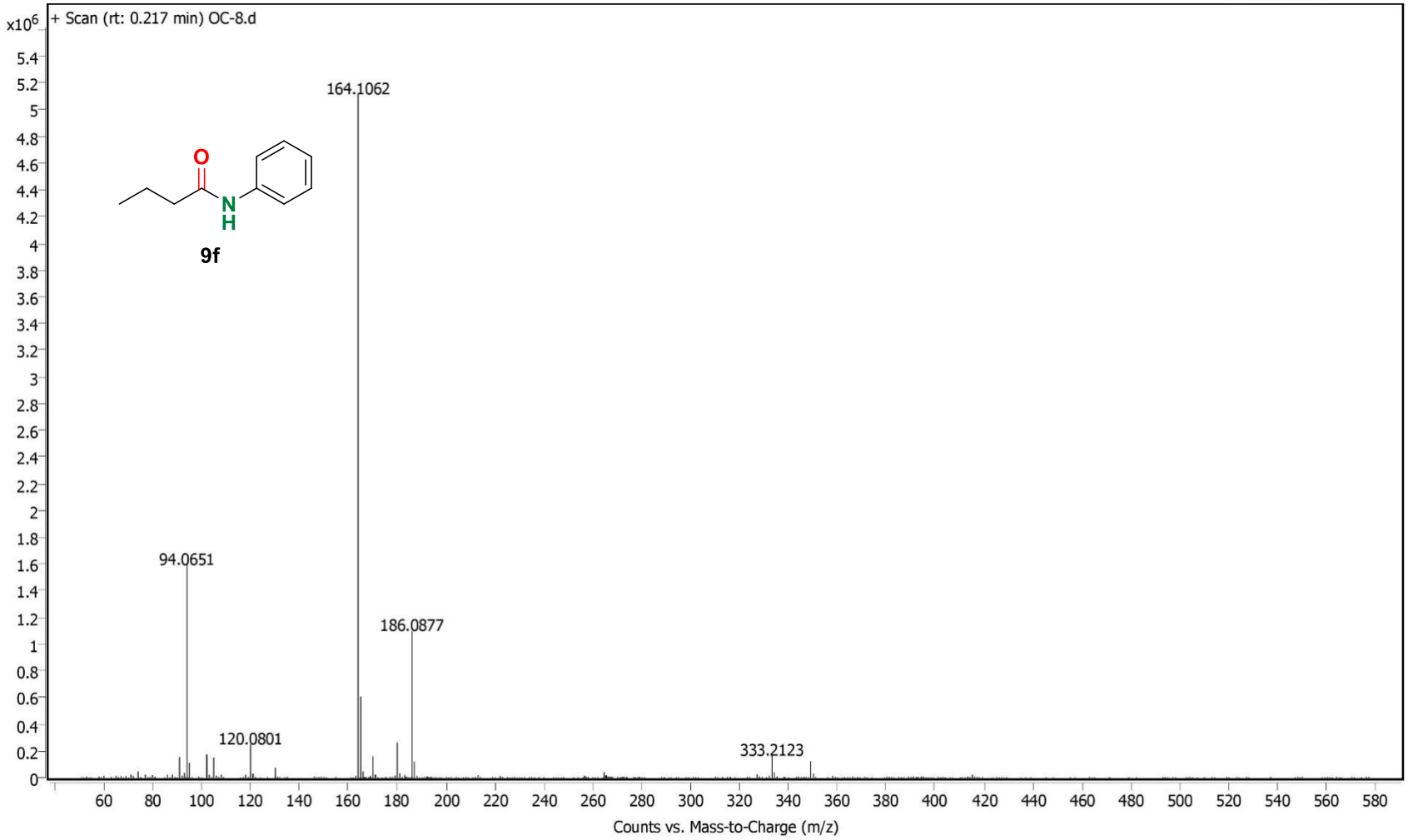


Figure S100. HRMS Spectrum of **9f**

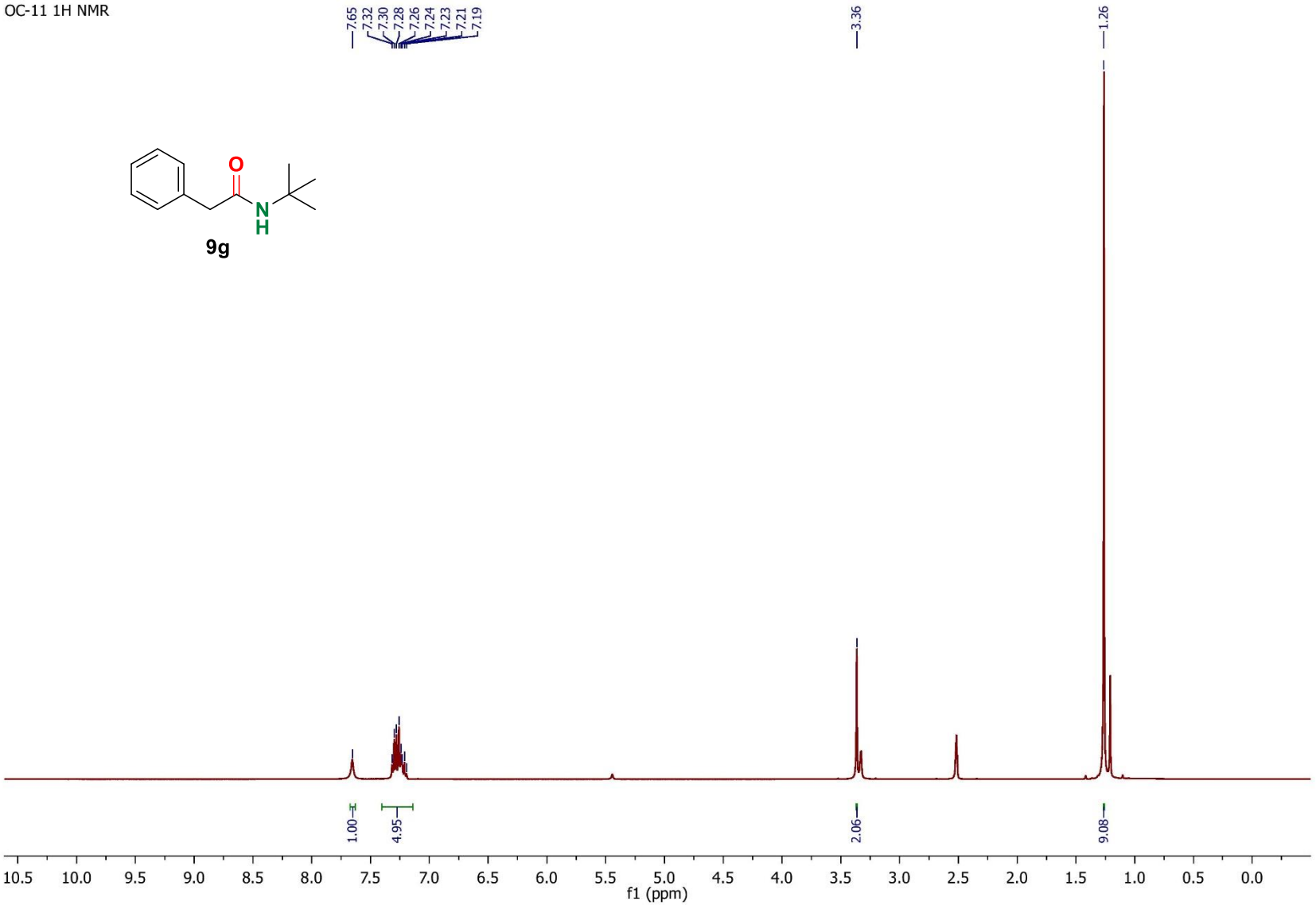


Figure S101. ^{1}H NMR Spectrum of **9g (400MHz, DMSO-d$_6$)**

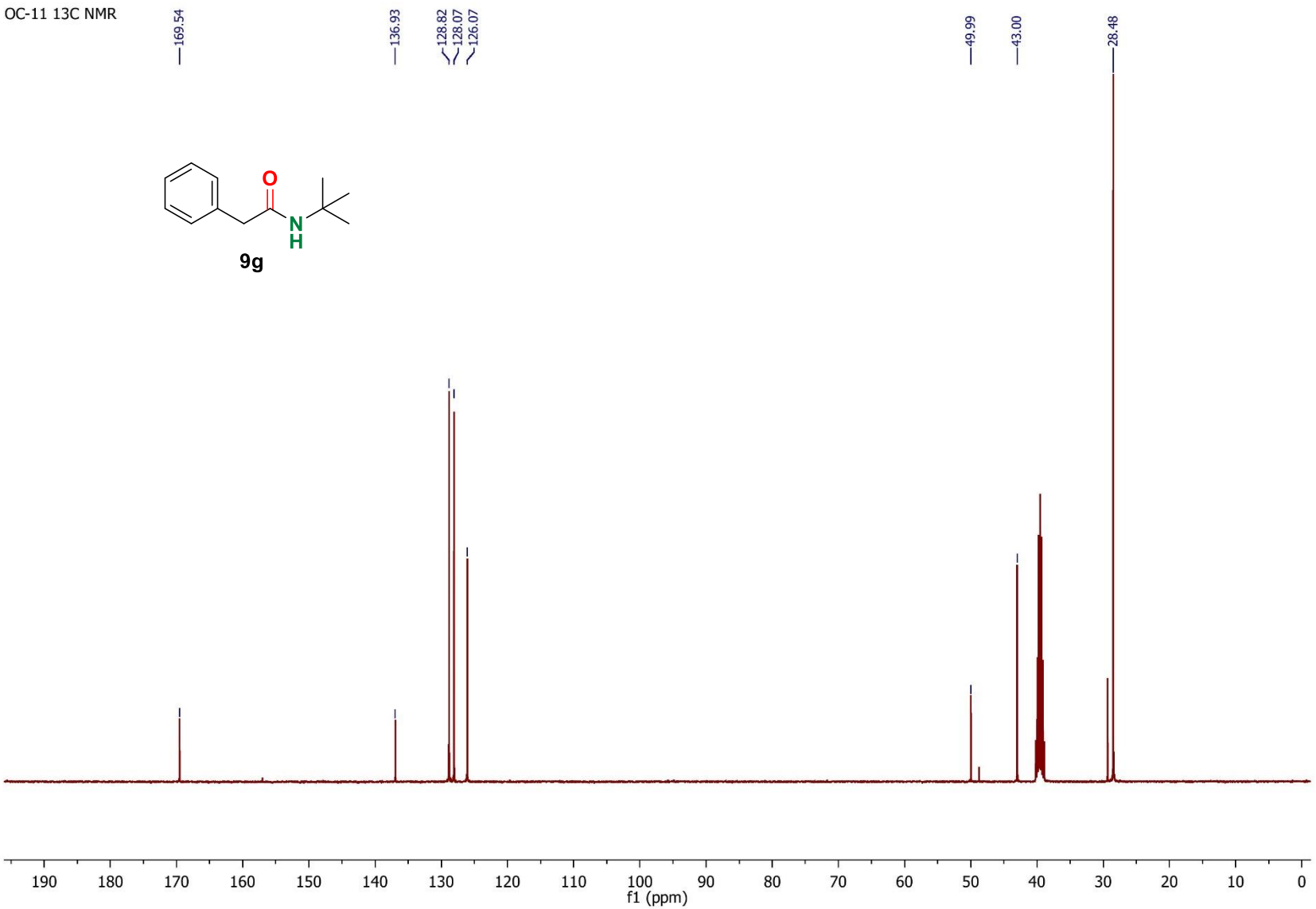


Figure S102. ^{13}C NMR Spectrum of **9g (101MHz, DMSO-d$_6$)**

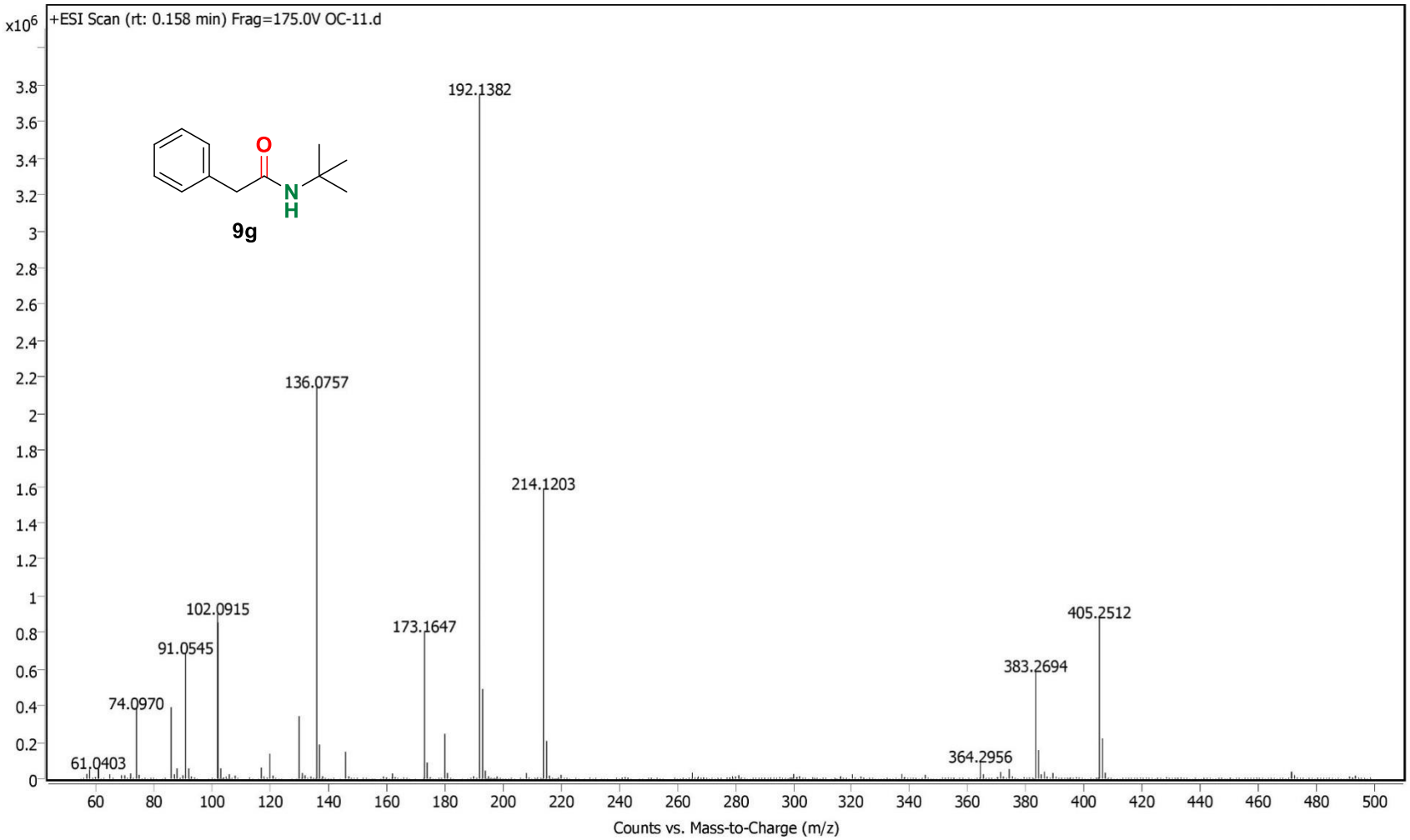


Figure S103. HRMS Spectrum of **9g**

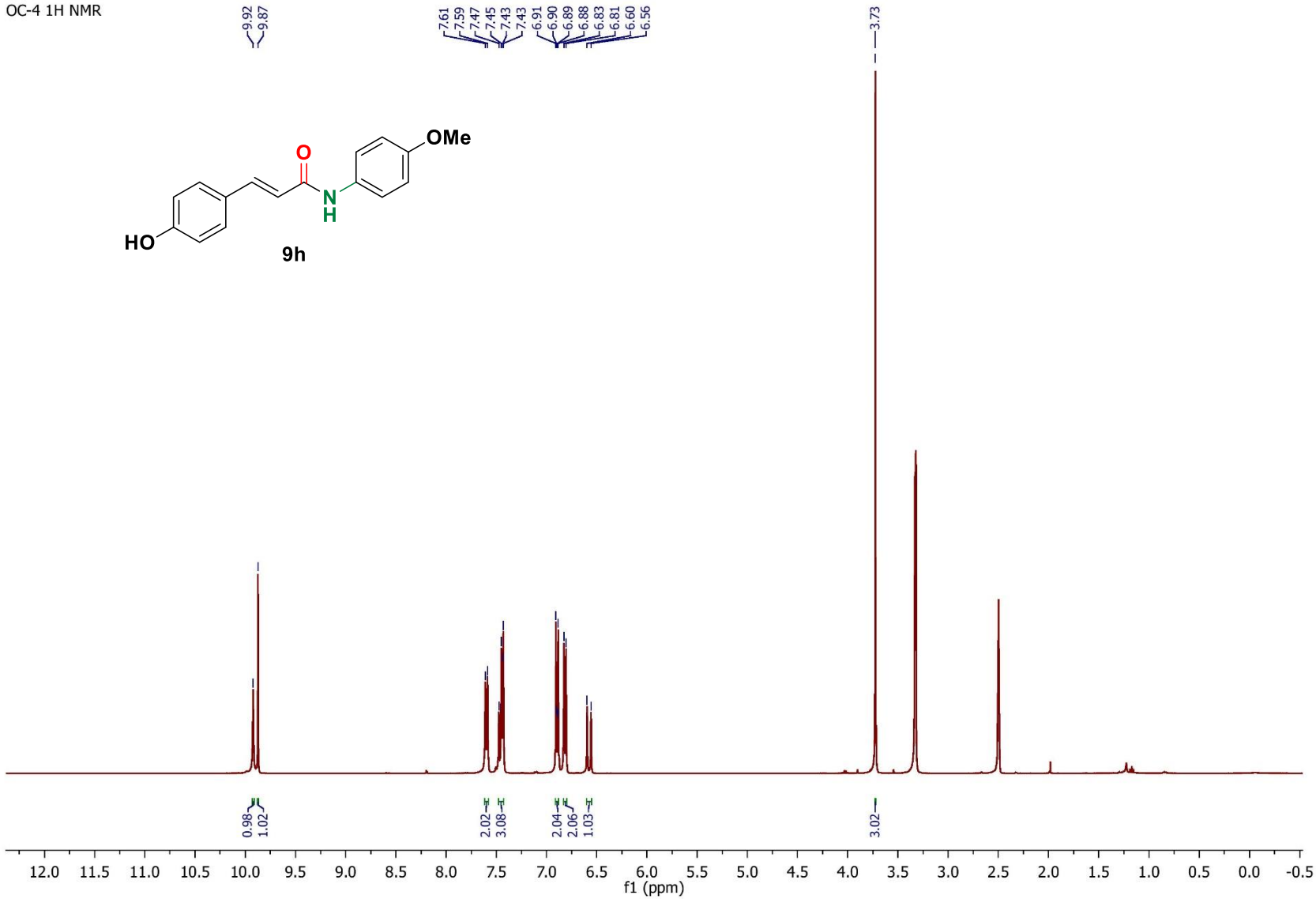


Figure S104. ^{1}H NMR Spectrum of **9h (400MHz, DMSO-d$_6$)**

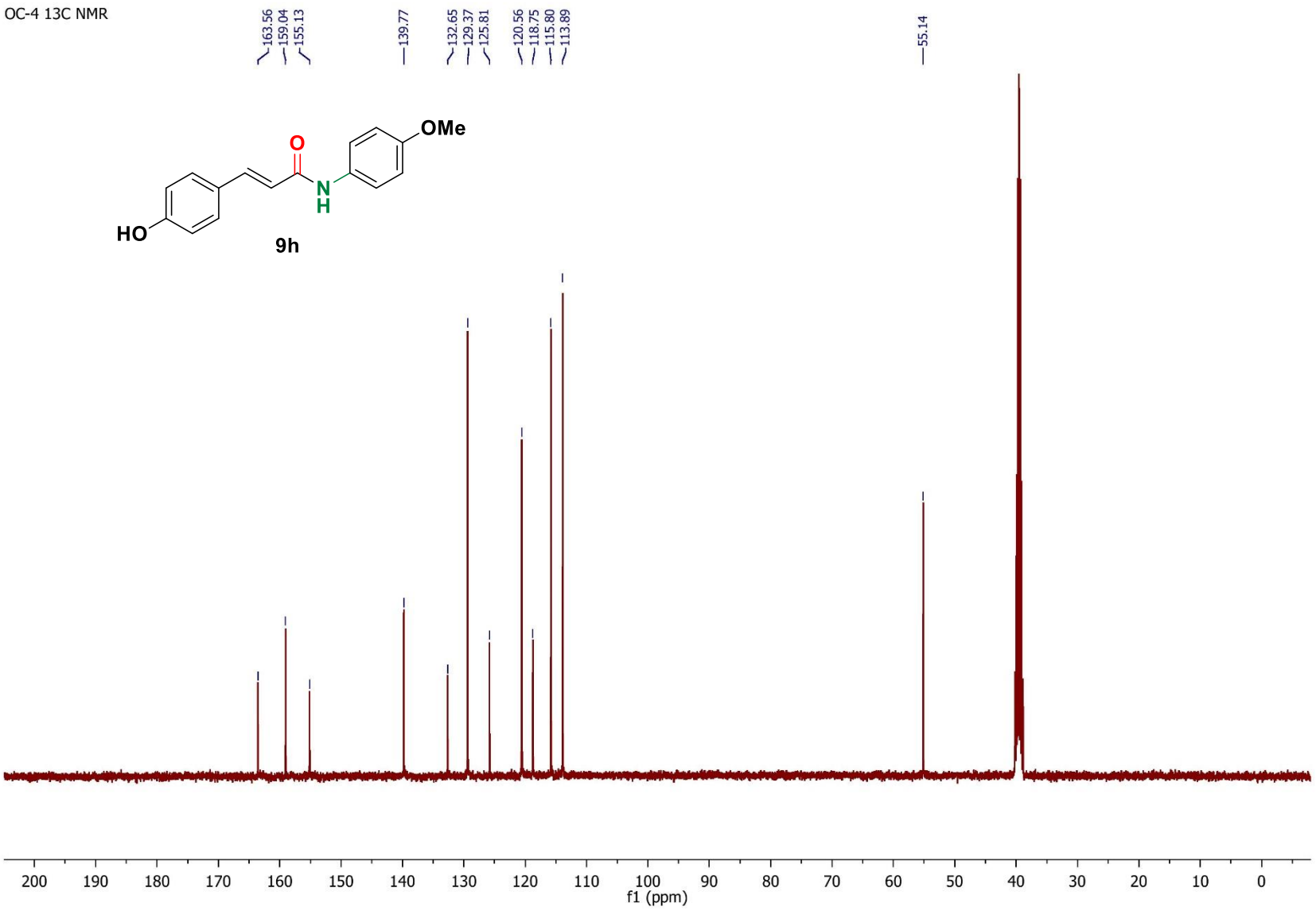


Figure S105. ^{13}C NMR Spectrum of **9h (101MHz, DMSO-d$_6$)**

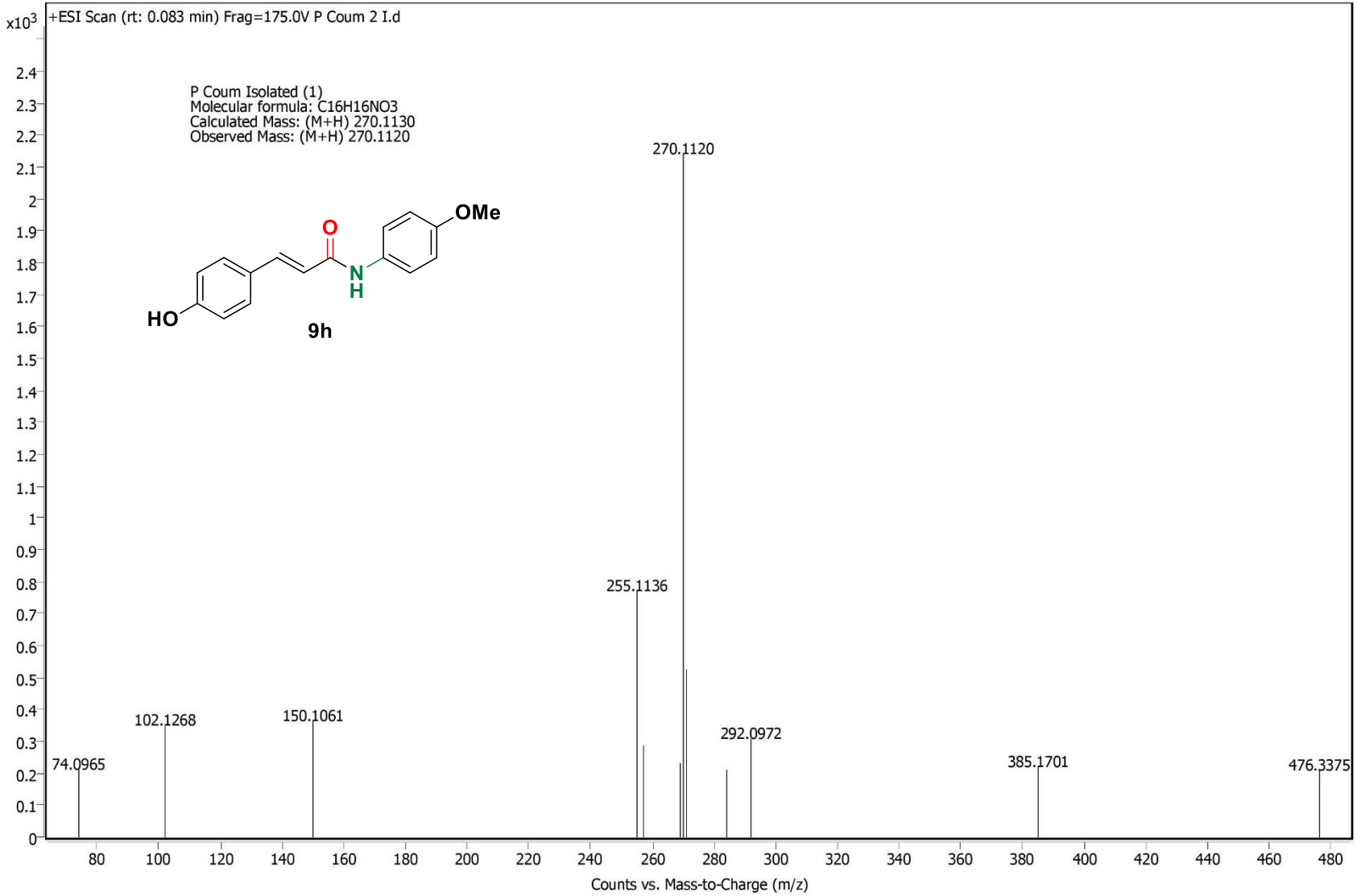


Figure S106. HRMS Spectrum of **9h**

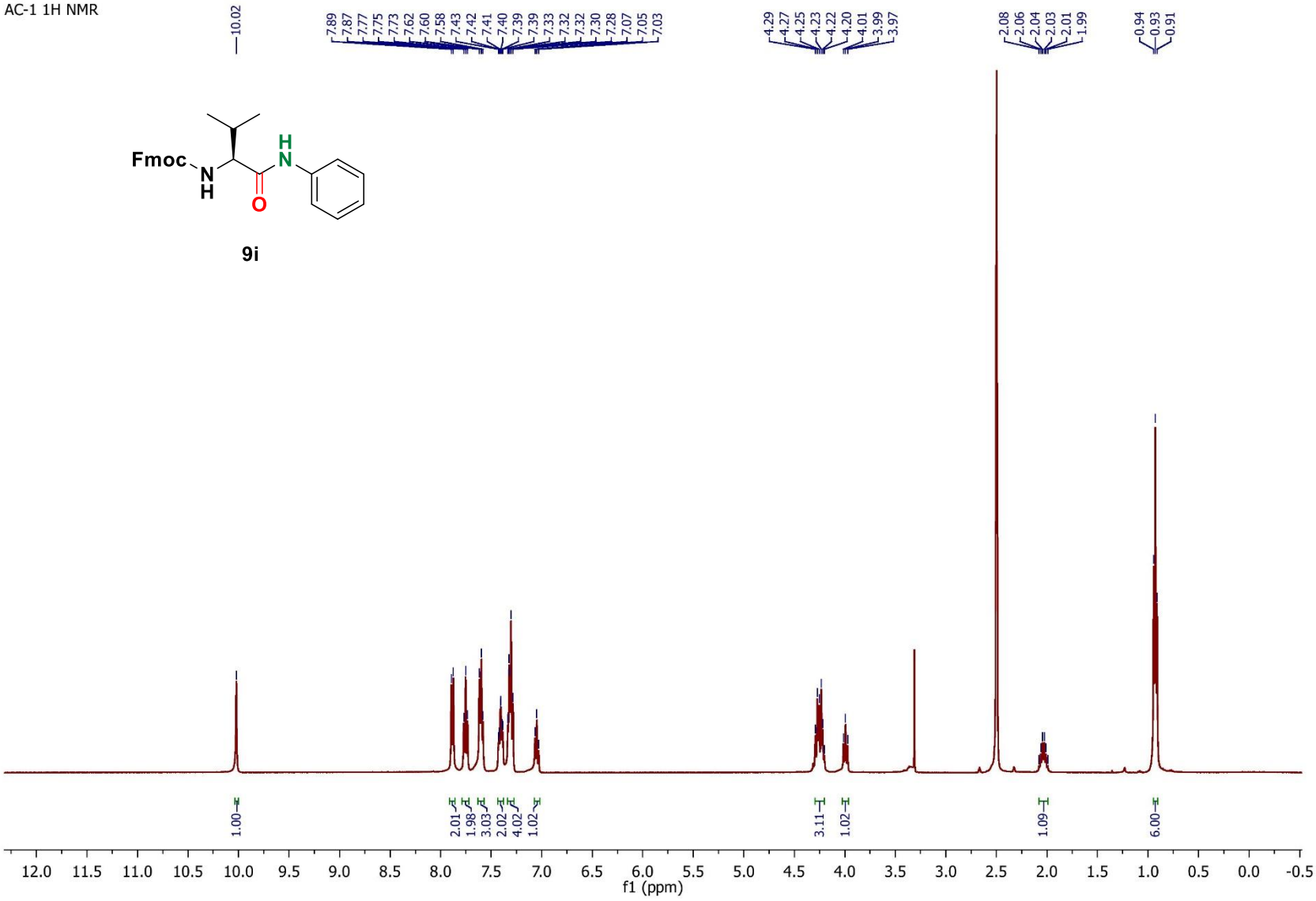


Figure S107. ^{1}H NMR Spectrum of **9i (400MHz, DMSO-d$_6$)**

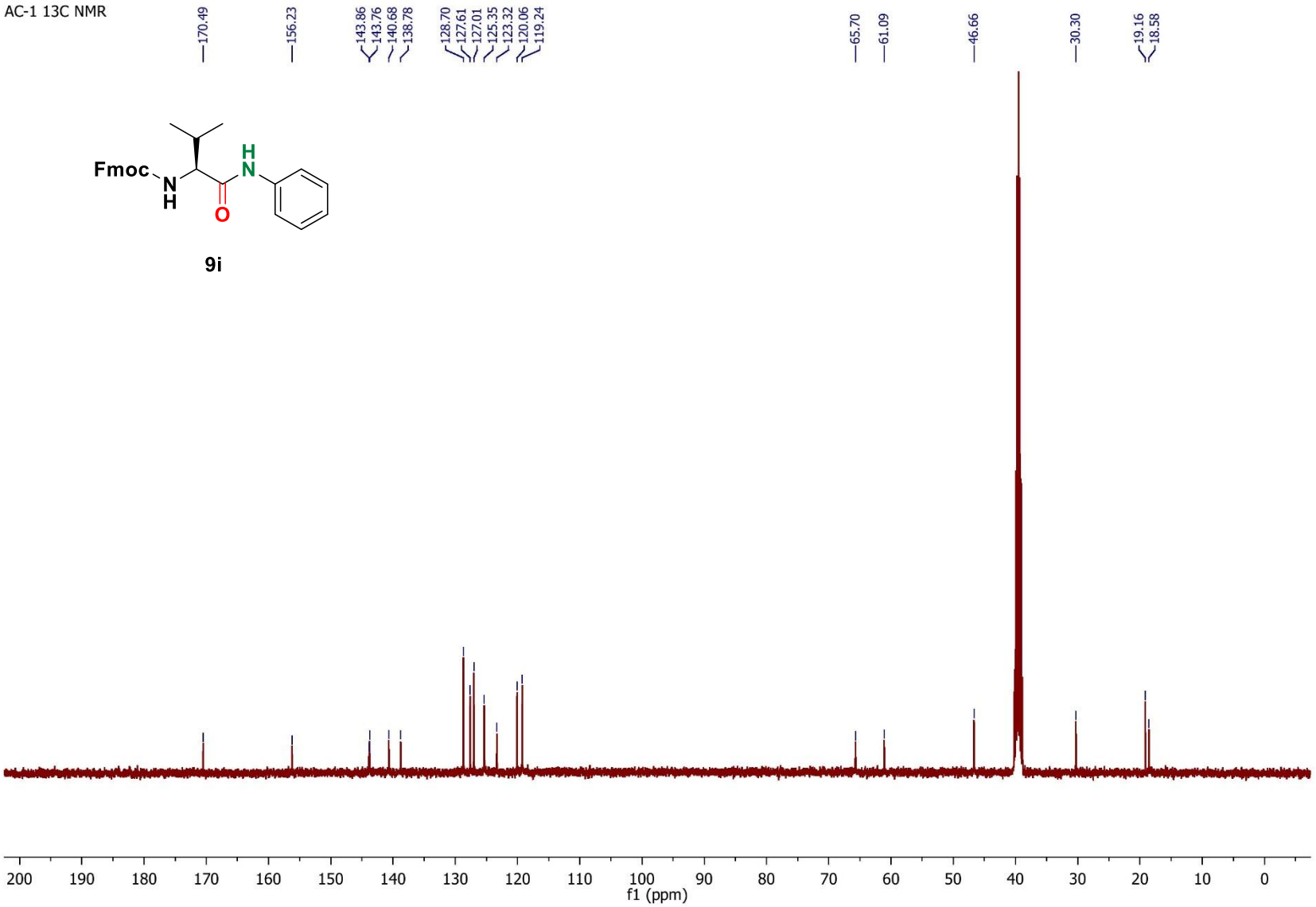


Figure S108. ^{13}C NMR Spectrum of **9i (101MHz, DMSO-d$_6$)**

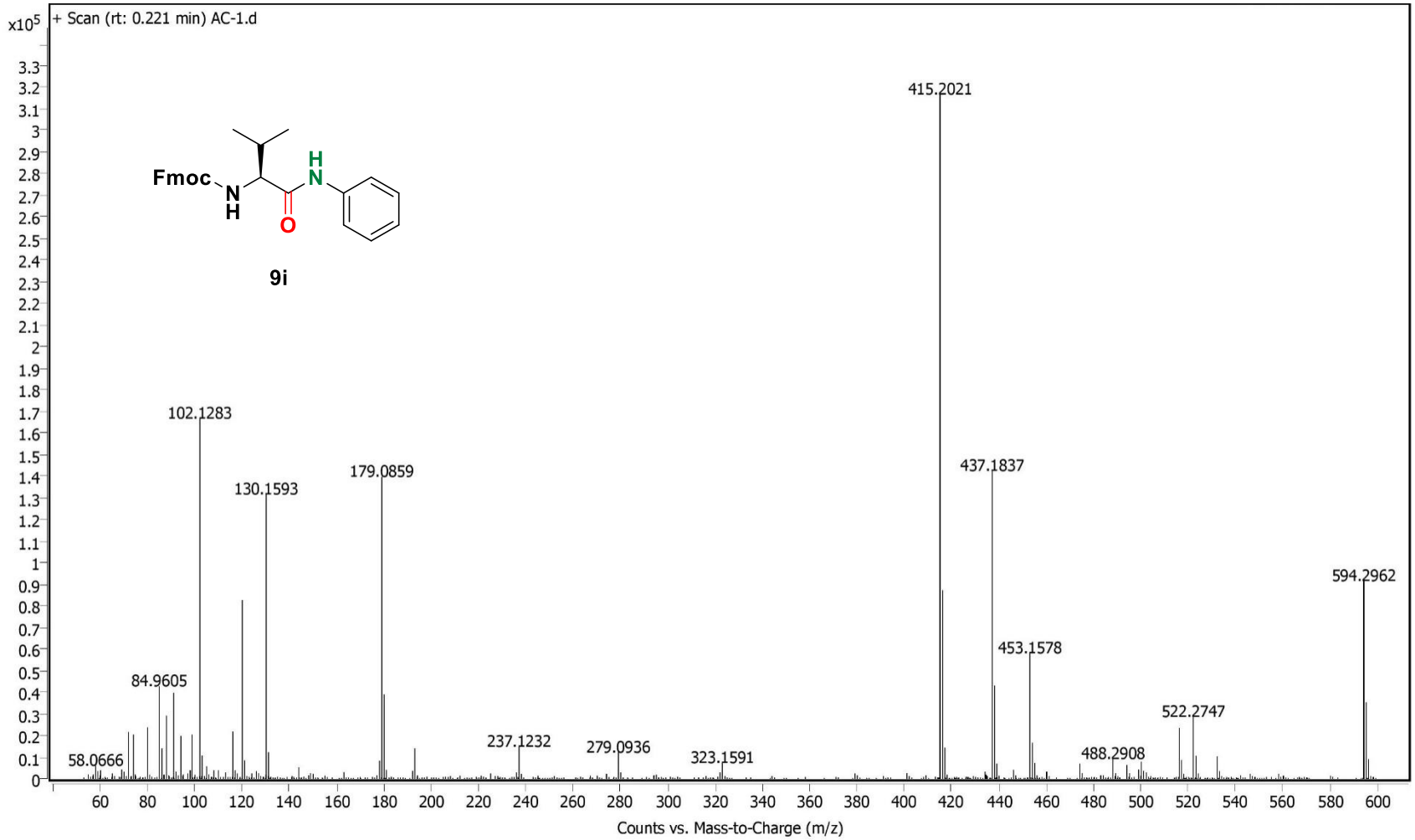


Figure S109. HRMS Spectrum of **9i**

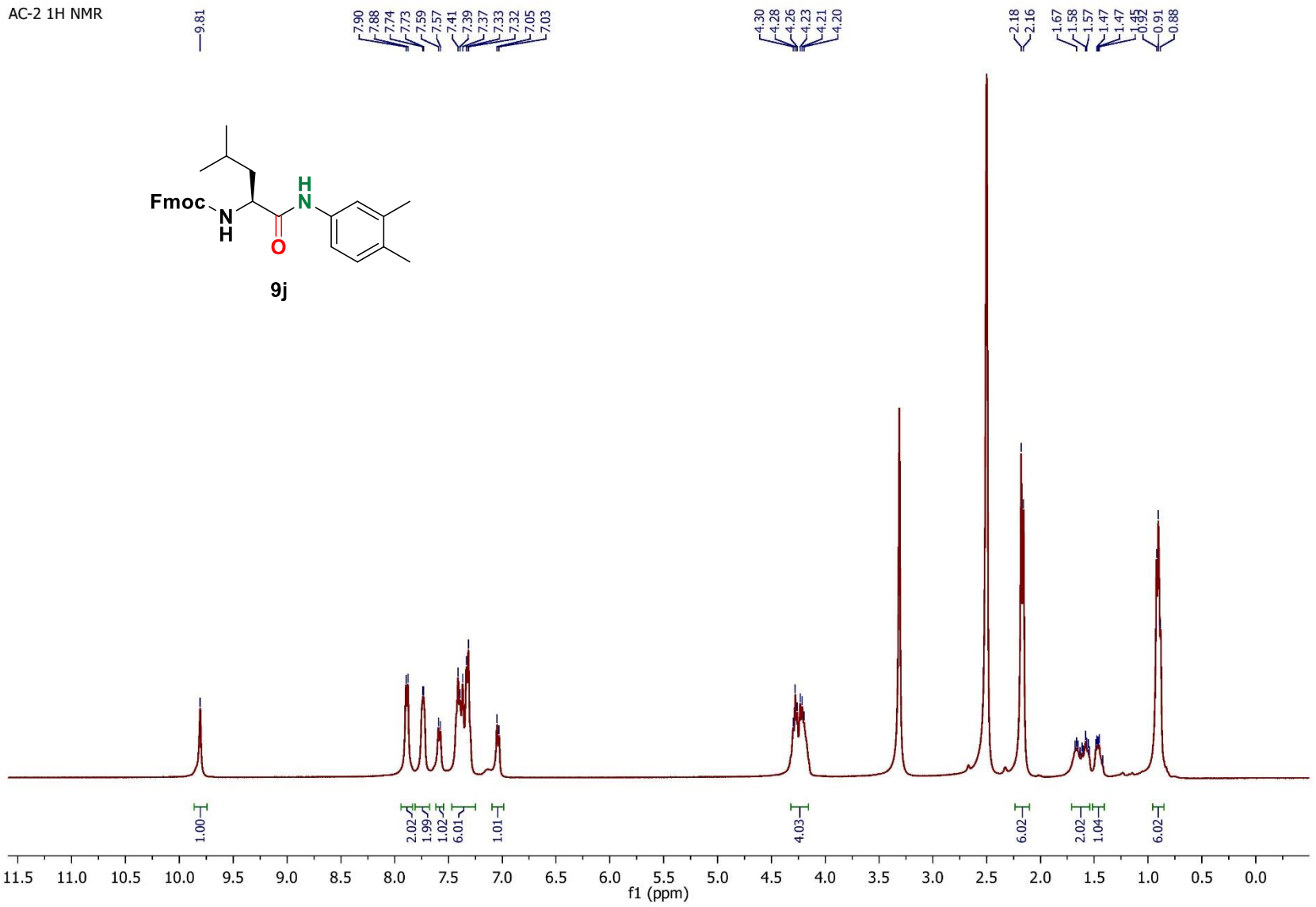


Figure S110. ^{1}H NMR Spectrum of **9j (400MHz, DMSO-d$_6$)**

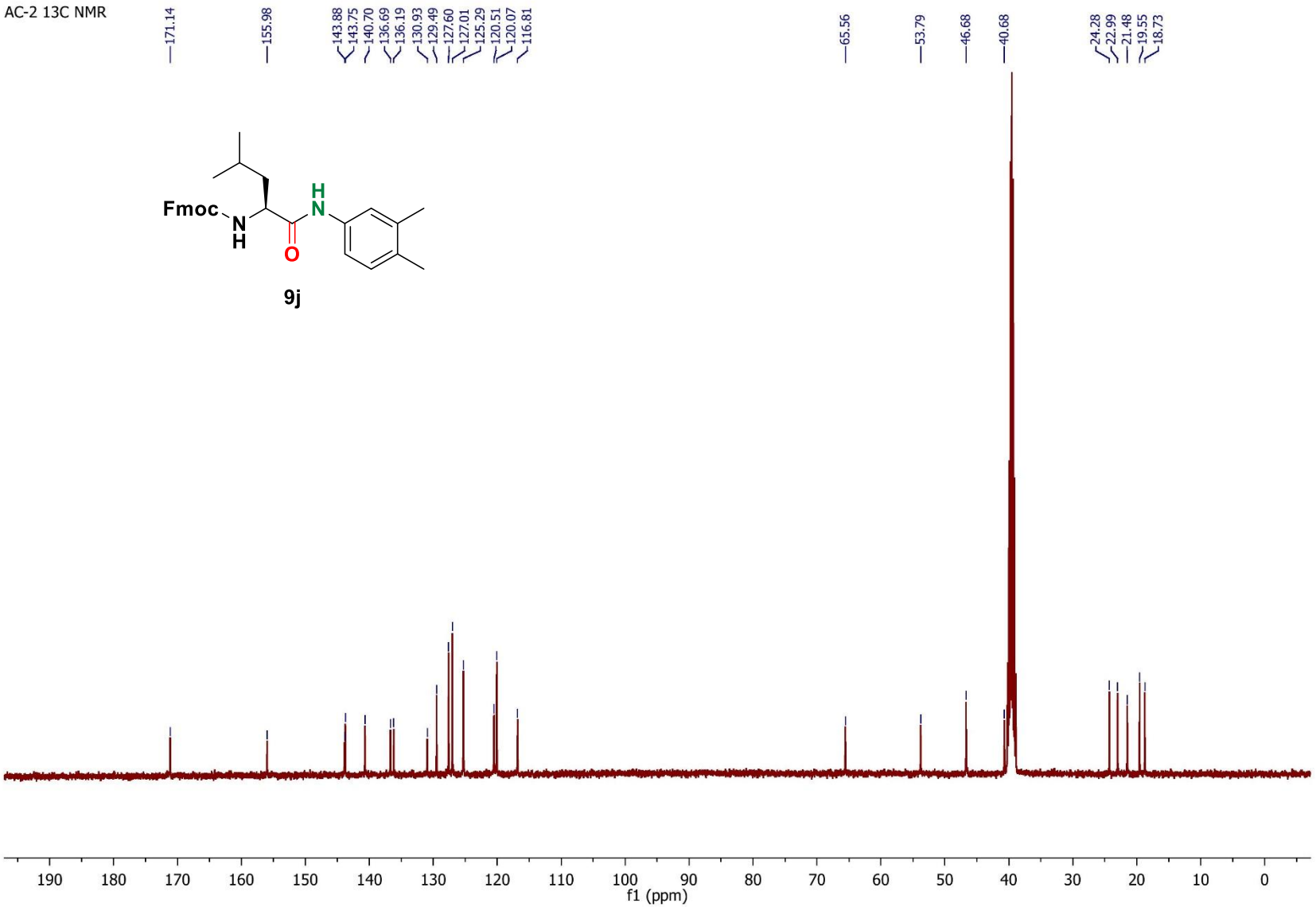


Figure S111. ^{13}C NMR Spectrum of **9j (101MHz, DMSO-d$_6$)**

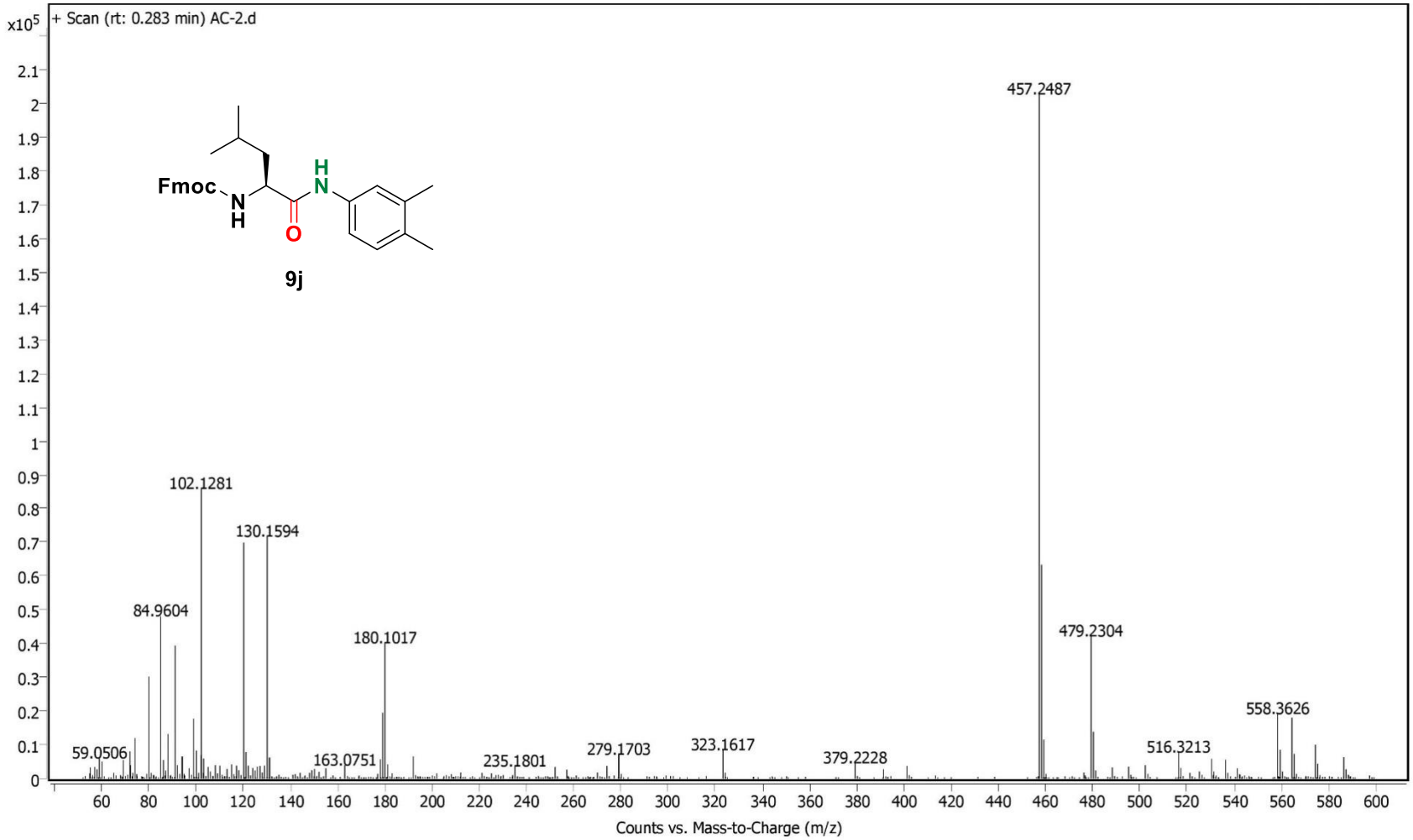


Figure S112. HRMS Spectrum of **9j**

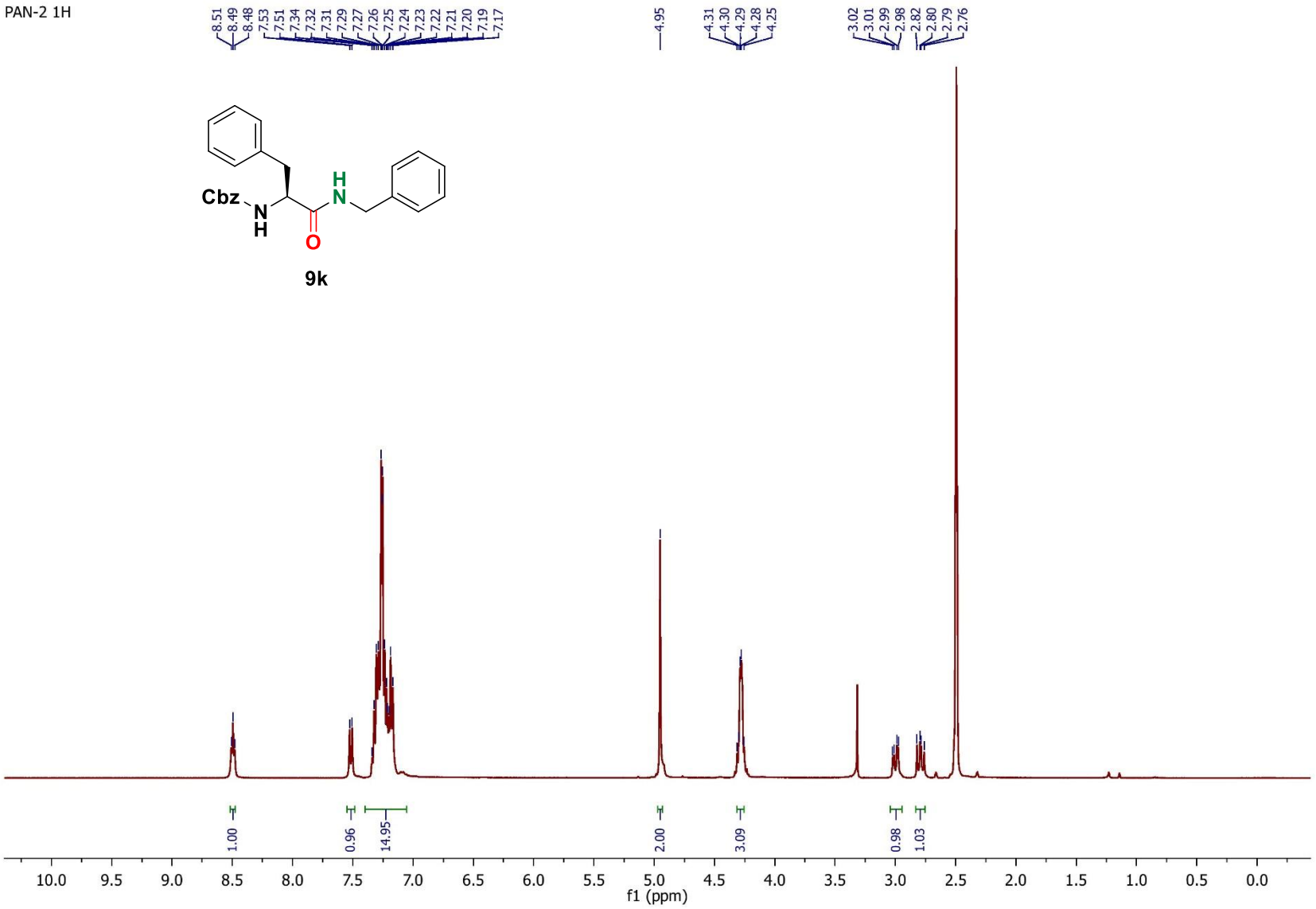


Figure S113. ^{1}H NMR Spectrum of **9k(400MHz, DMSO-d$_6$)**

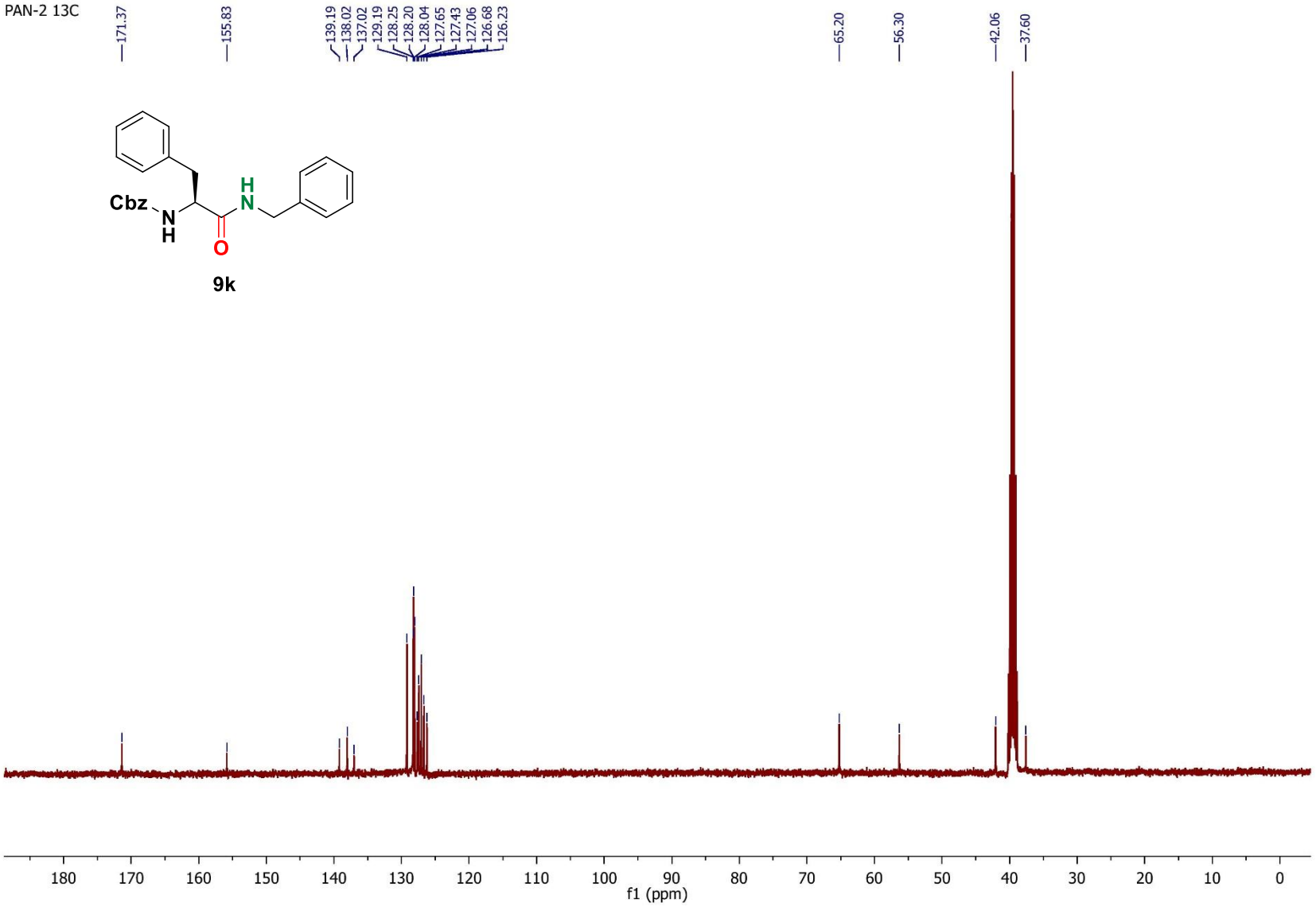


Figure S114. ^{13}C NMR Spectrum of **9k (101MHz, DMSO-d$_6$)**

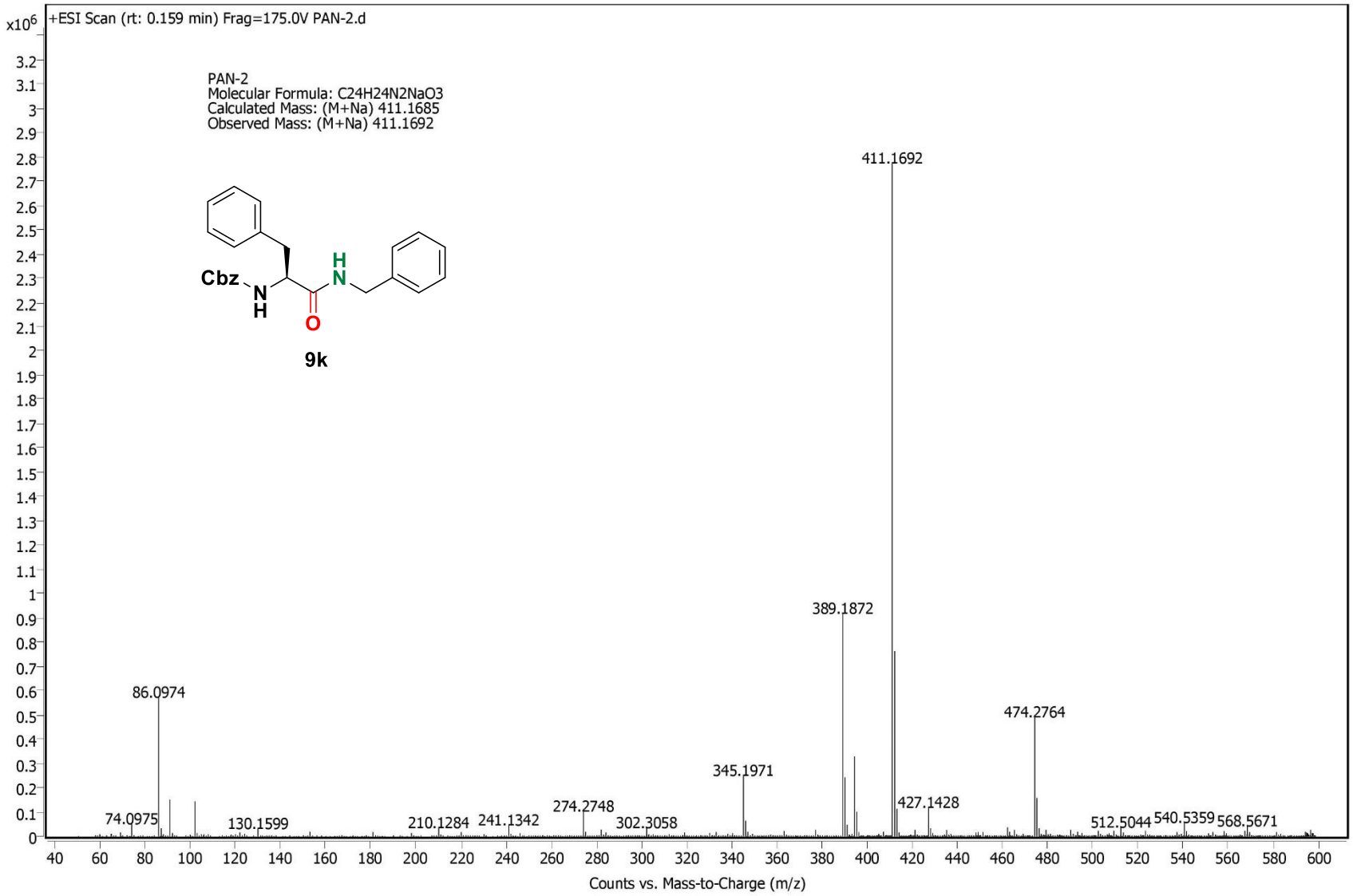


Figure S115. HRMS Spectrum of **9k**

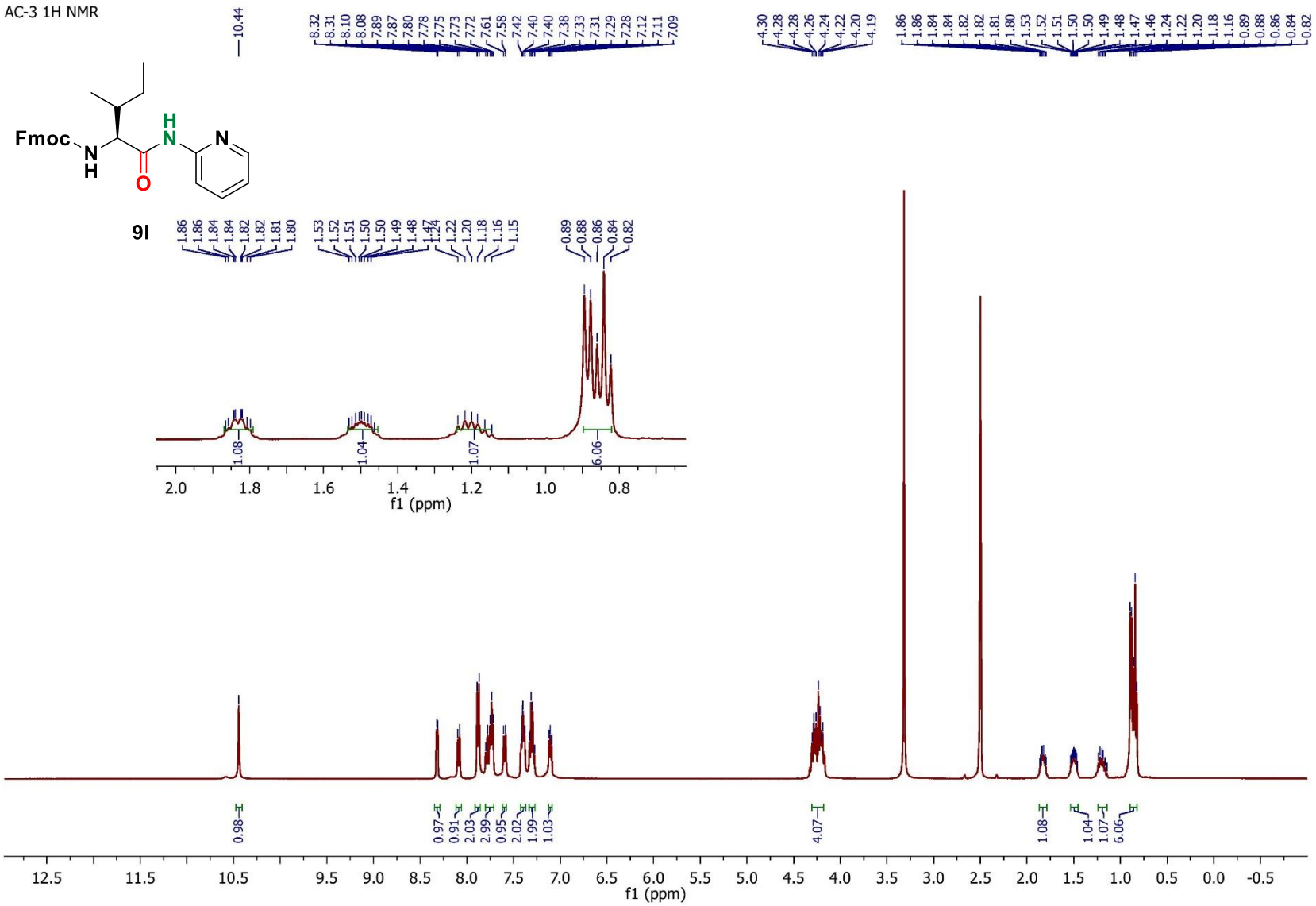


Figure S116. ^{1}H NMR Spectrum of **9l(400MHz, DMSO-d$_6$)**

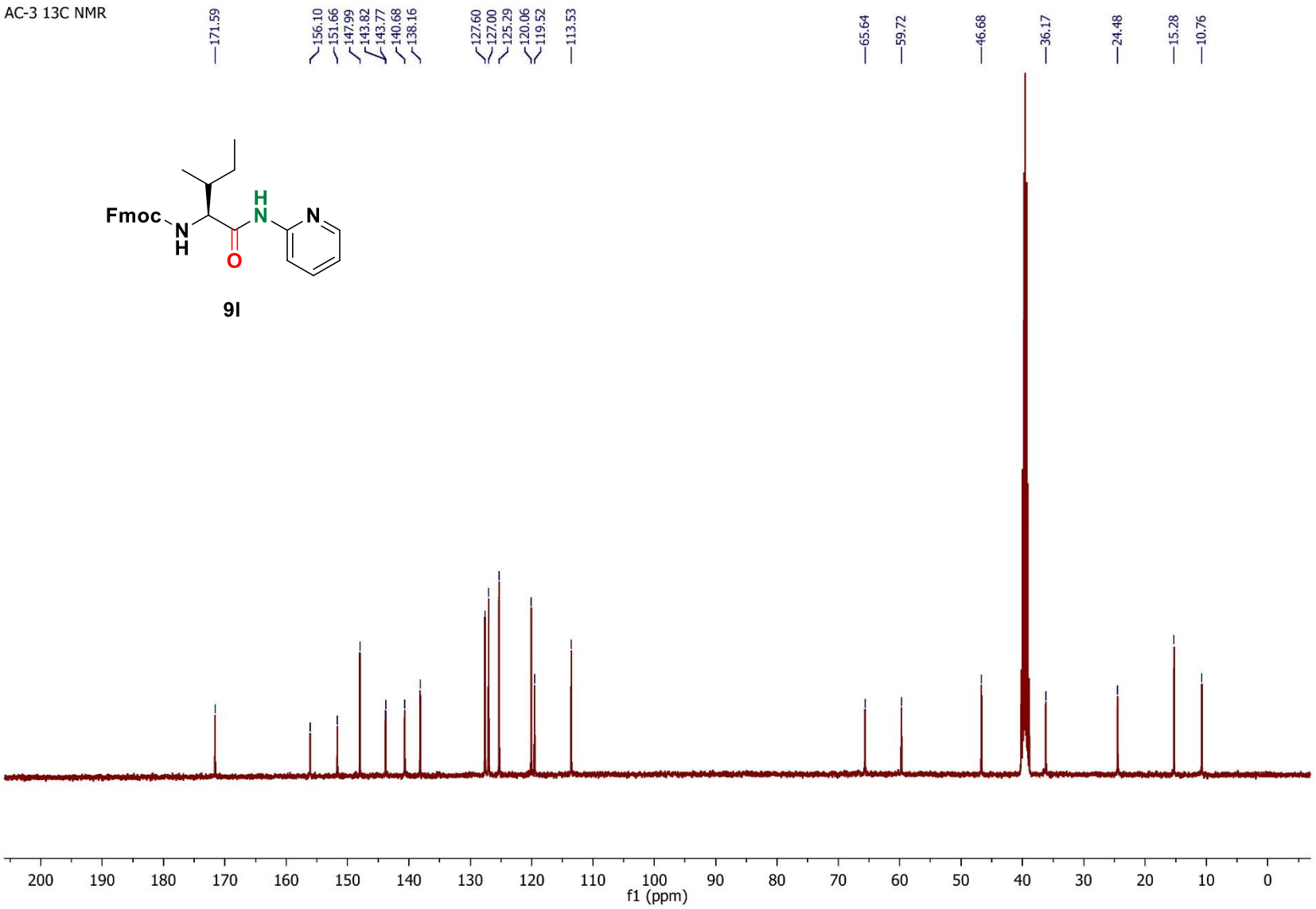


Figure S117. ^{13}C NMR Spectrum of **9l (101MHz, DMSO-d$_6$)**

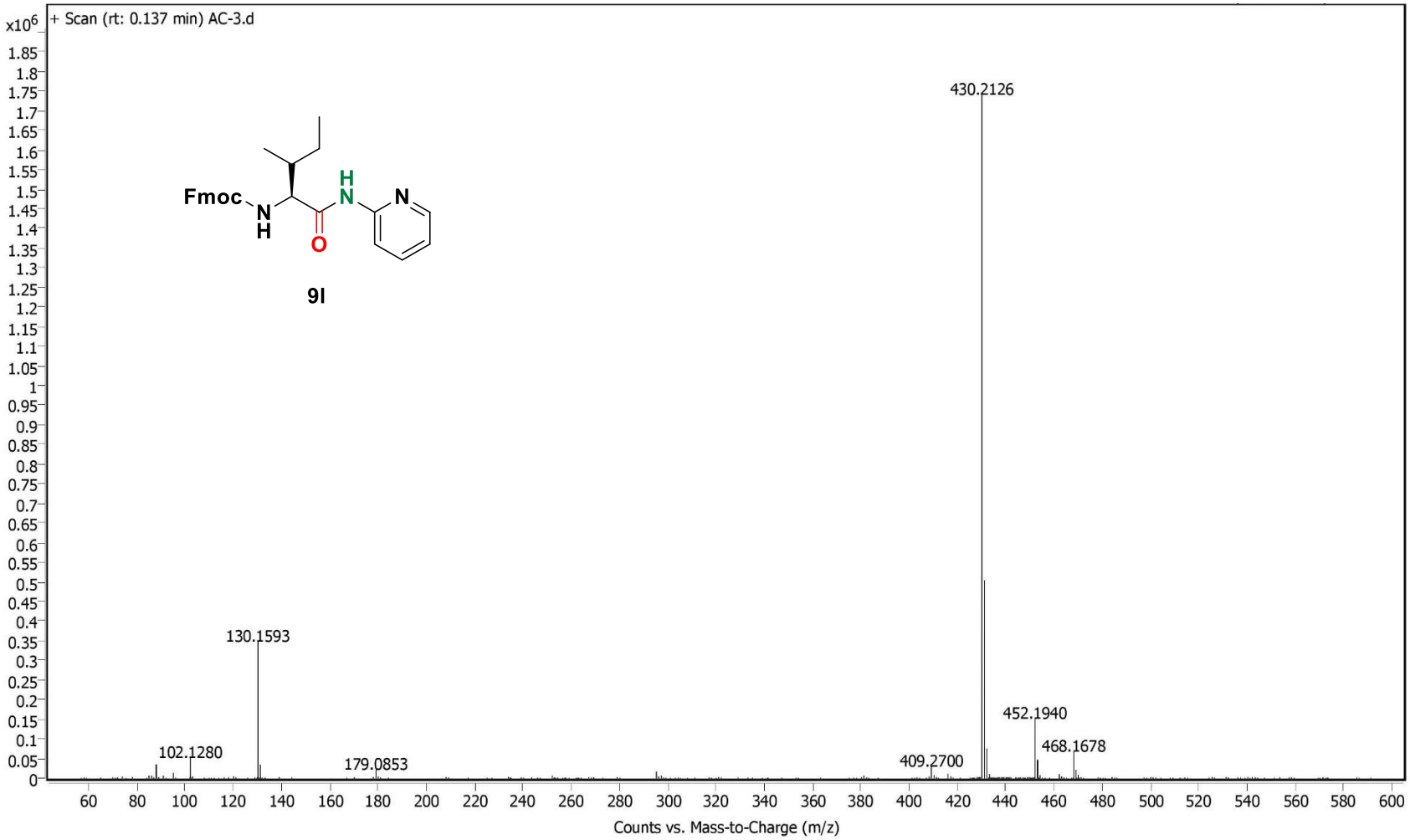


Figure S118. HRMS Spectrum of **9l**

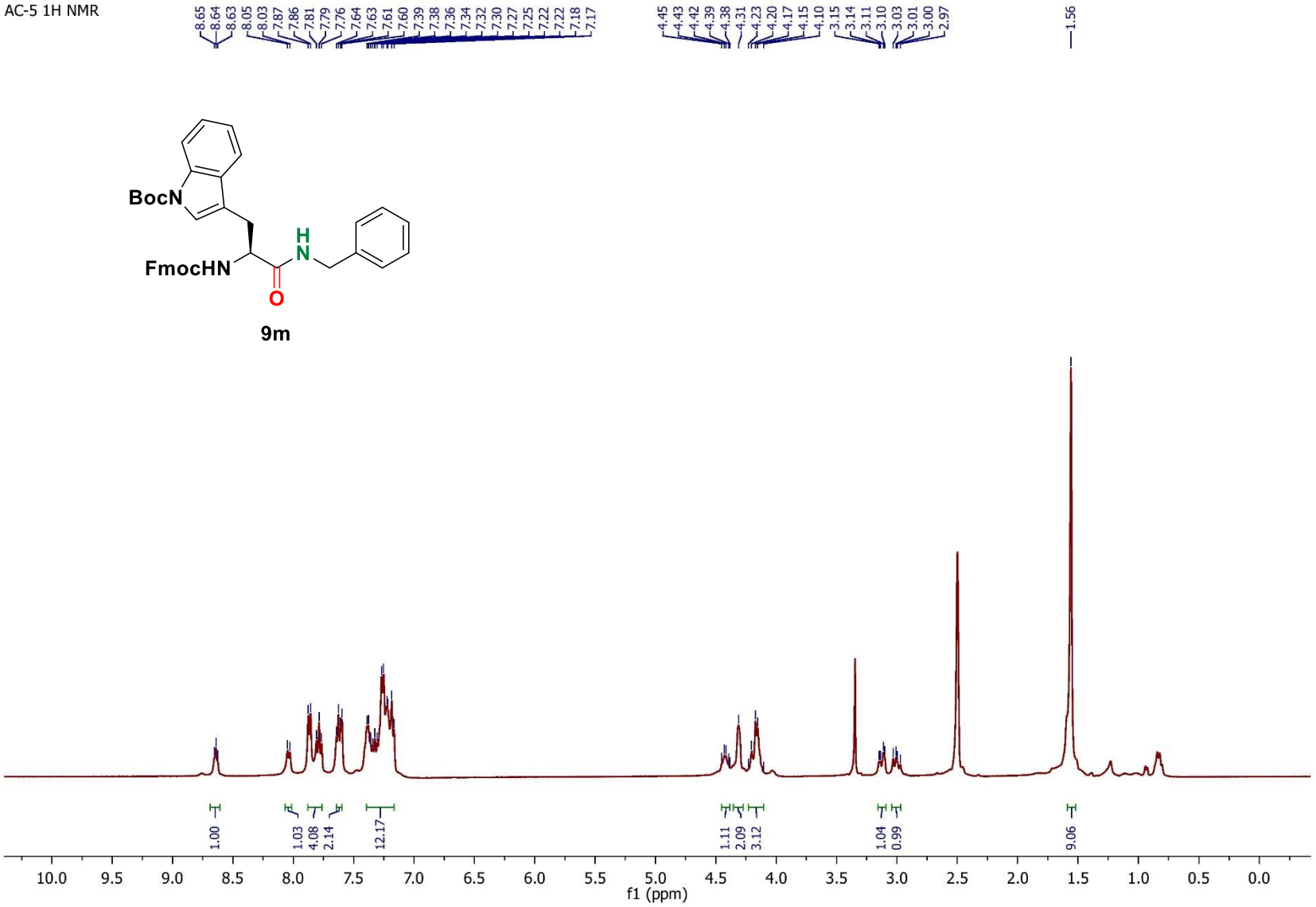


Figure S119. ^{1}H NMR Spectrum of **9m (400MHz, DMSO-d$_6$)**

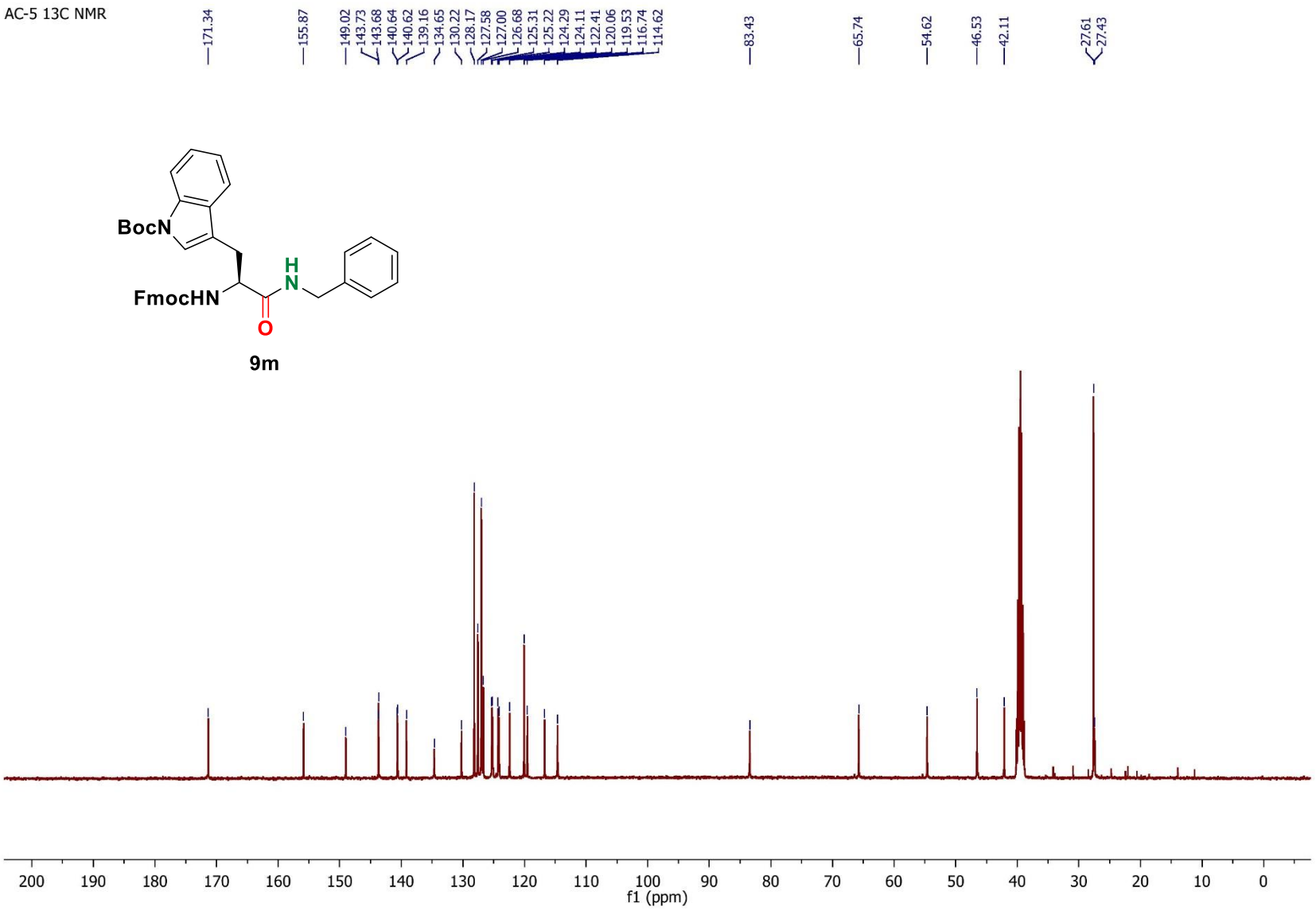


Figure S120. ^{13}C NMR Spectrum of **9m (101MHz, DMSO-d$_6$)**

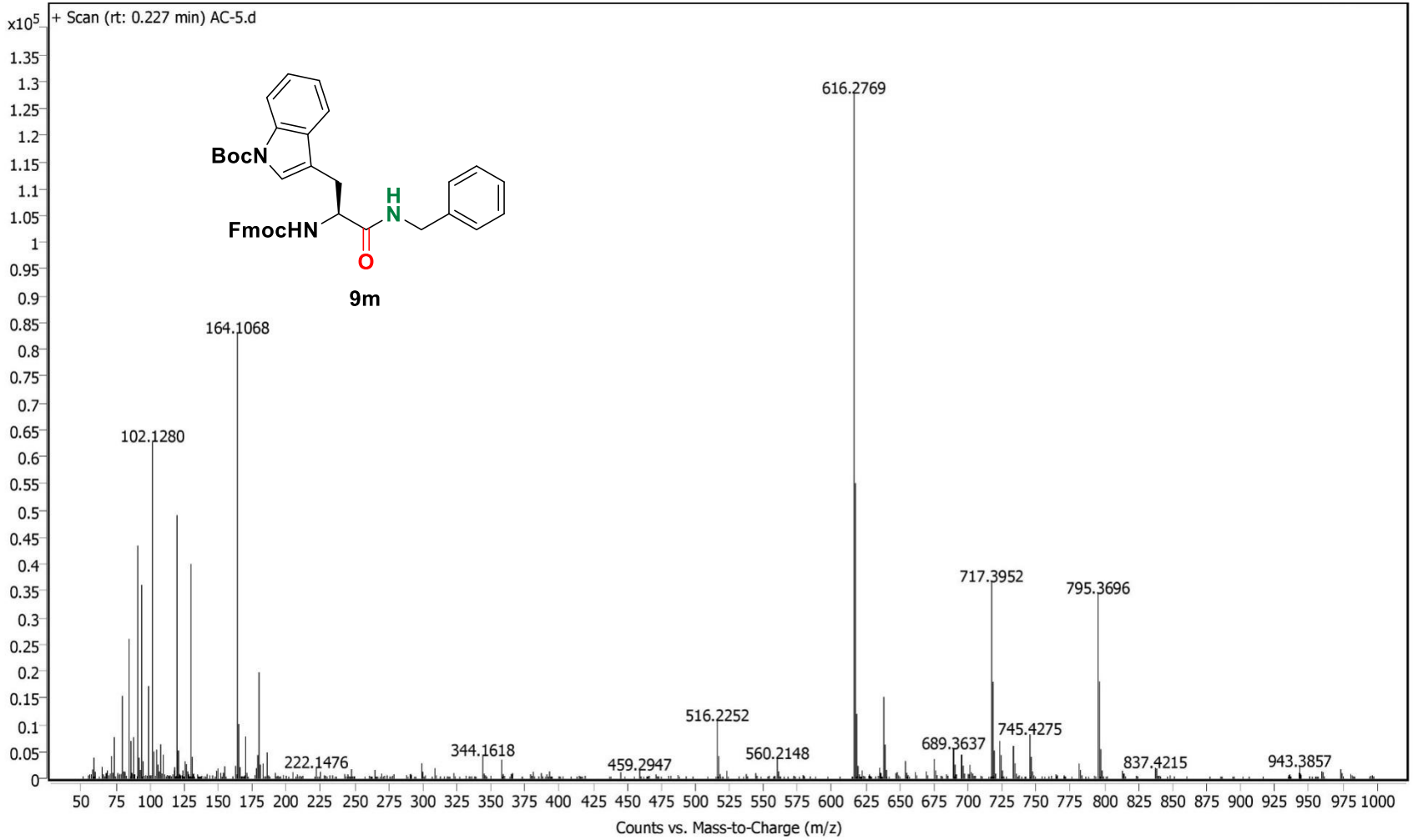


Figure S121. HRMS Spectrum of **9m**

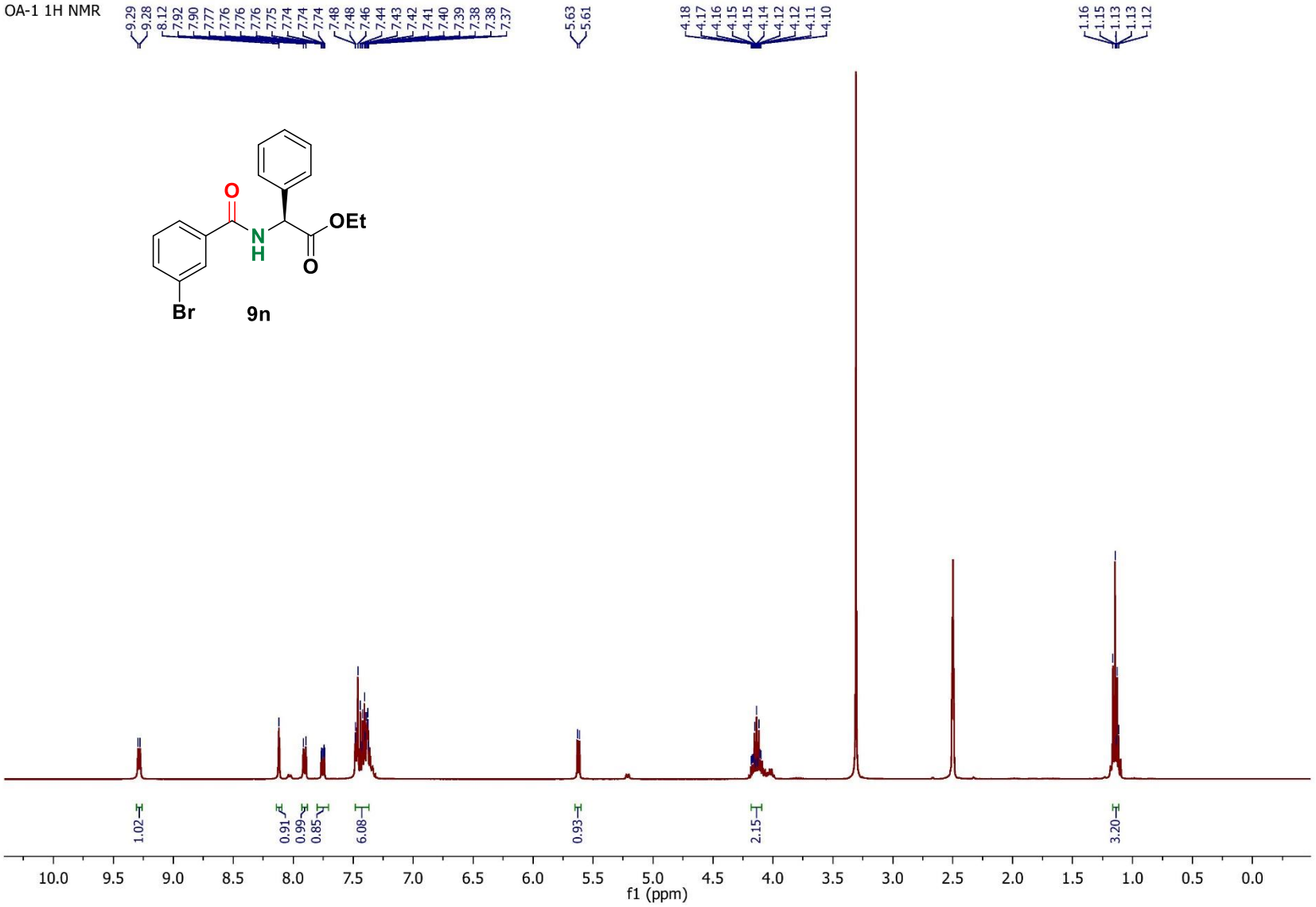


Figure S122. ^{1}H NMR Spectrum of **9n (400MHz, DMSO-d$_6$)**

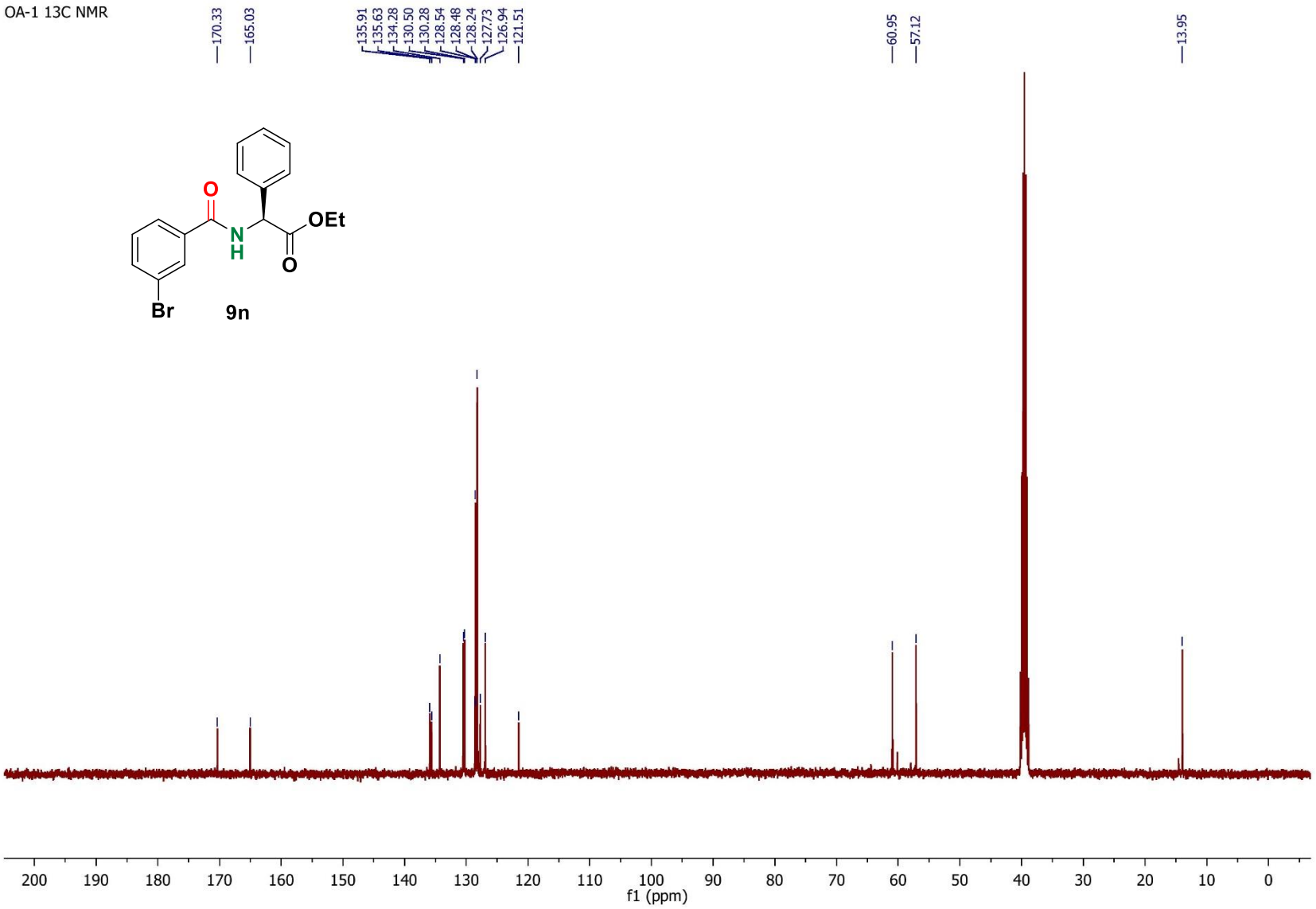


Figure S123. ^{13}C NMR Spectrum of **9n (101MHz, DMSO-d$_6$)**

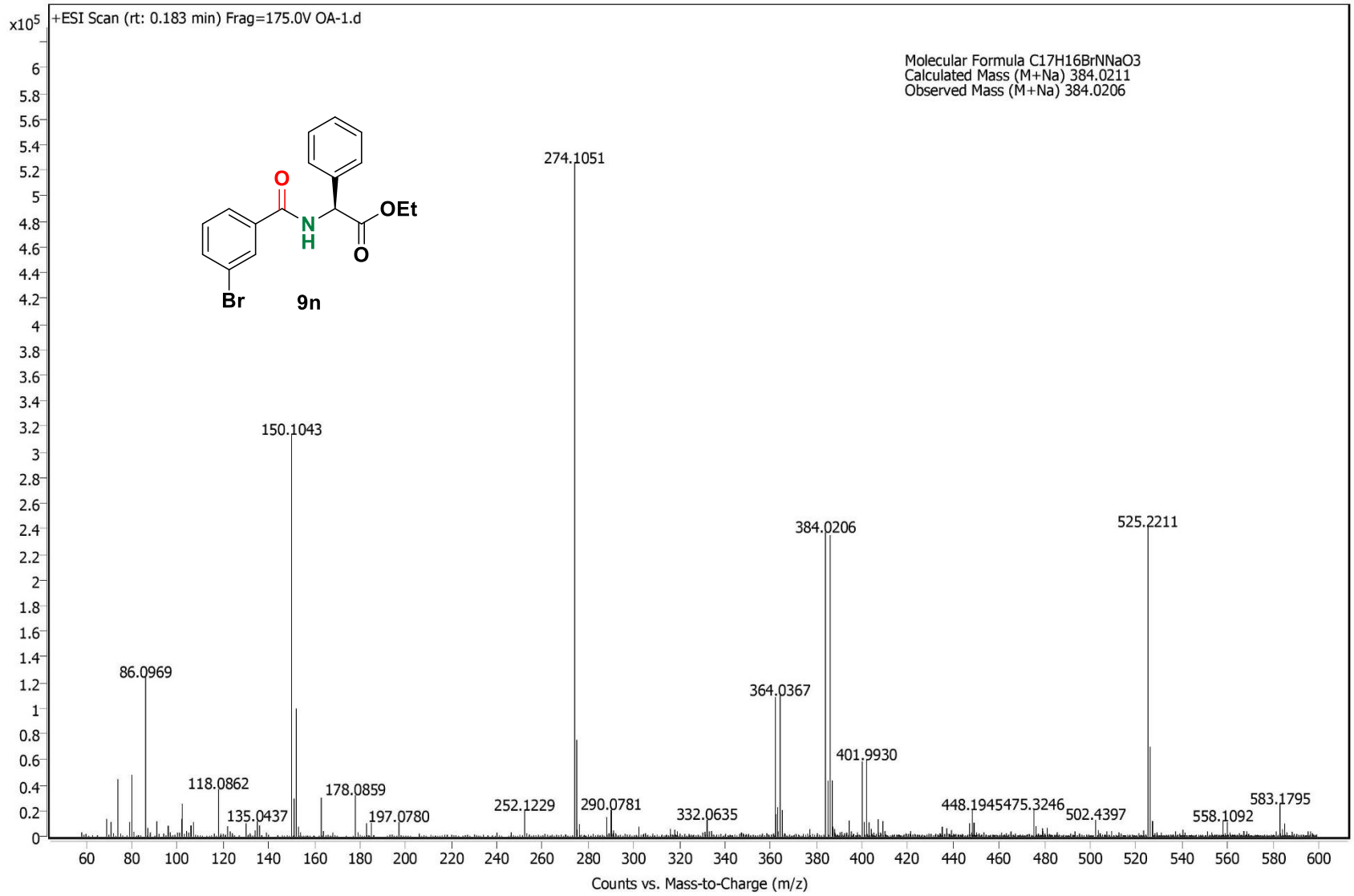


Figure S124. HRMS Spectrum of **9n**

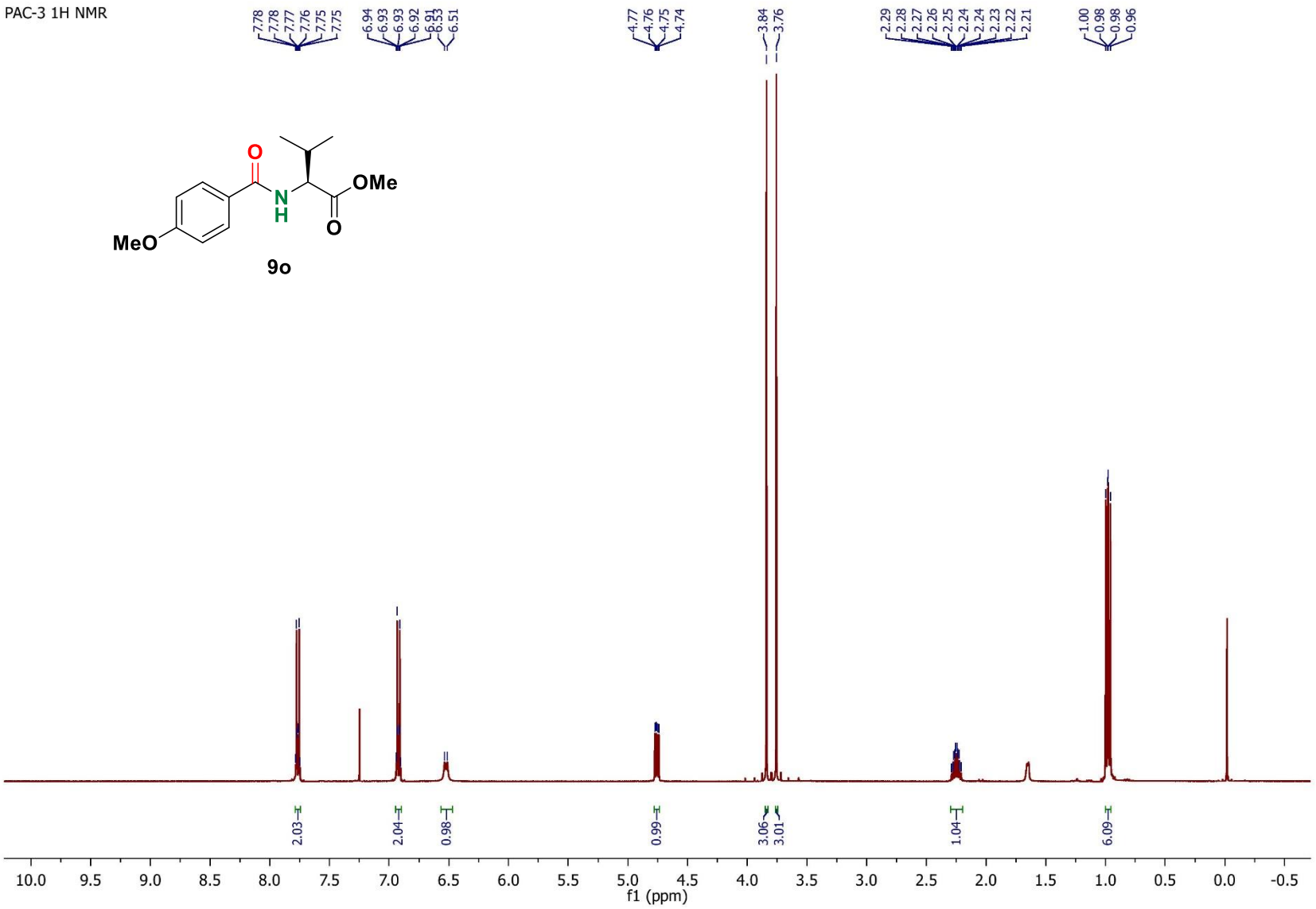


Figure S125. ^{1}H NMR Spectrum of **9o (400MHz, $CDCl_3$)**

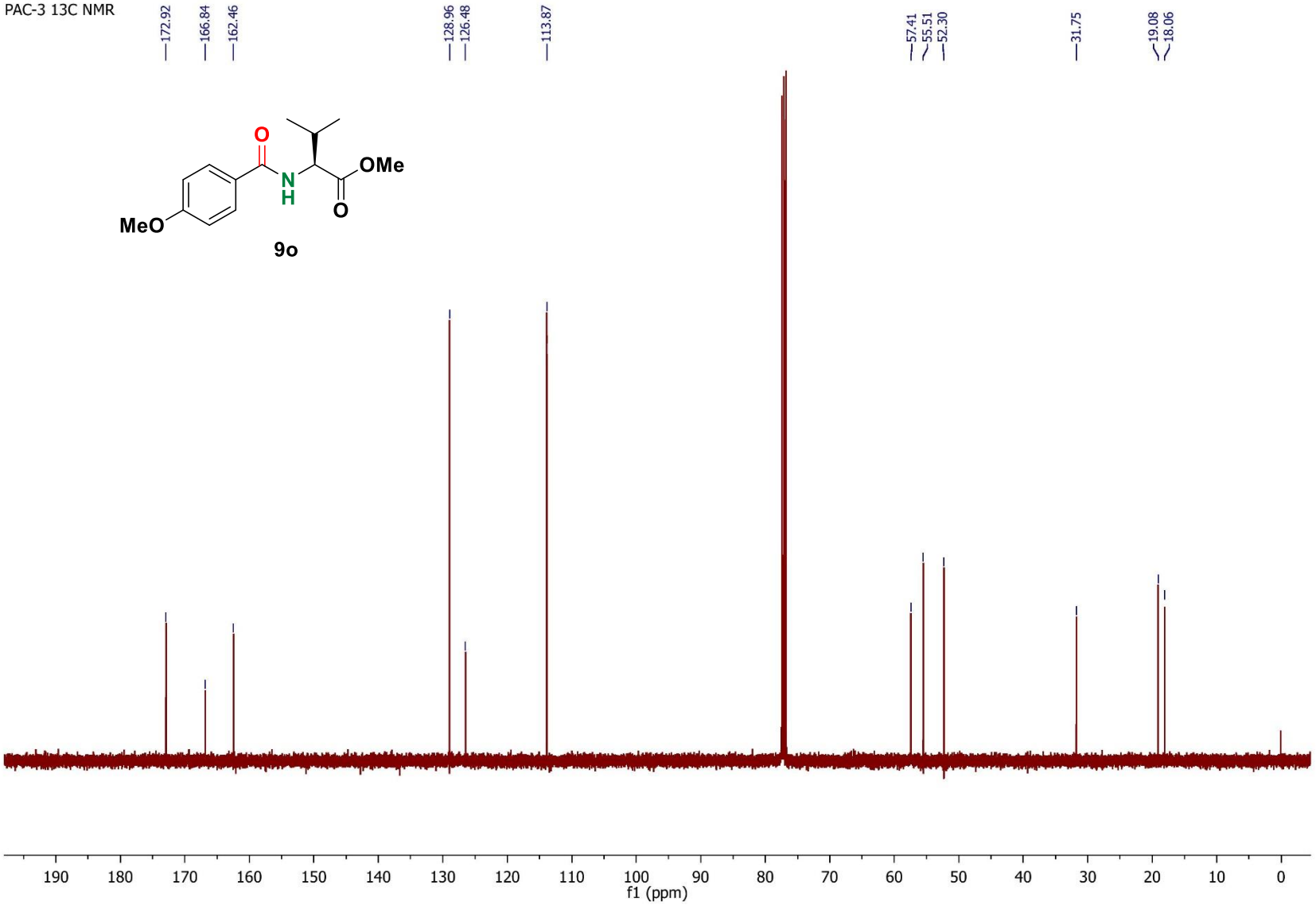


Figure S126. ^{13}C NMR Spectrum of **9o (101MHz, $CDCl_3$)**

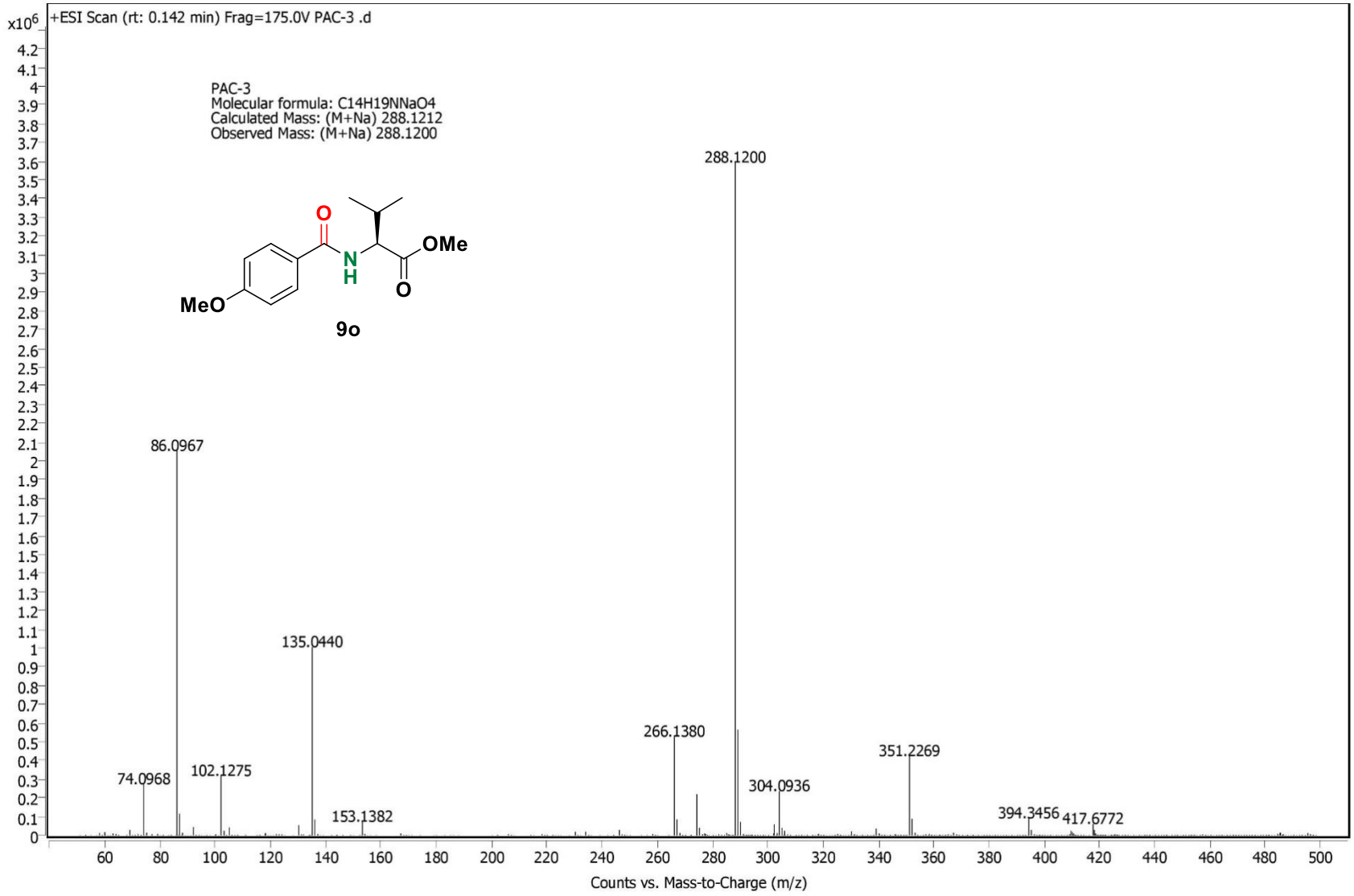


Figure S127. HRMS Spectrum of **9o**

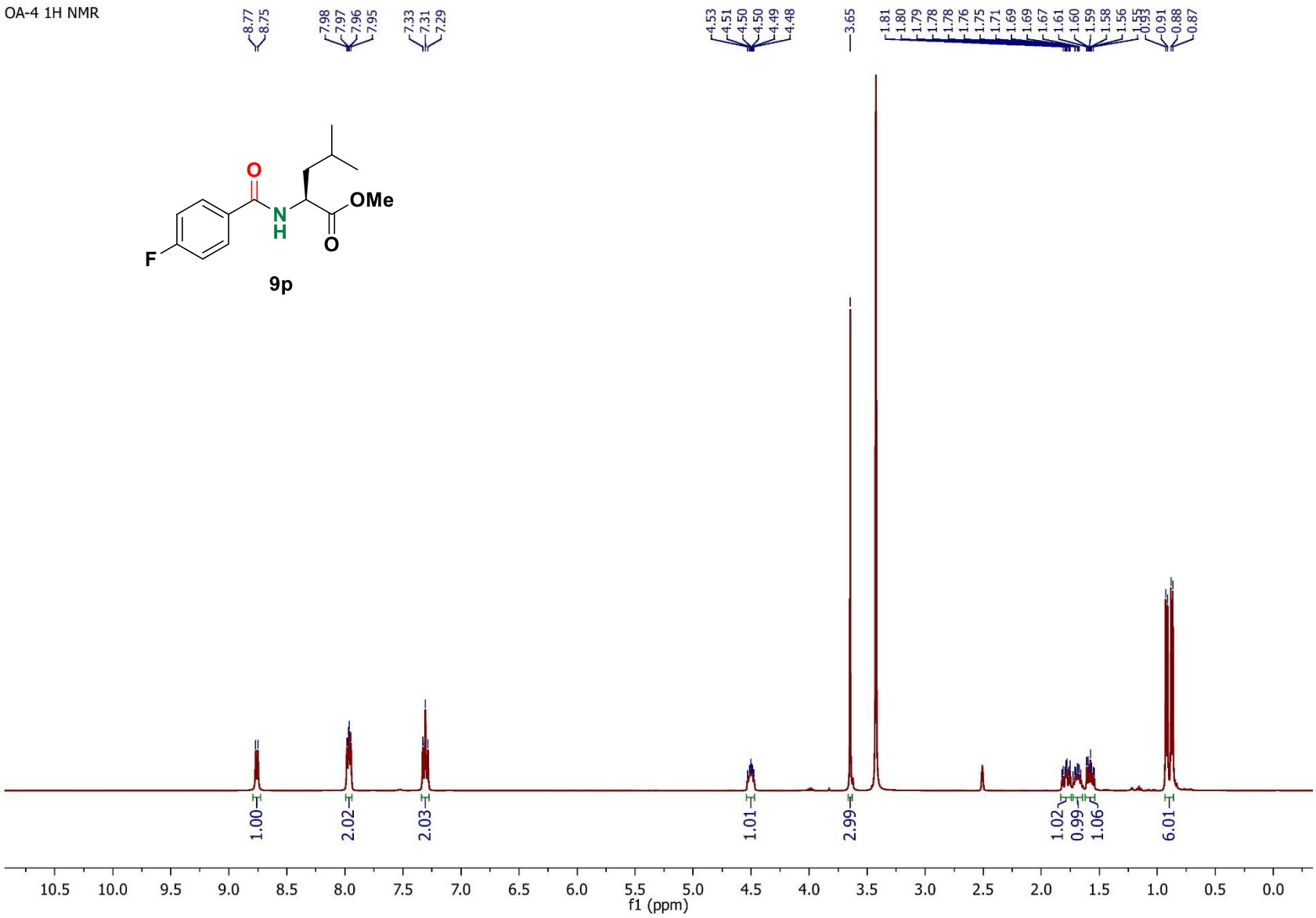


Figure S128. ^{1}H NMR Spectrum of **9p (400MHz, DMSO-d$_6$)**

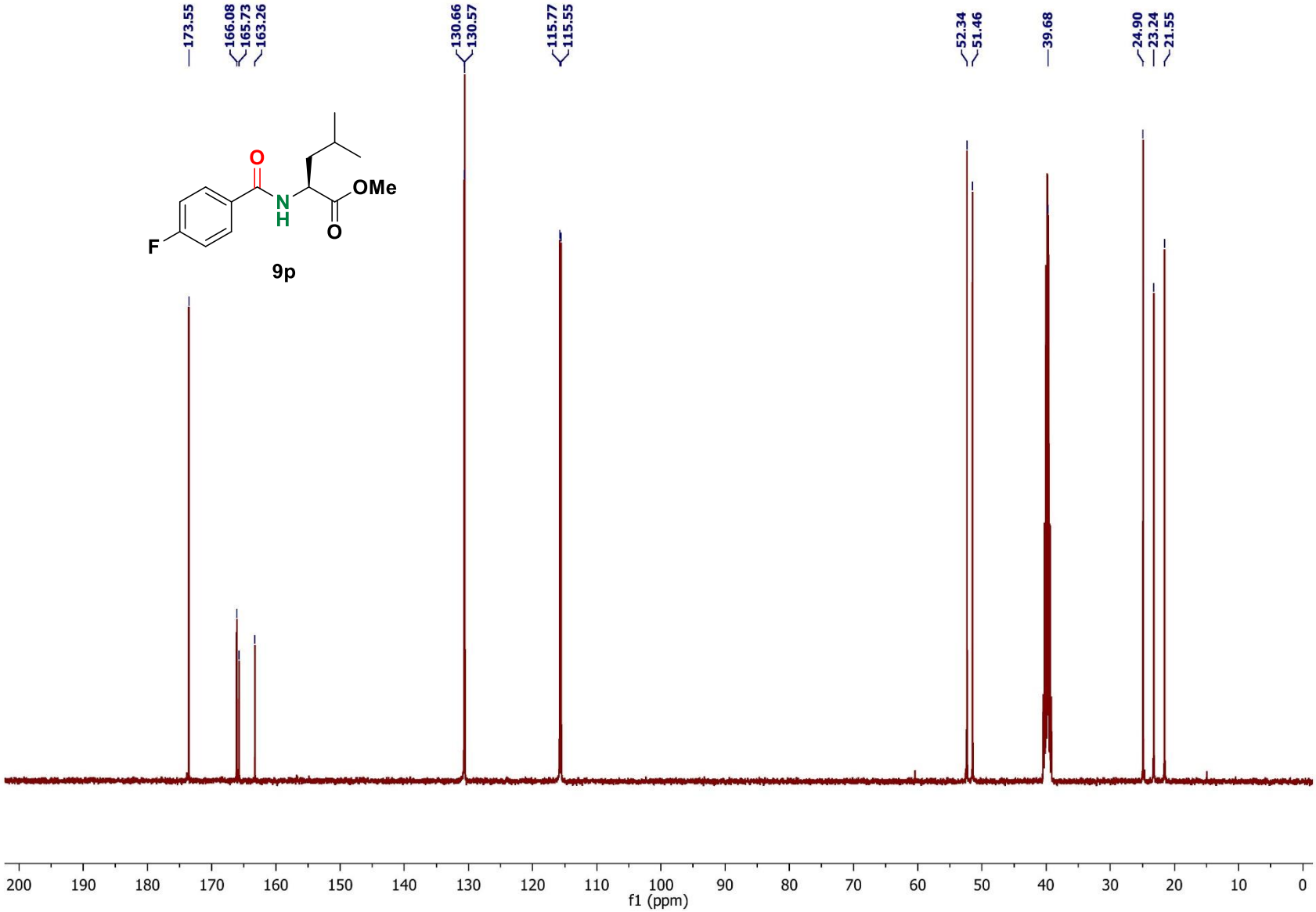


Figure S129. ^{13}C NMR Spectrum of **9p (101MHz, DMSO-d$_6$)**

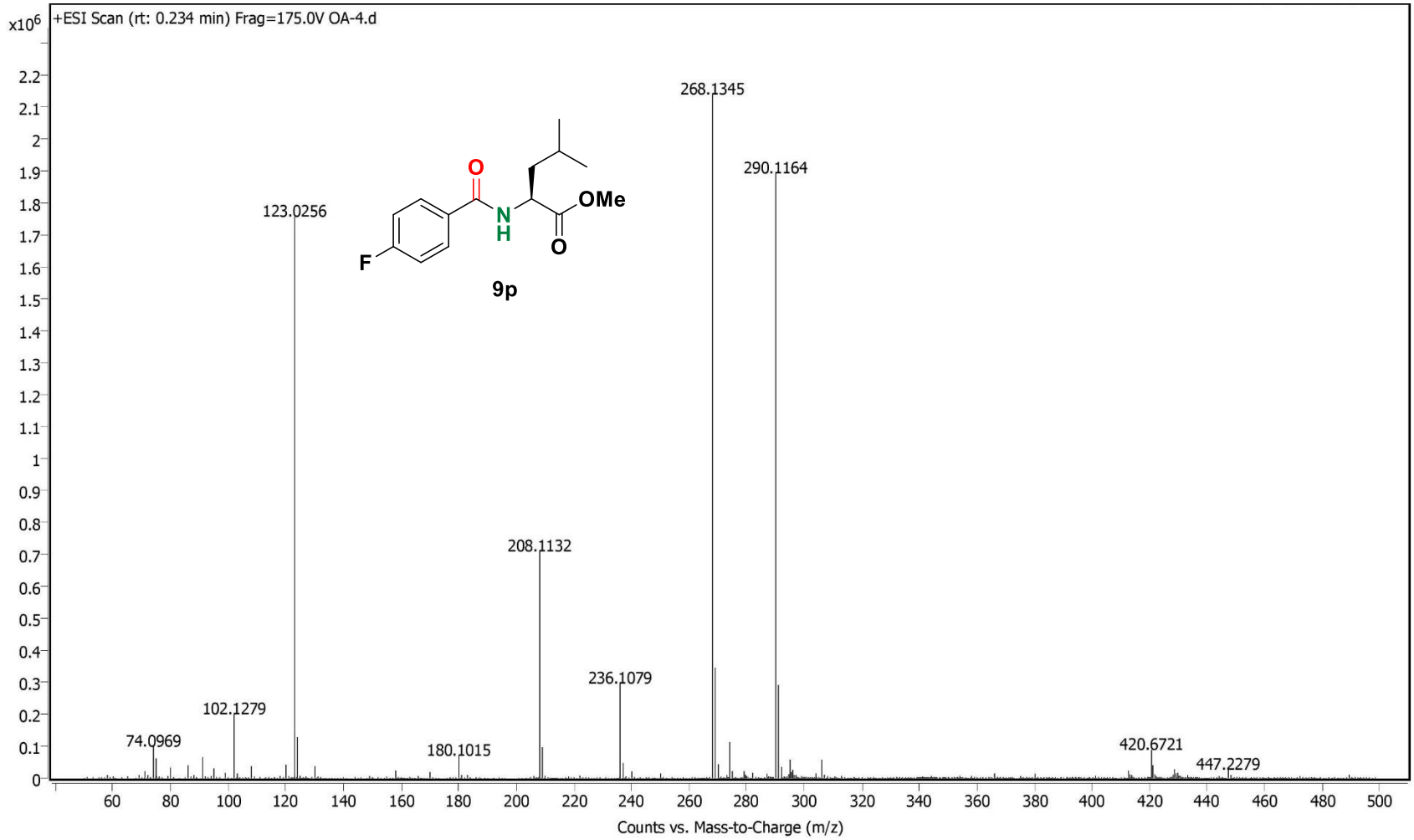


Figure S130. HRMS Spectrum of **9p**

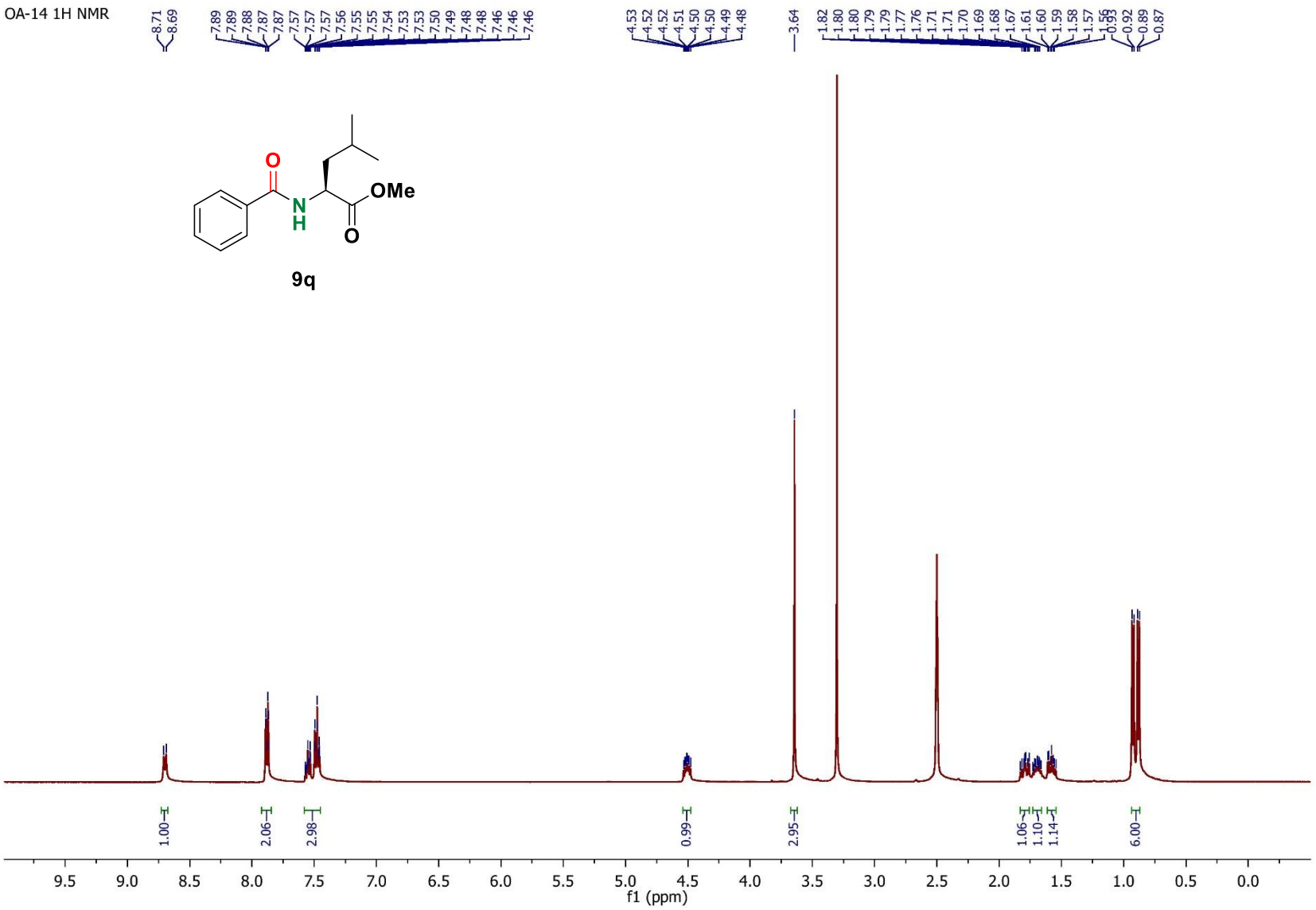


Figure S131. ^{1}H NMR Spectrum of **9q (400MHz, DMSO-d$_6$)**

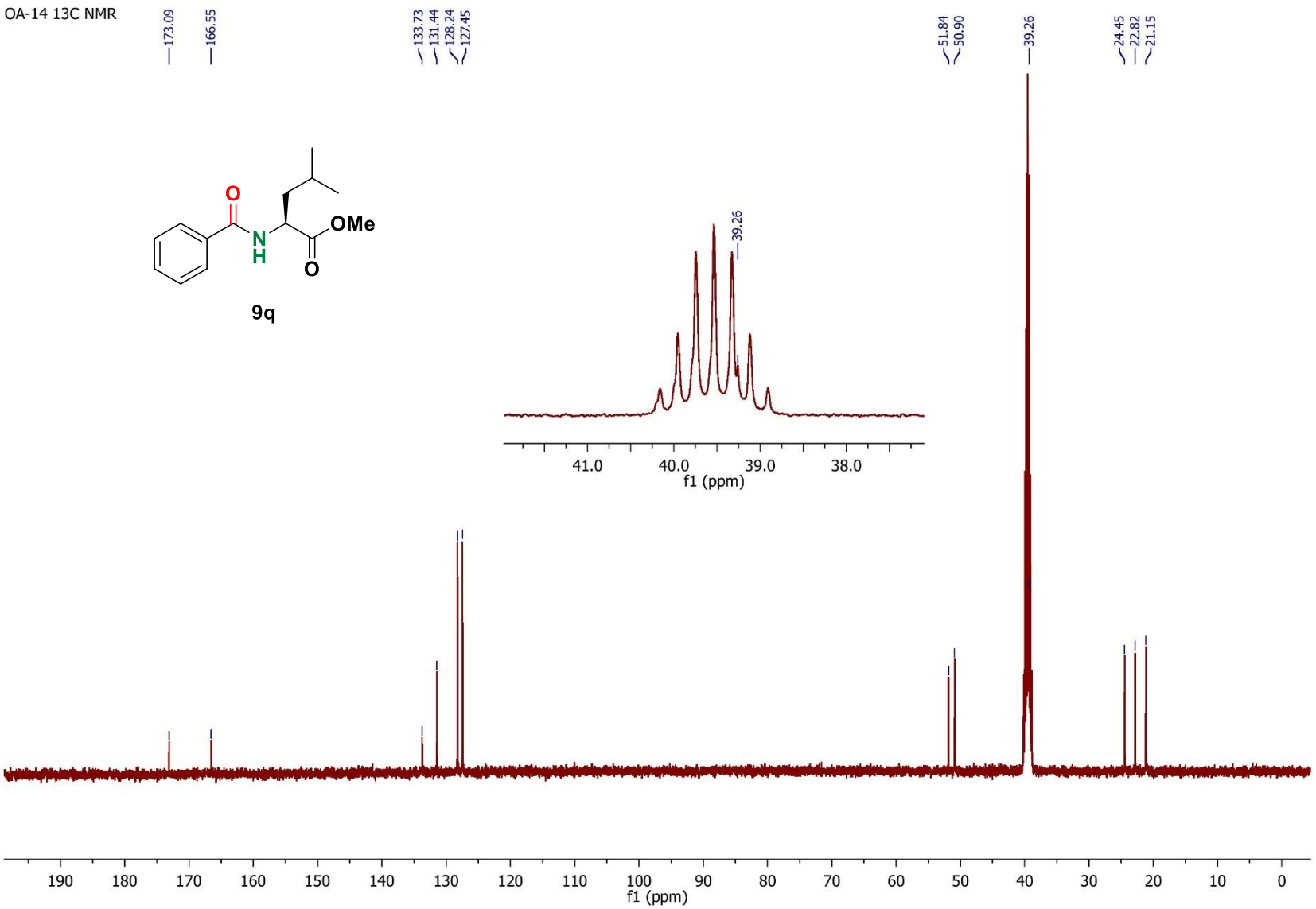


Figure S132. ^{13}C NMR Spectrum of **9q(101MHz, DMSO-d$_6$)**

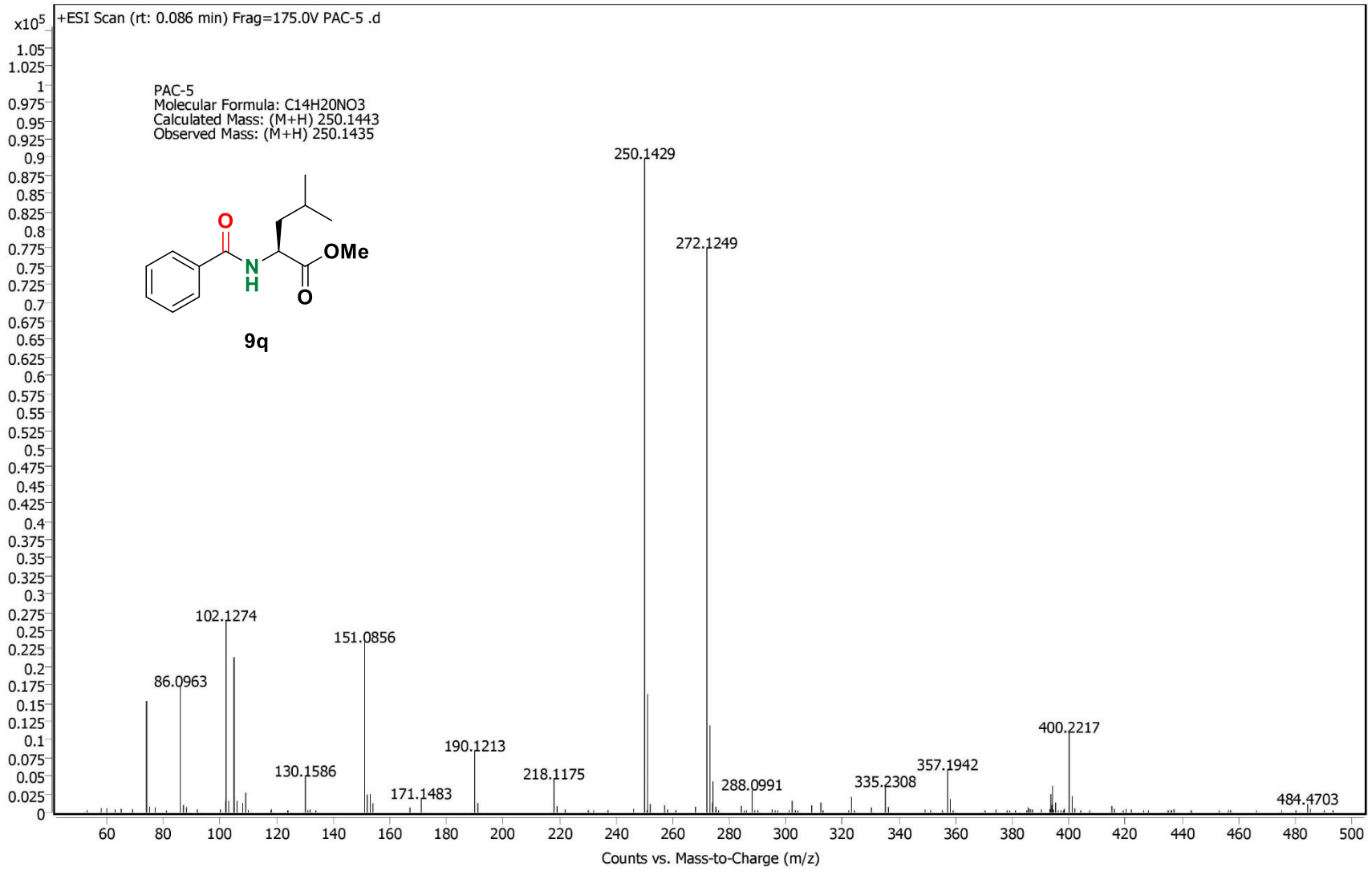


Figure S133. HRMS Spectrum of **9q**

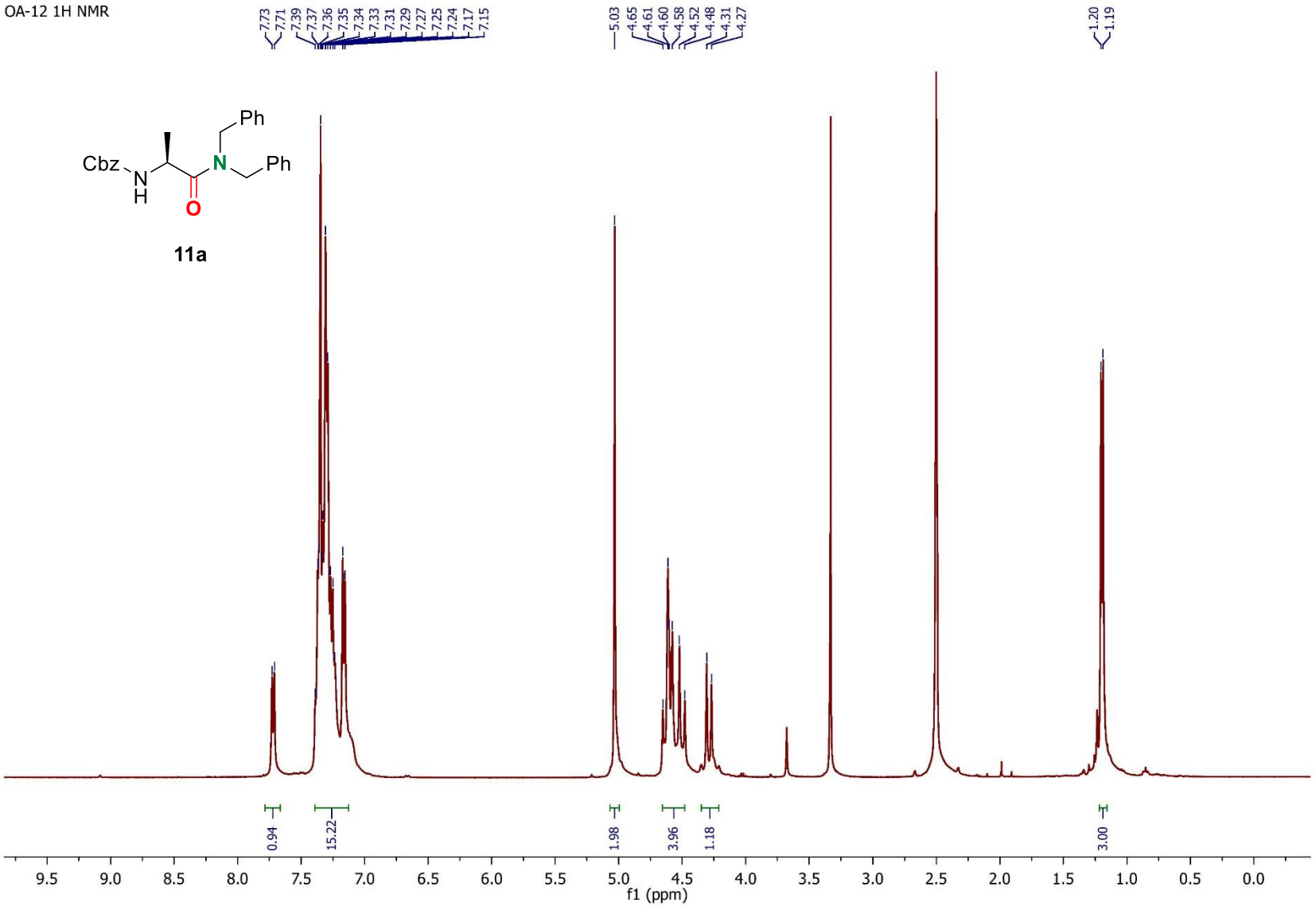


Figure S134. ^{1}H NMR Spectrum of **11a (400MHz, DMSO-d$_6$)**

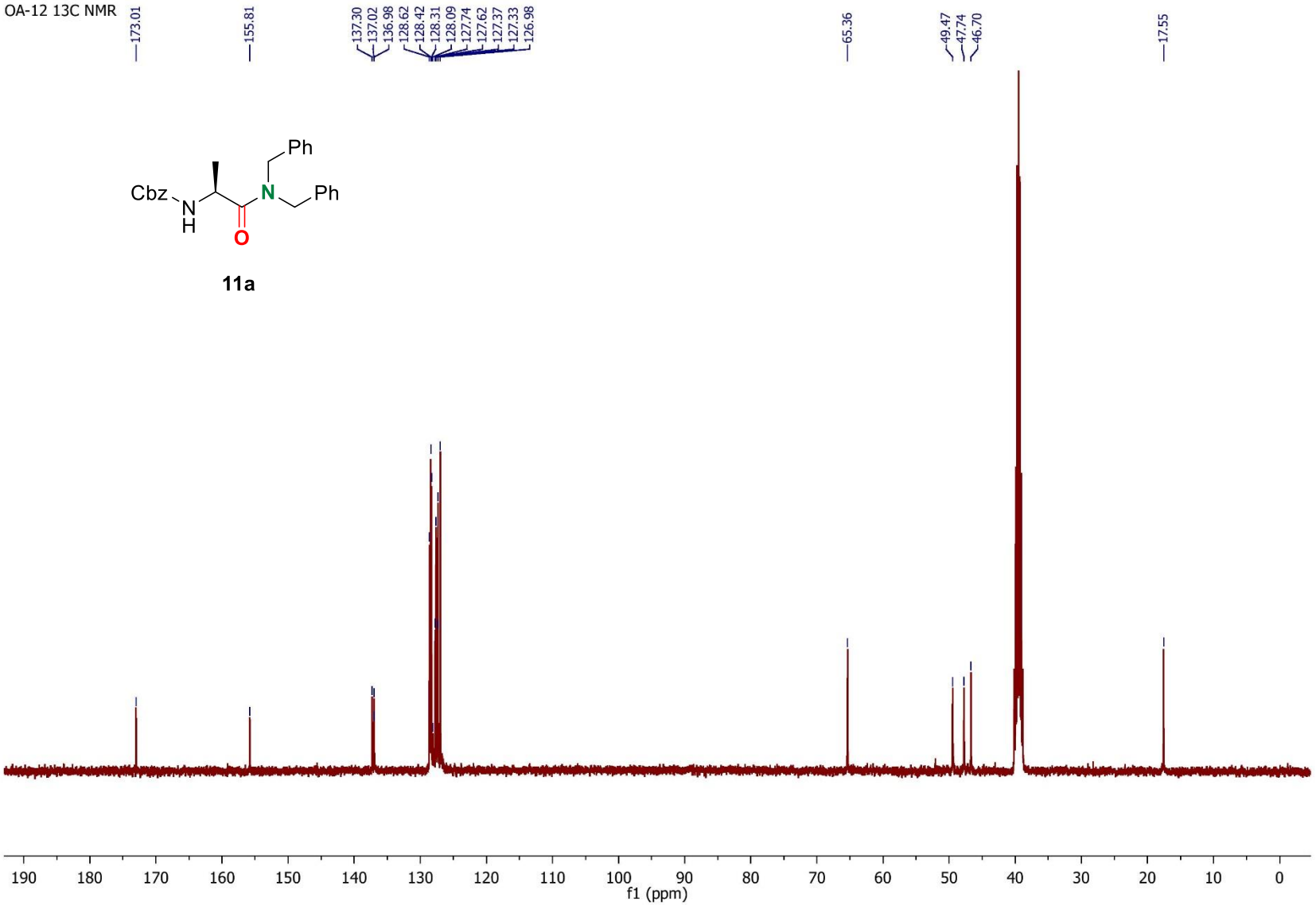


Figure S135. ^{13}C NMR Spectrum of **11a (101MHz, DMSO-d$_6$)**

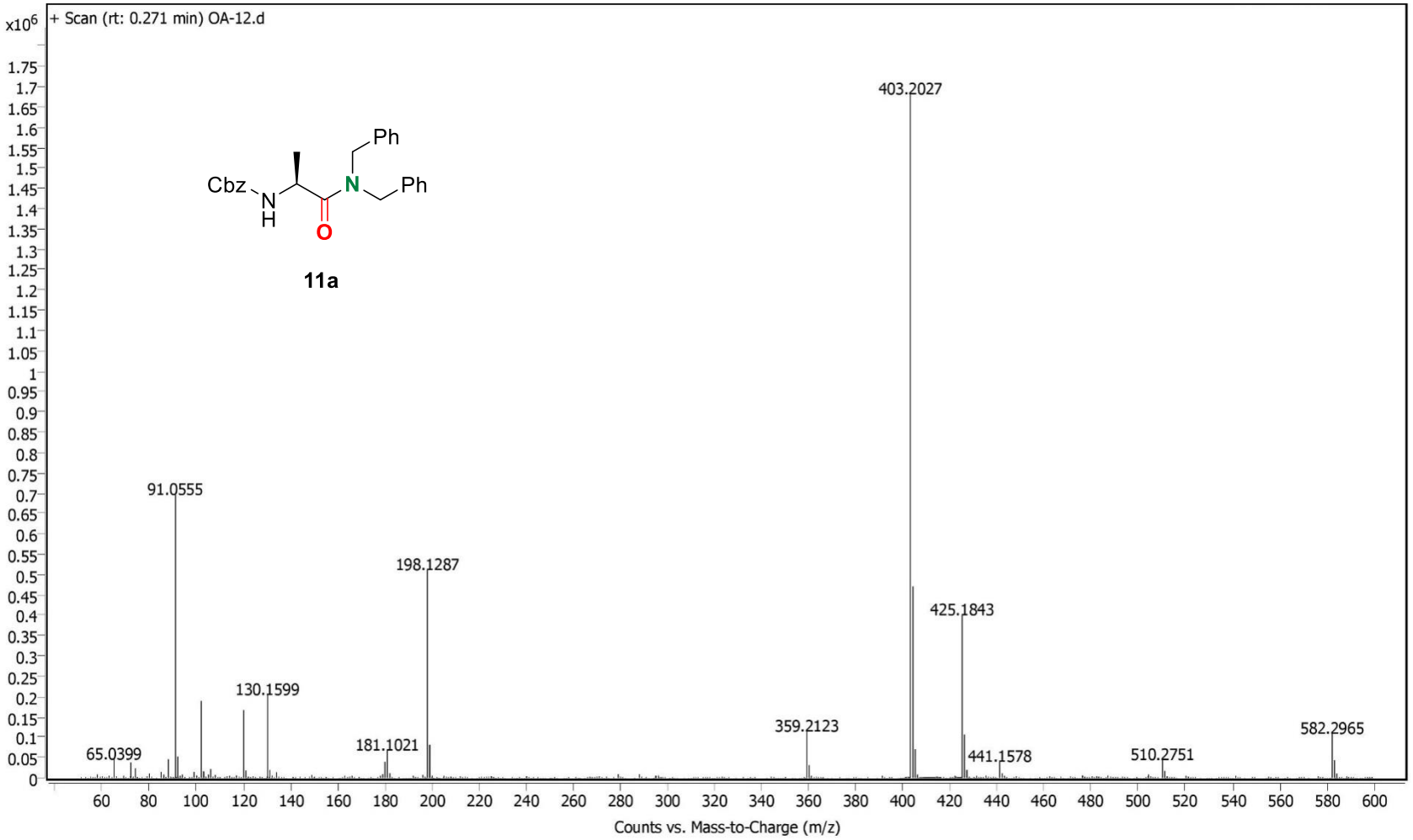


Figure S136. HRMS Spectrum of **11a**

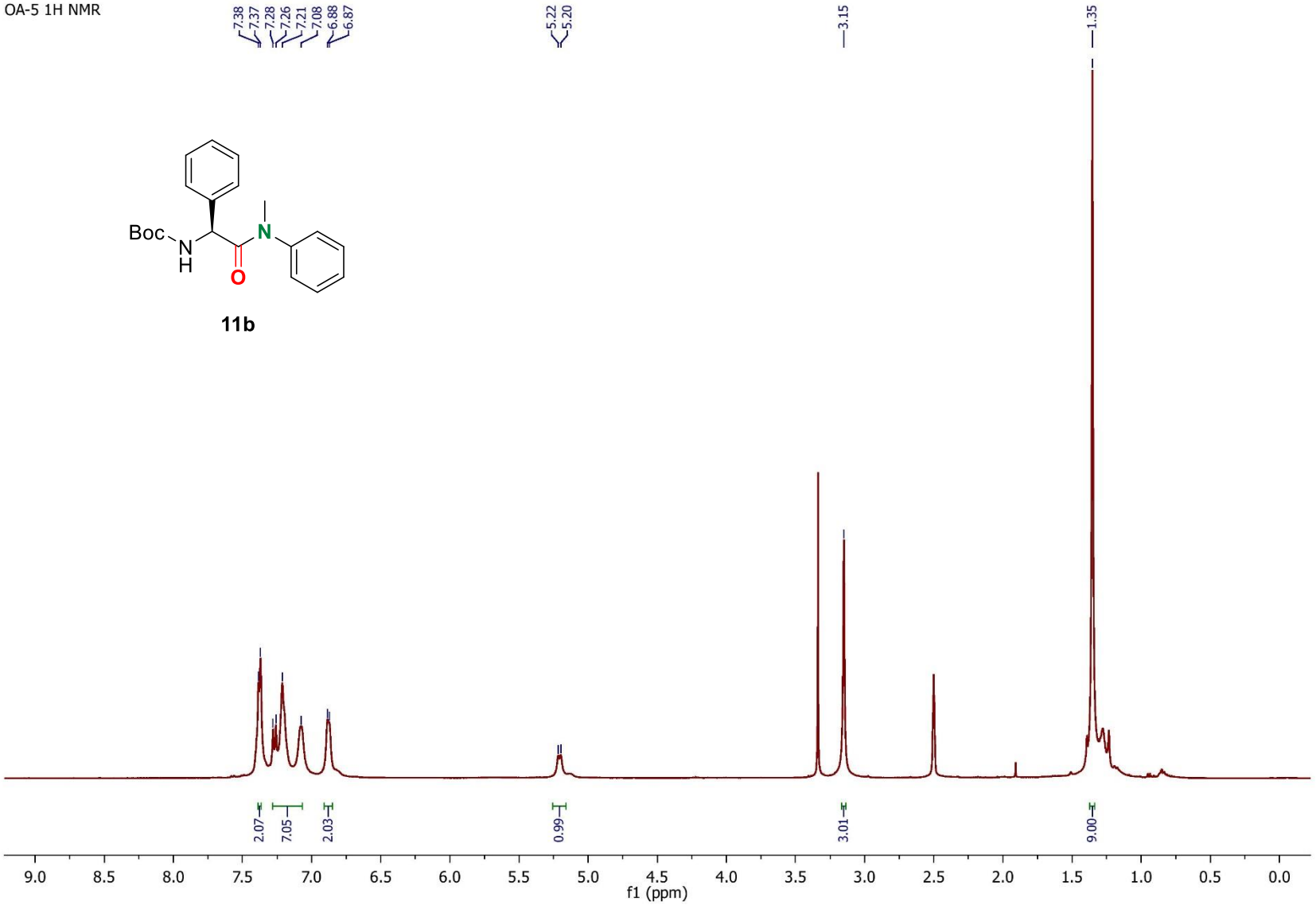


Figure S137. ^{1}H NMR Spectrum of **11b (400MHz, DMSO-d$_6$)**

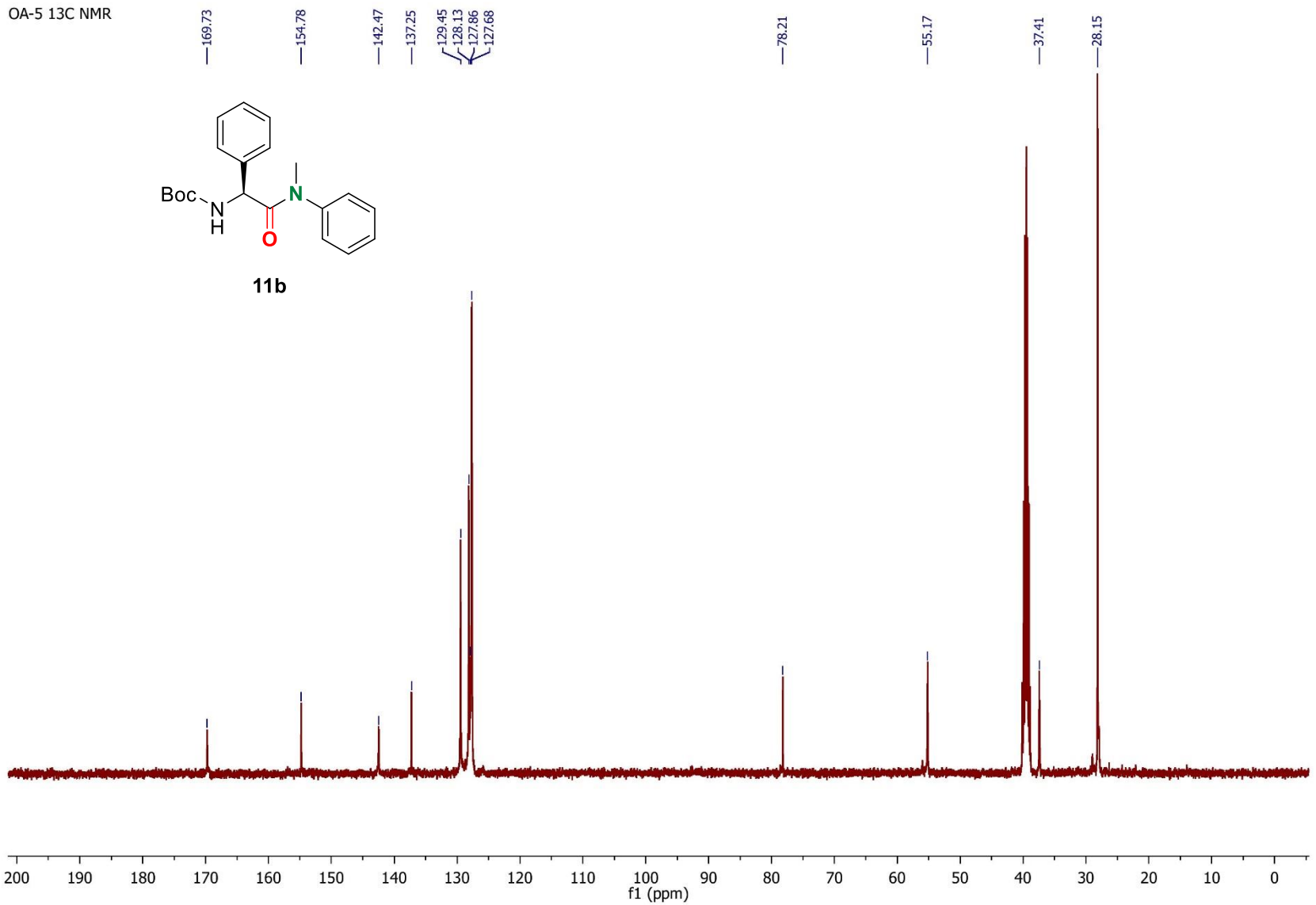


Figure S138. ^{13}C NMR Spectrum of **11b (101MHz, DMSO-d$_6$)**

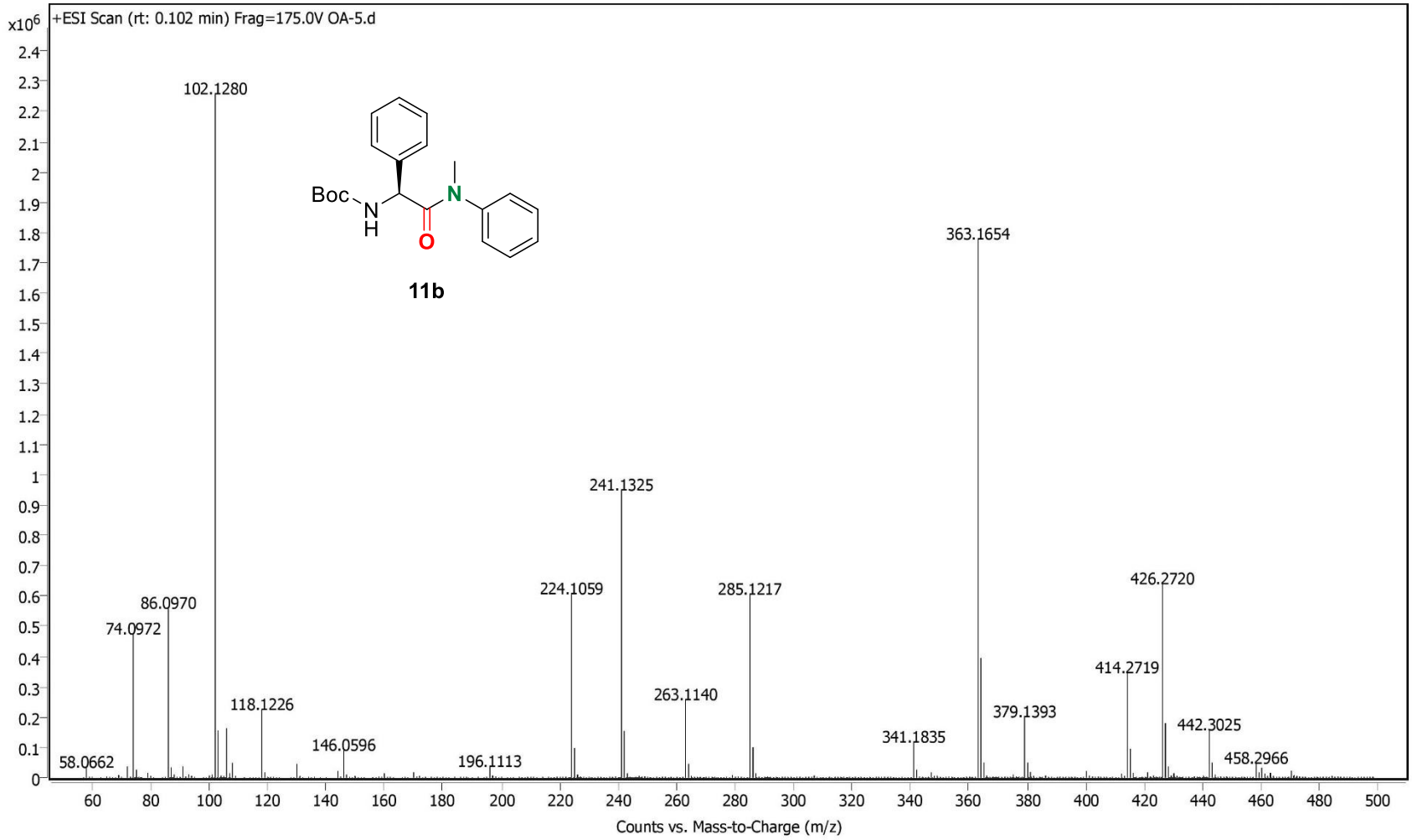


Figure S139. HRMS Spectrum of **11b**

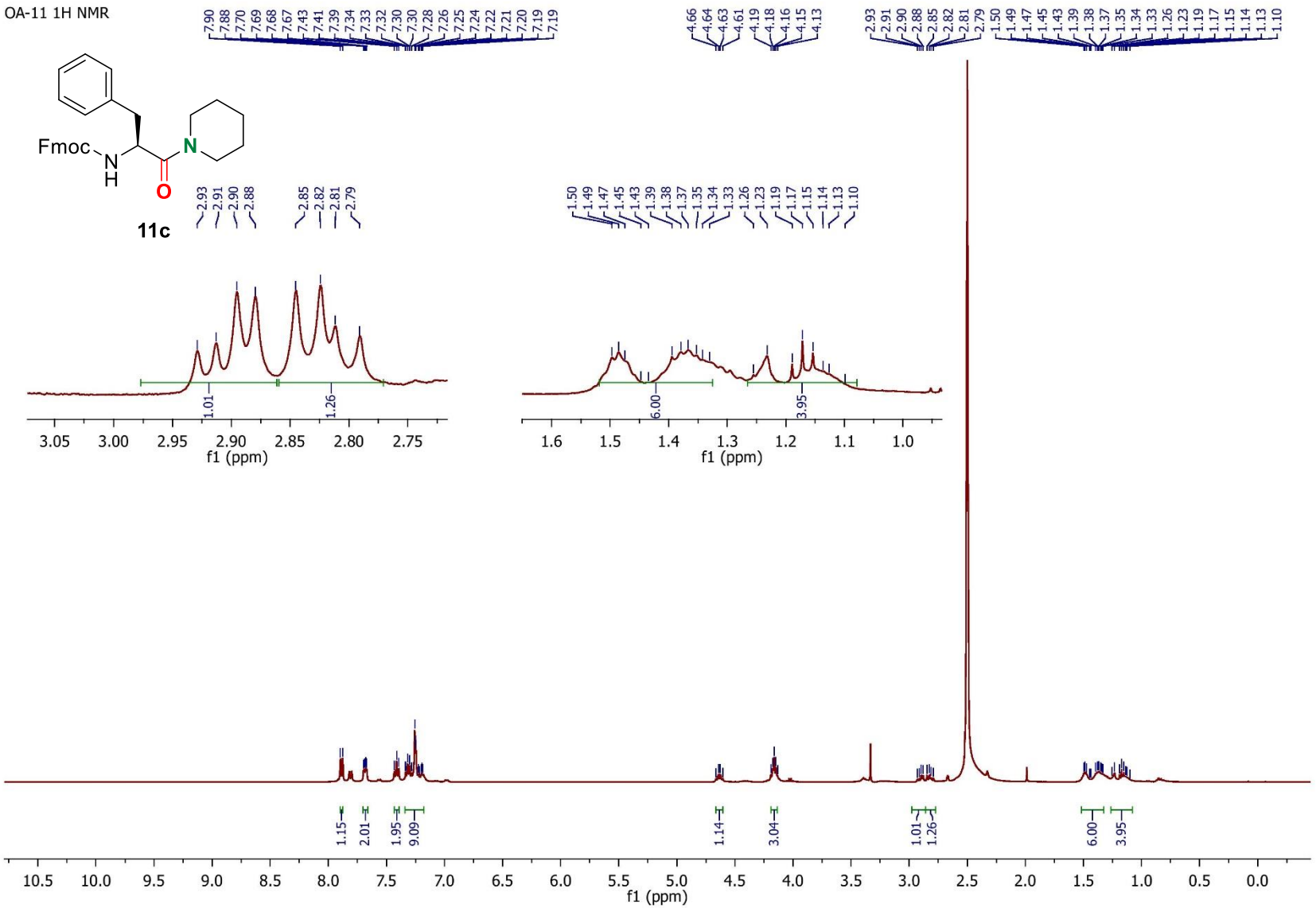


Figure S140. ^{1}H NMR Spectrum of **11c (400MHz, DMSO-d$_6$)**

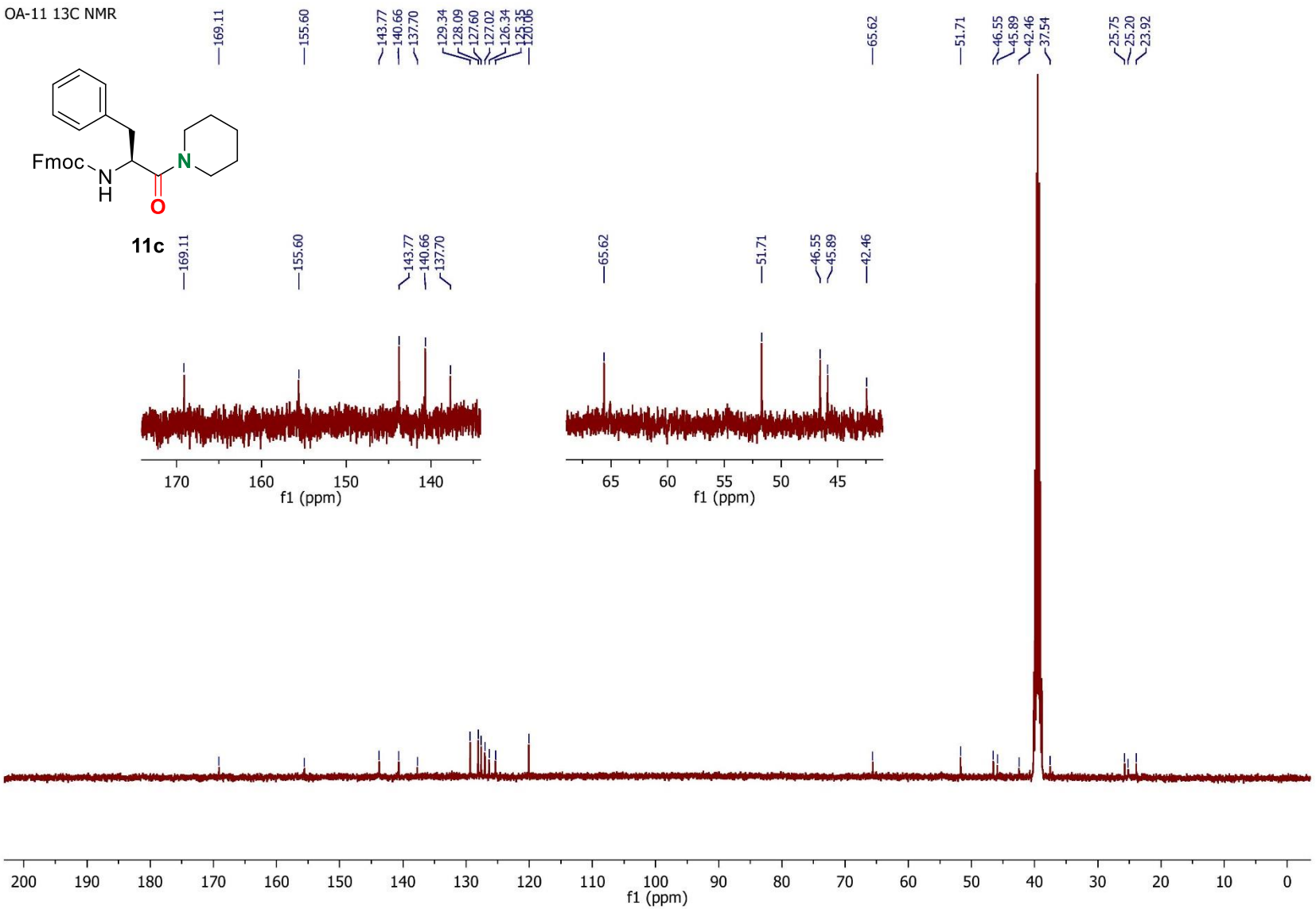


Figure S141. ^{13}C NMR Spectrum of **11c (101MHz, DMSO-d$_6$)**

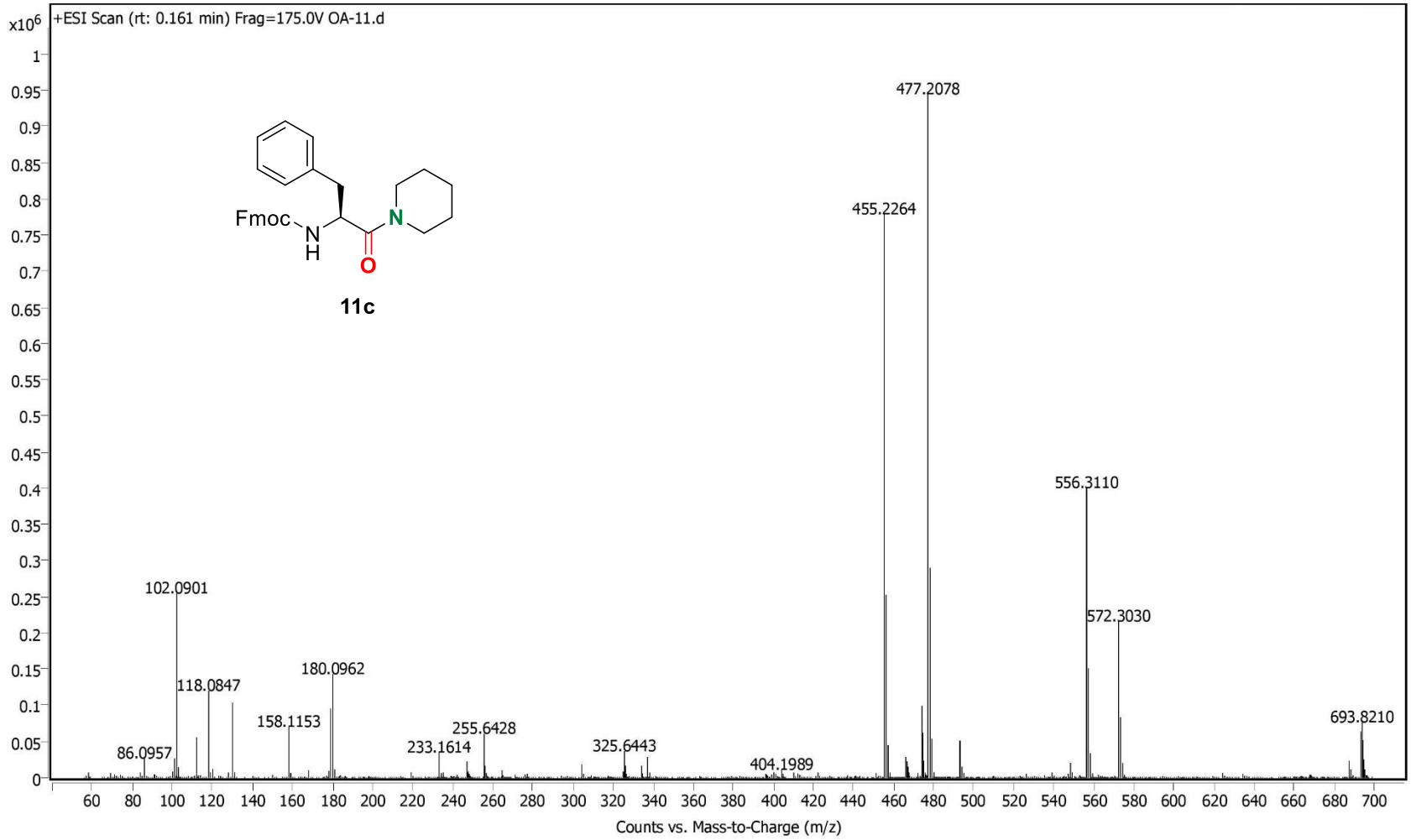


Figure S142. HRMS Spectrum of **11c**

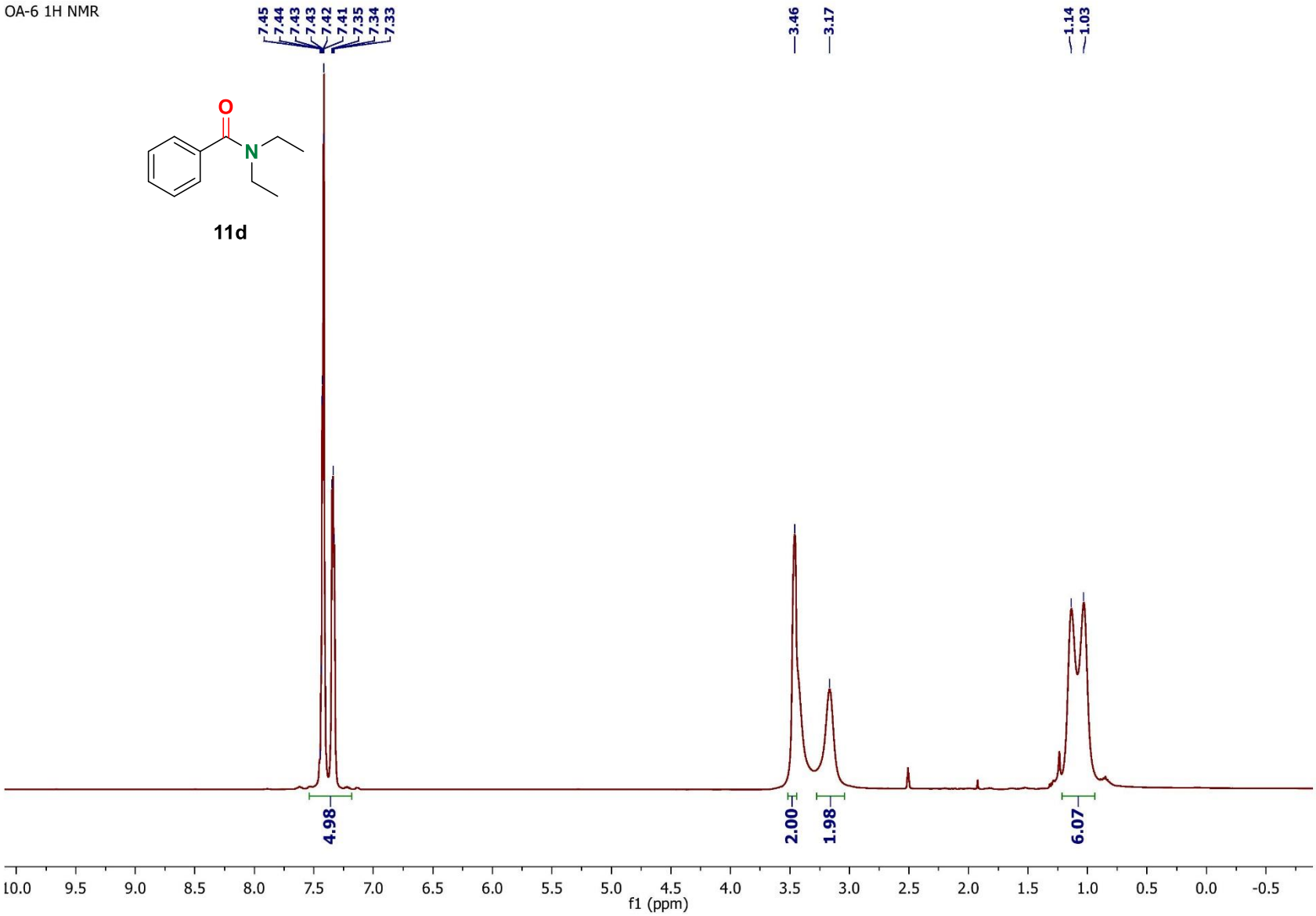


Figure S143. ^{1}H NMR Spectrum of **11d (400MHz, DMSO-d$_6$)**

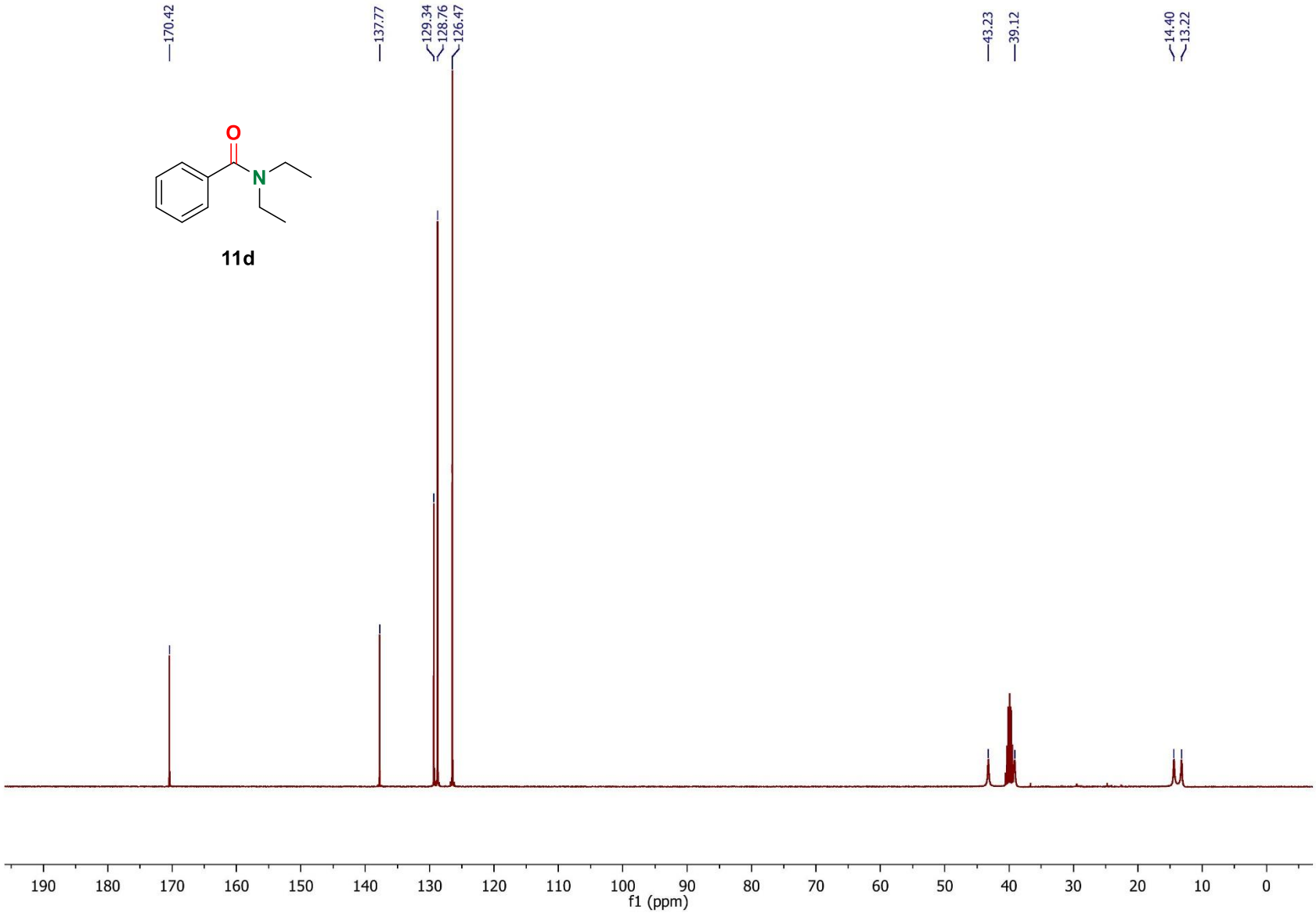


Figure S144. ^{13}C NMR Spectrum of **11d (101MHz, DMSO-d$_6$)**

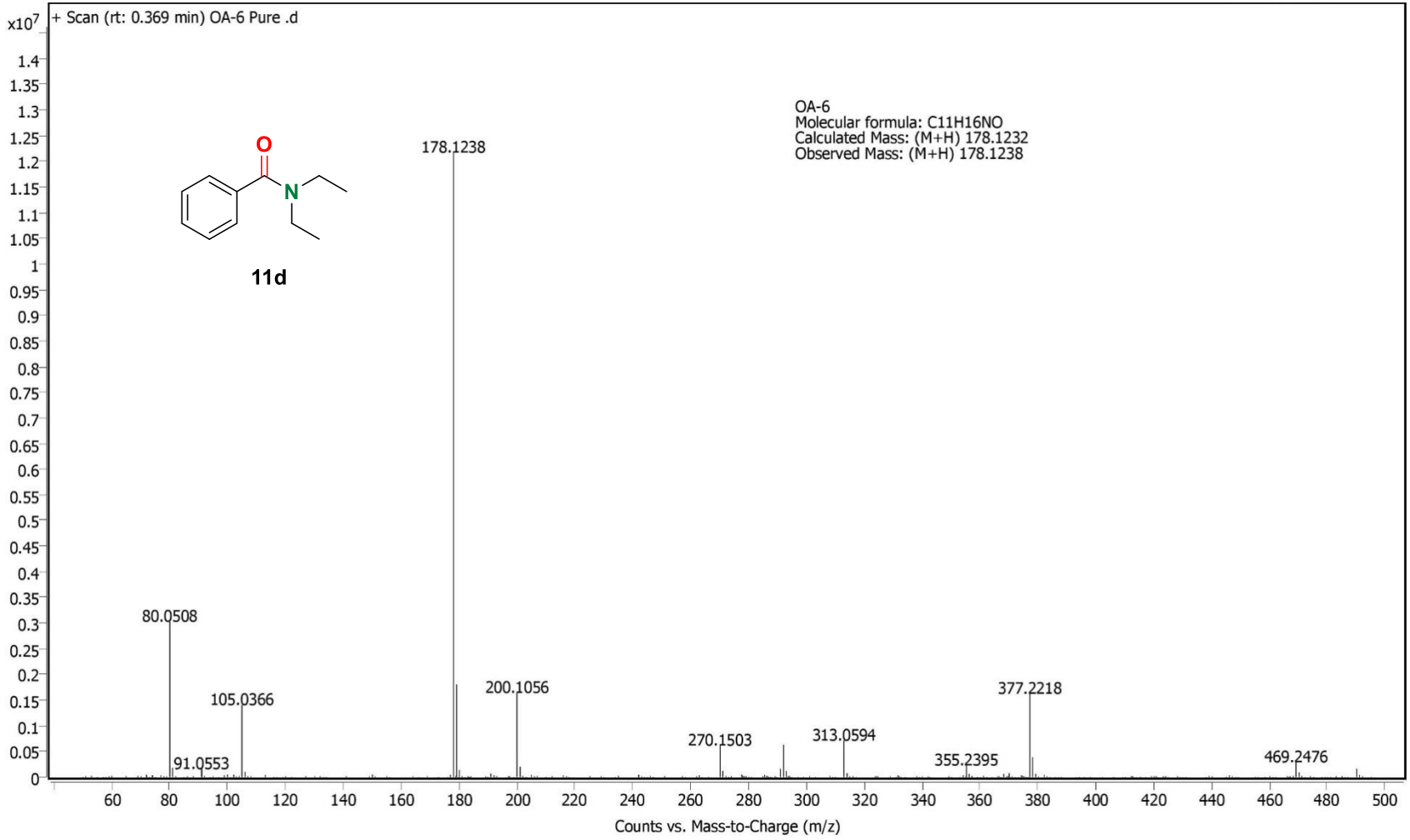


Figure S145. HRMS Spectrum of **11d**

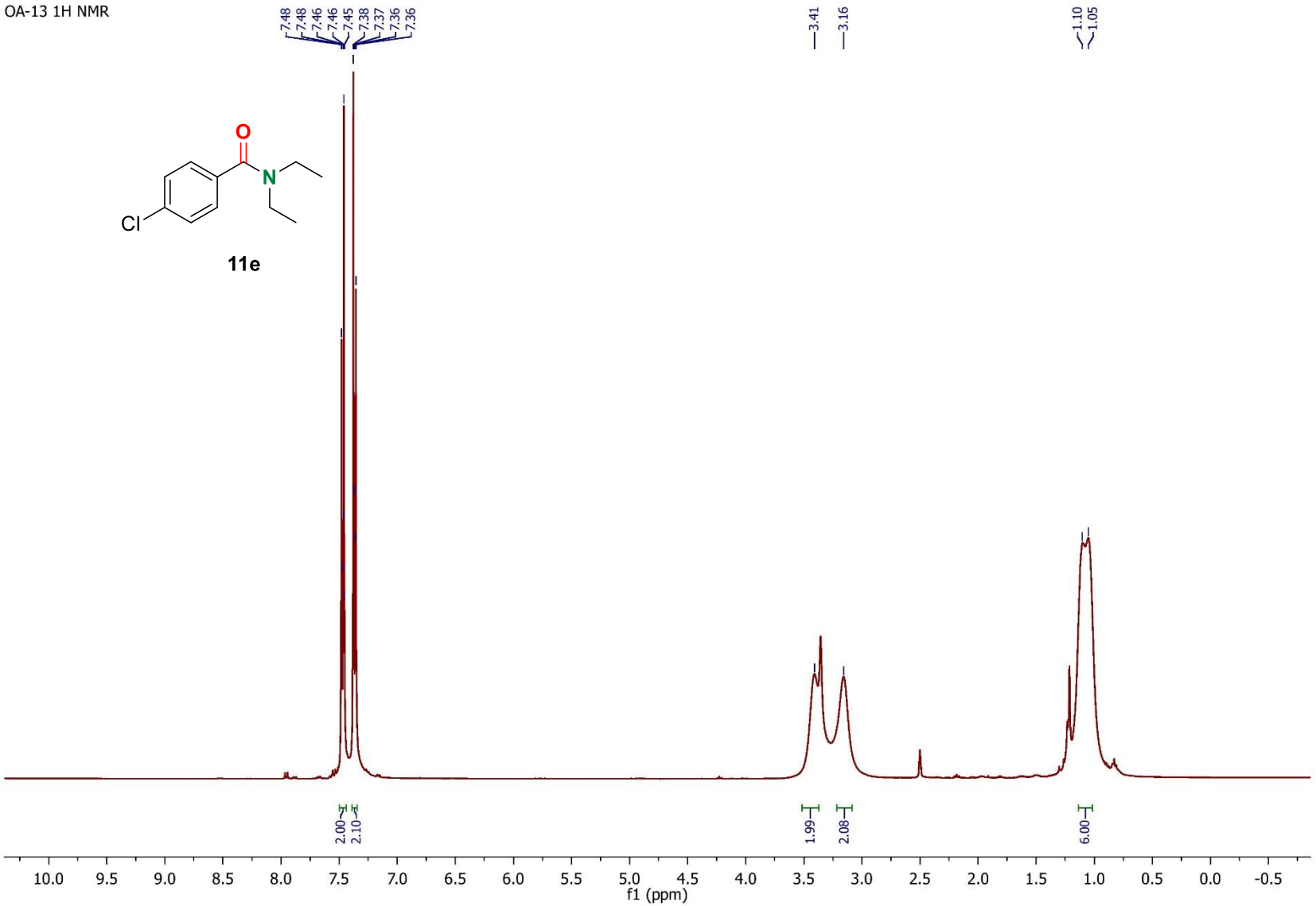


Figure S146. ^{1}H NMR Spectrum of **11e (400MHz, DMSO-d$_6$)**

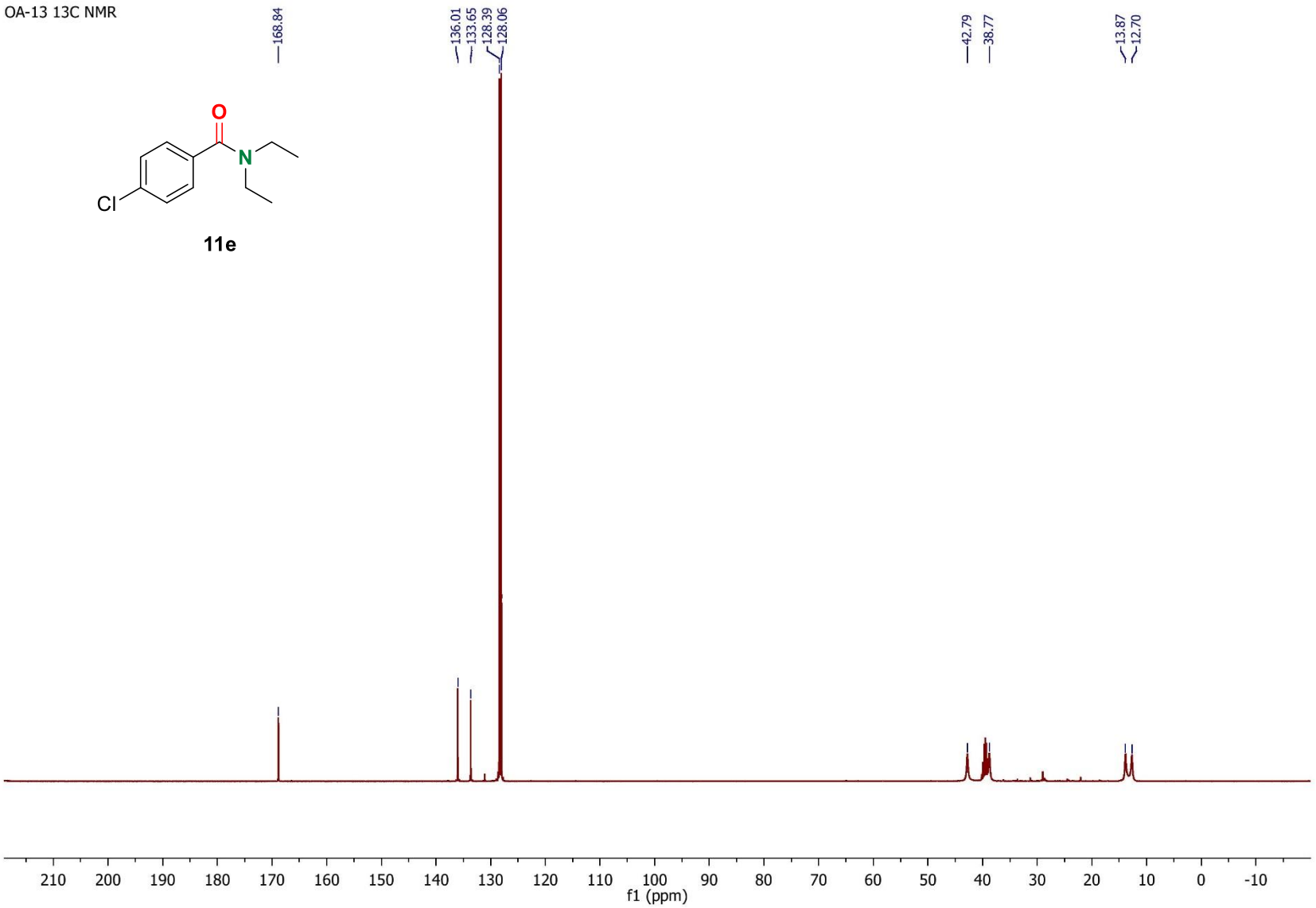


Figure S147. ^{13}C NMR Spectrum of **11e (101MHz, DMSO-d$_6$)**

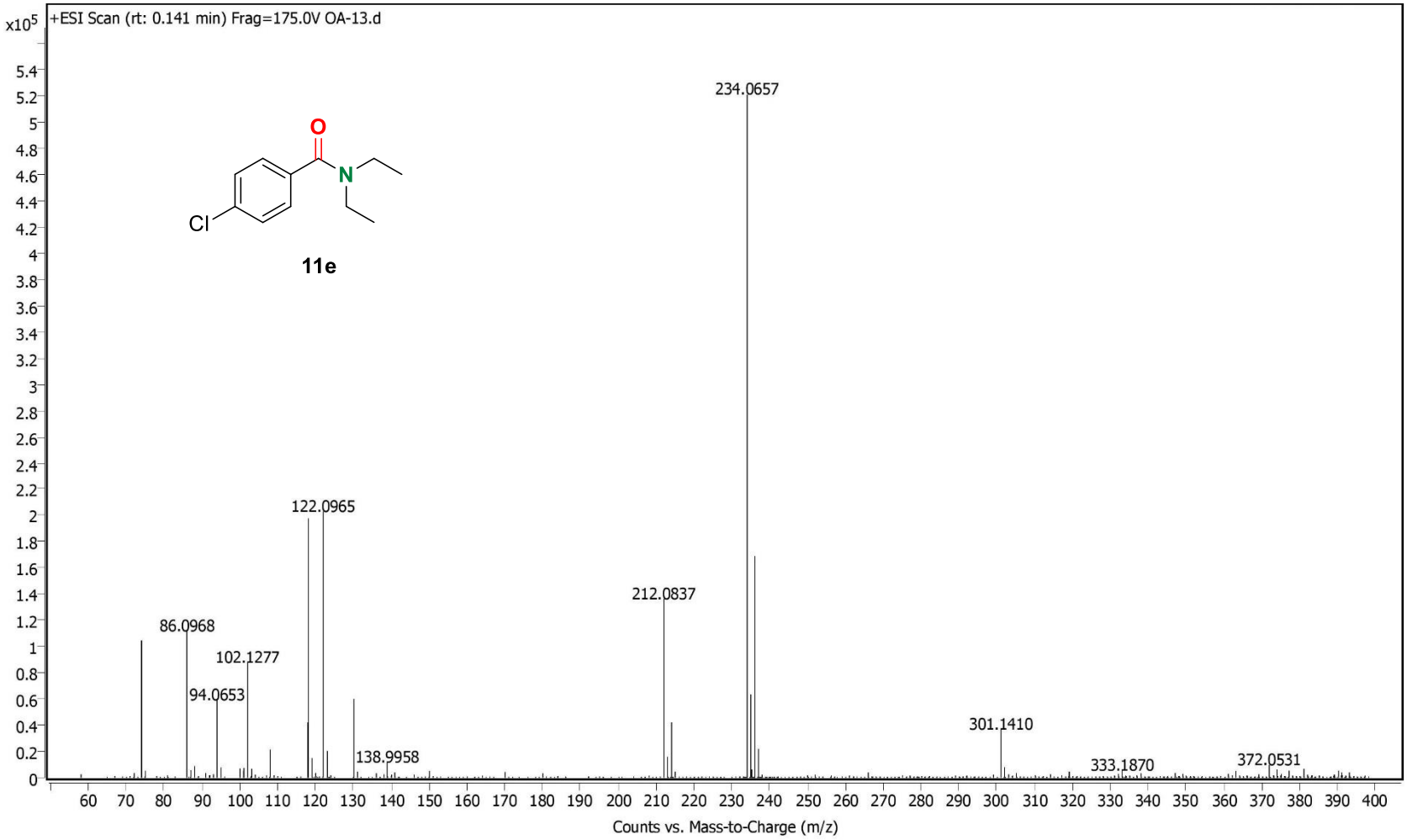


Figure S148. HRMS Spectrum of **11e**

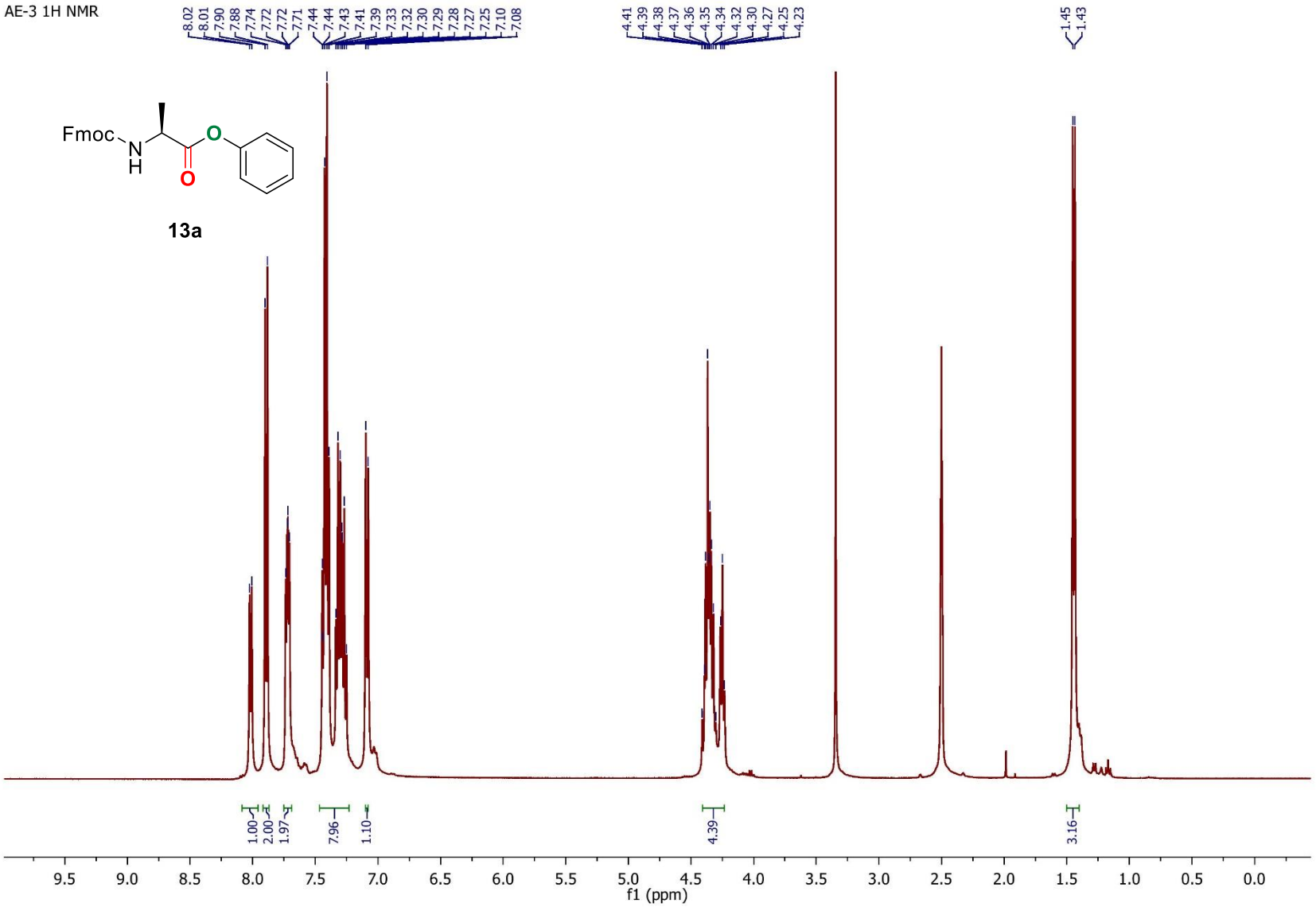


Figure S149. ^{1}H NMR Spectrum of **13a (400MHz, DMSO-d$_6$)**

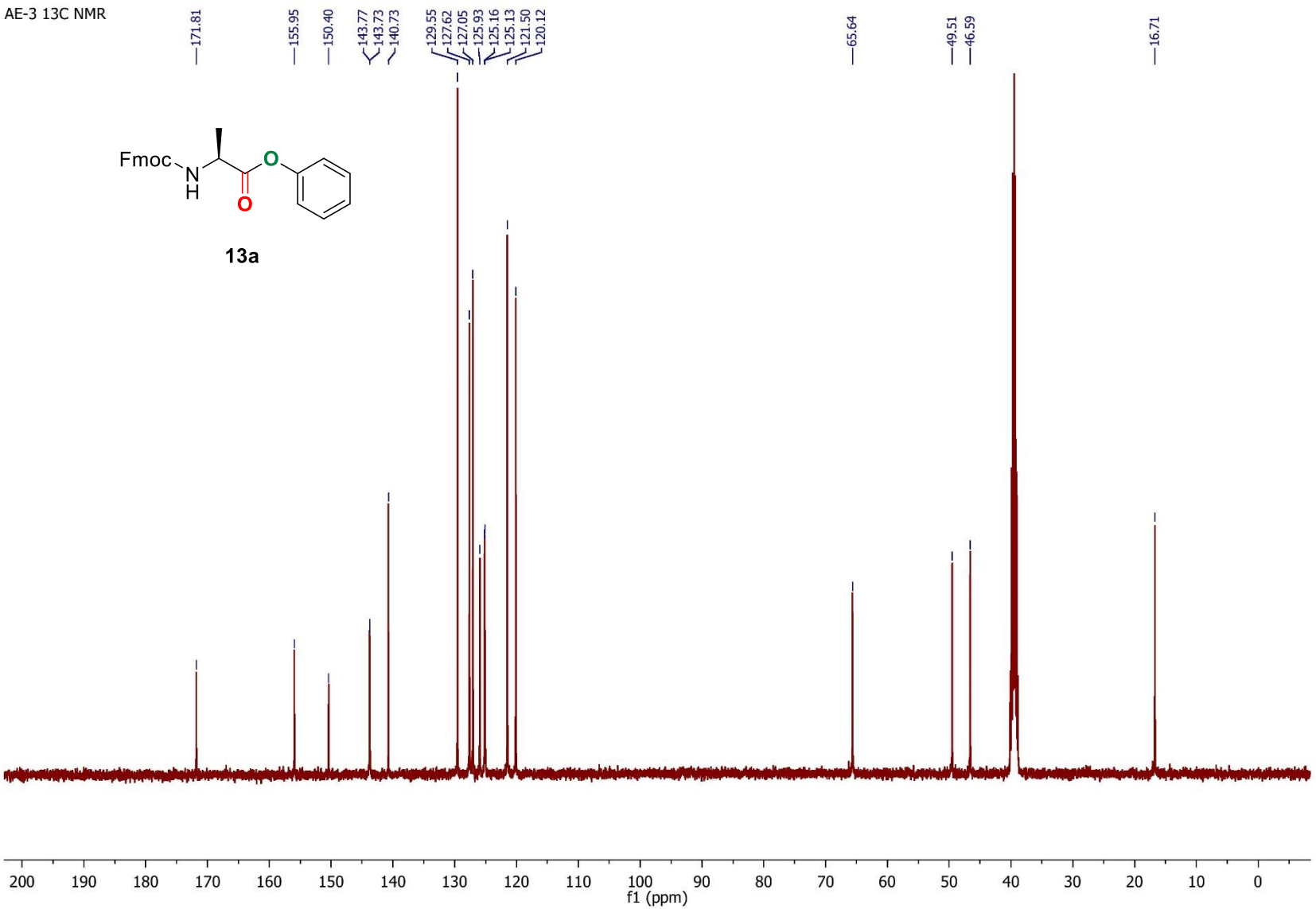


Figure S150. ^{13}C NMR Spectrum of **13a (101MHz, DMSO-d$_6$)**

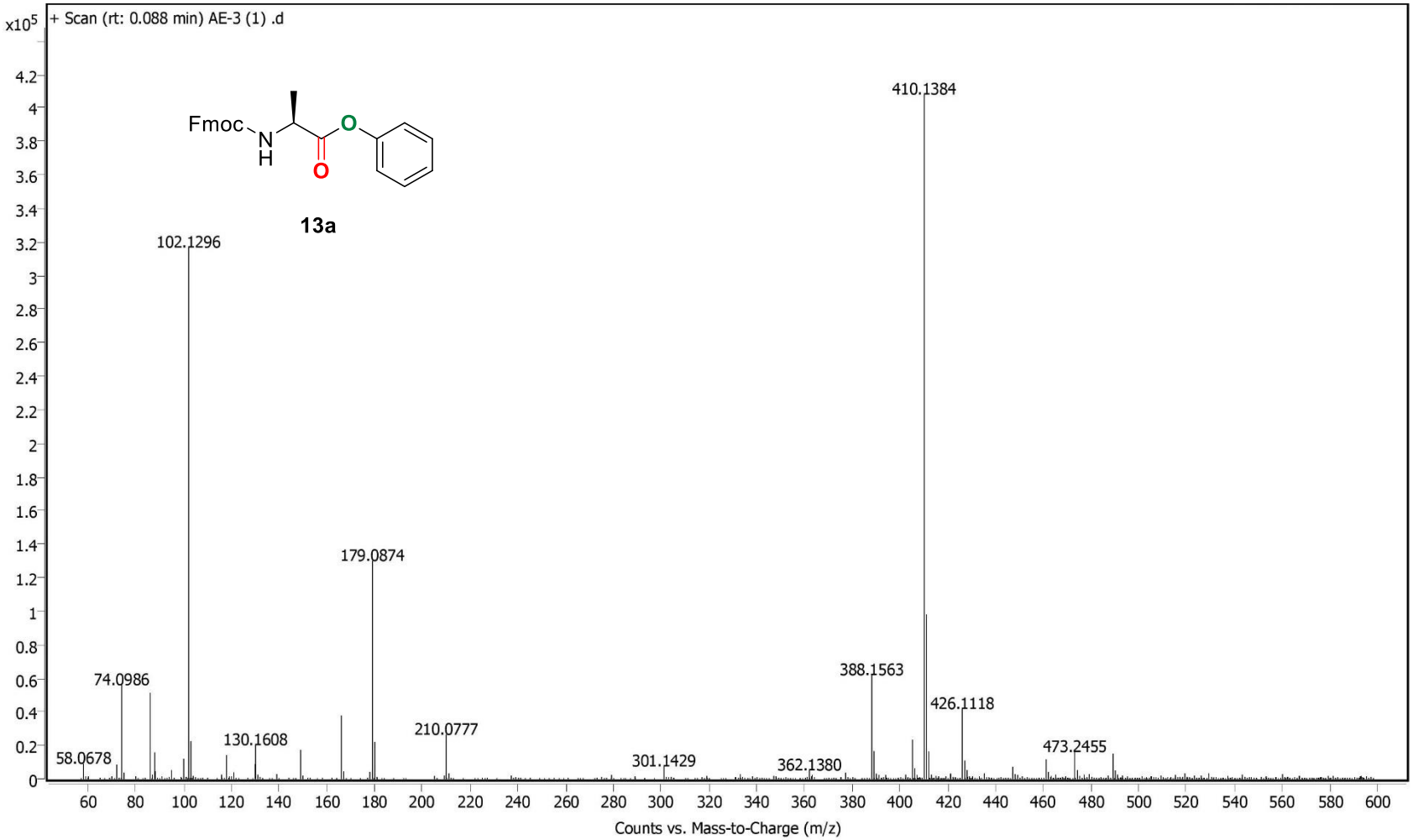


Figure S151. HRMS Spectrum of **13a**

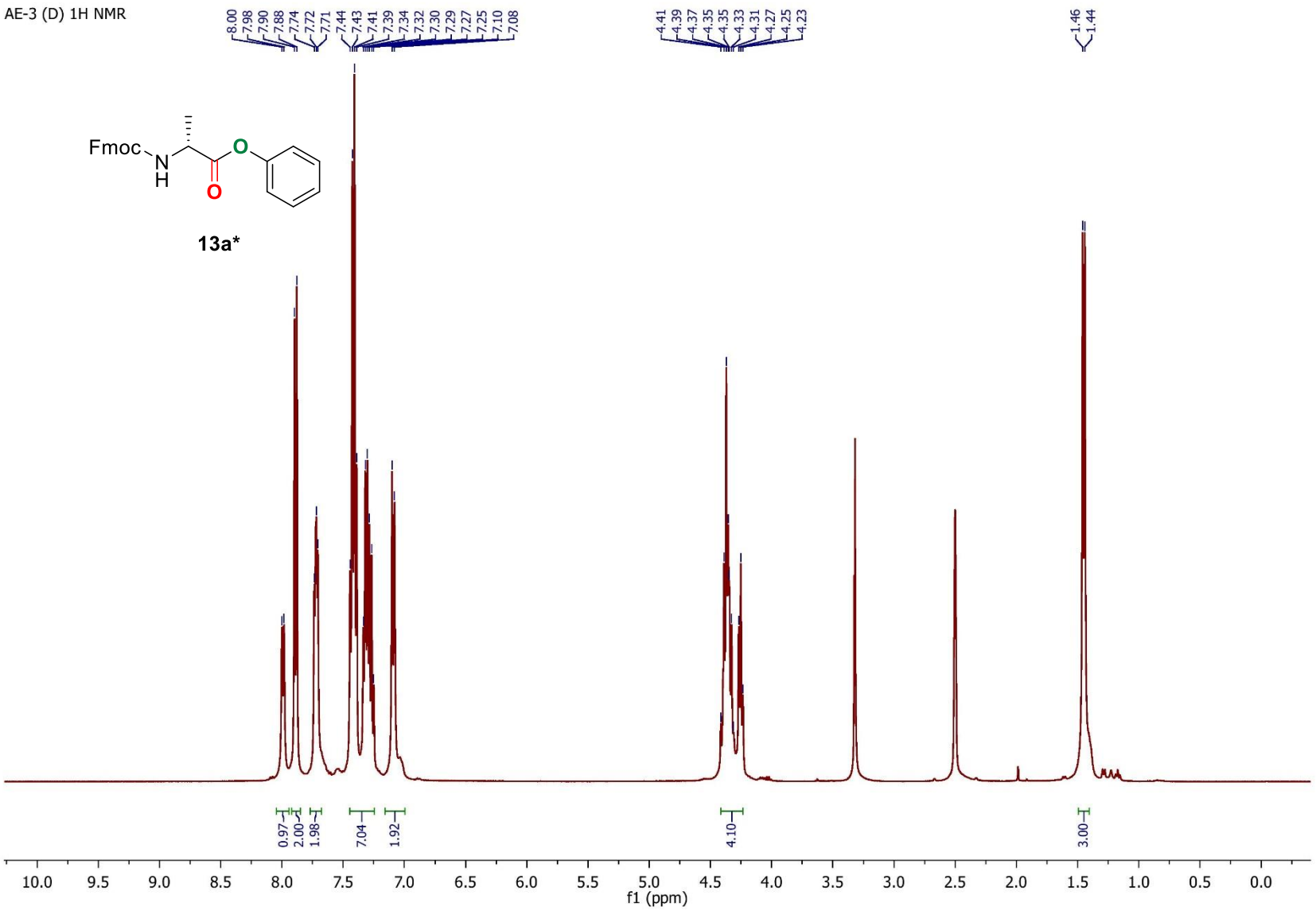


Figure S152. ^{1}H NMR Spectrum of **13a* (400MHz, DMSO-d$_6$)**

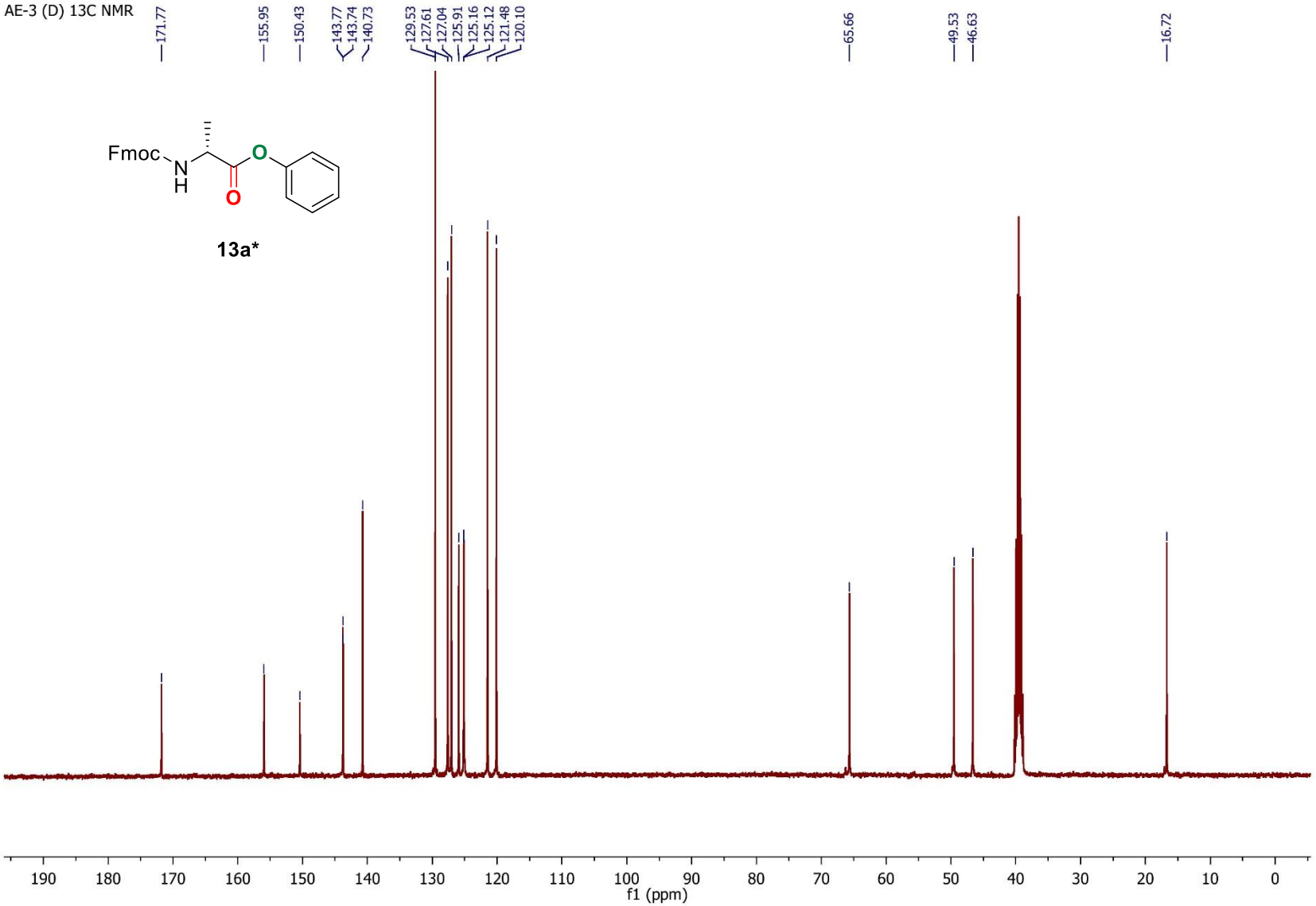


Figure S153. ^{13}C NMR Spectrum of **13a*(101MHz, DMSO-d$_6$)**

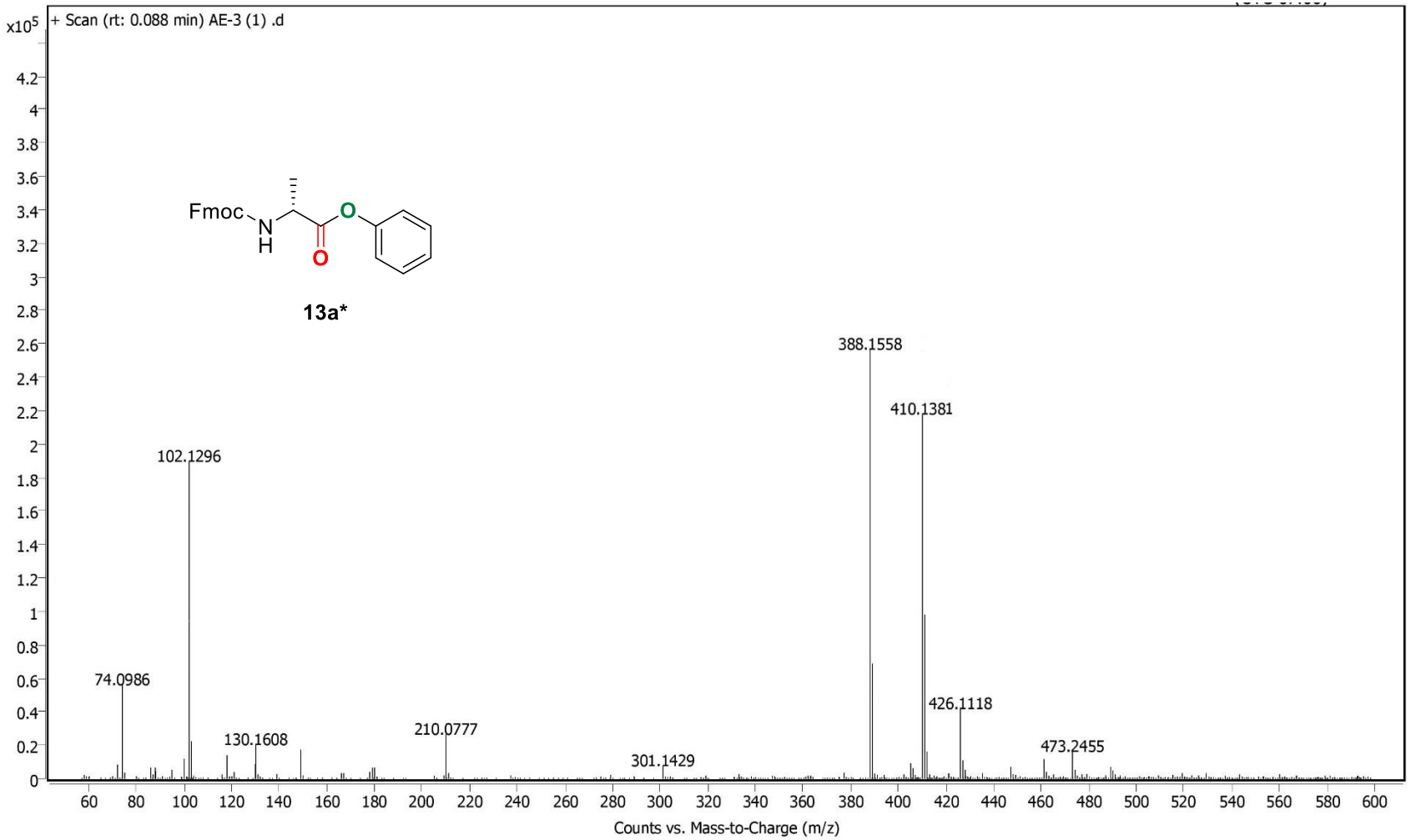


Figure S154. HRMS Spectrum of **13a***

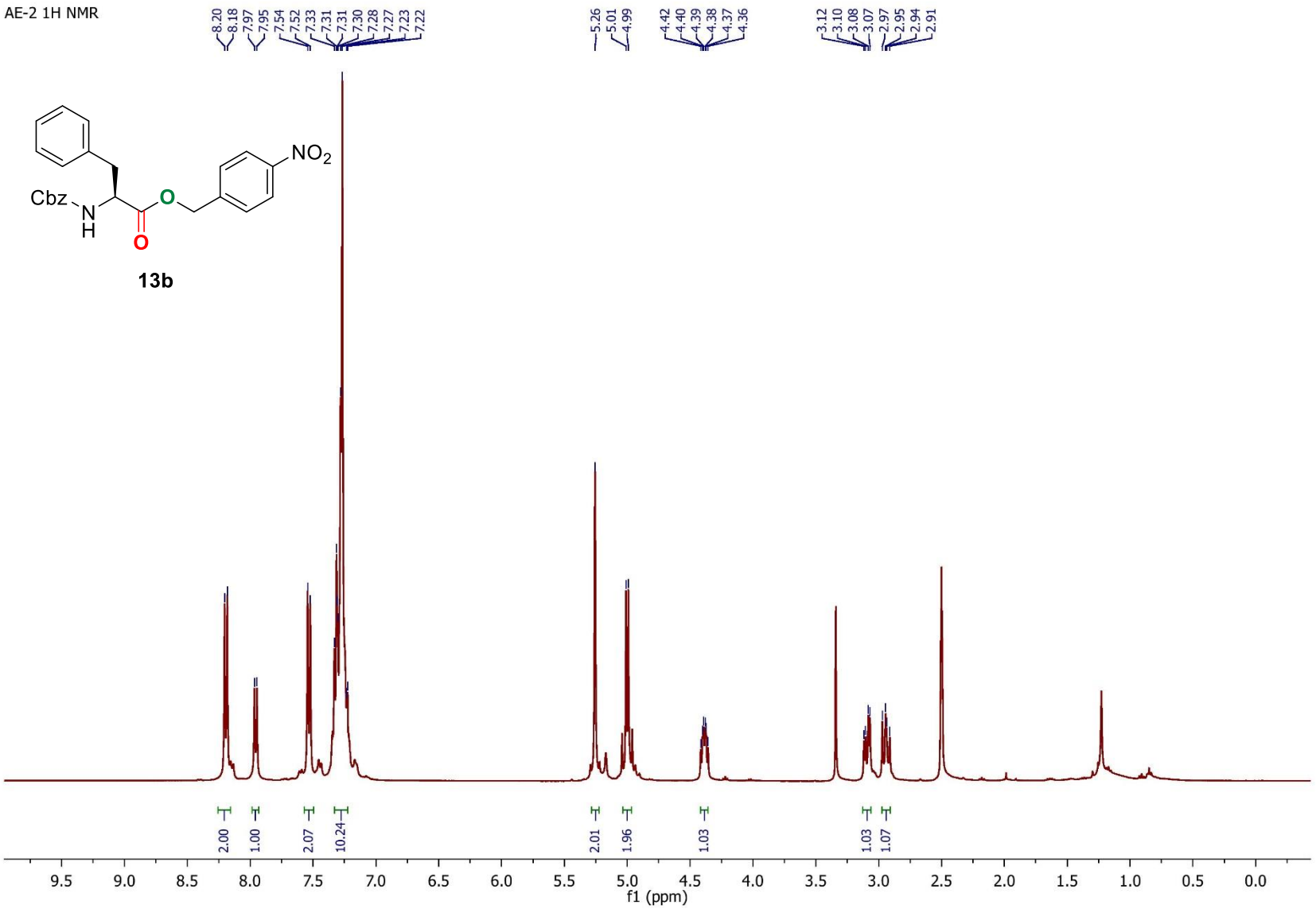


Figure S155. ^{1}H NMR Spectrum of **13b (400MHz, DMSO-d$_6$)**

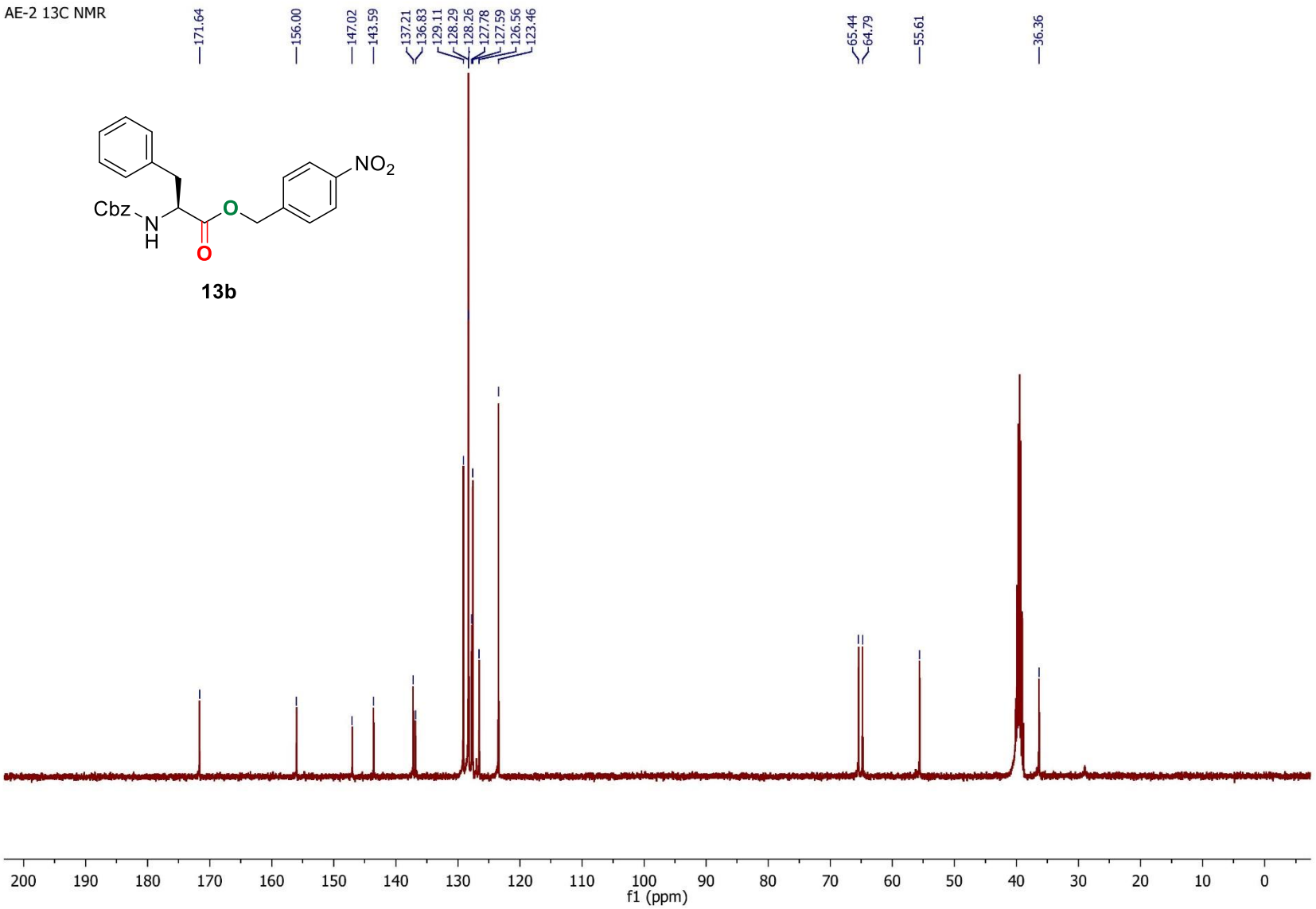


Figure S156. ^{13}C NMR Spectrum of **13b(101MHz, DMSO-d$_6$)**

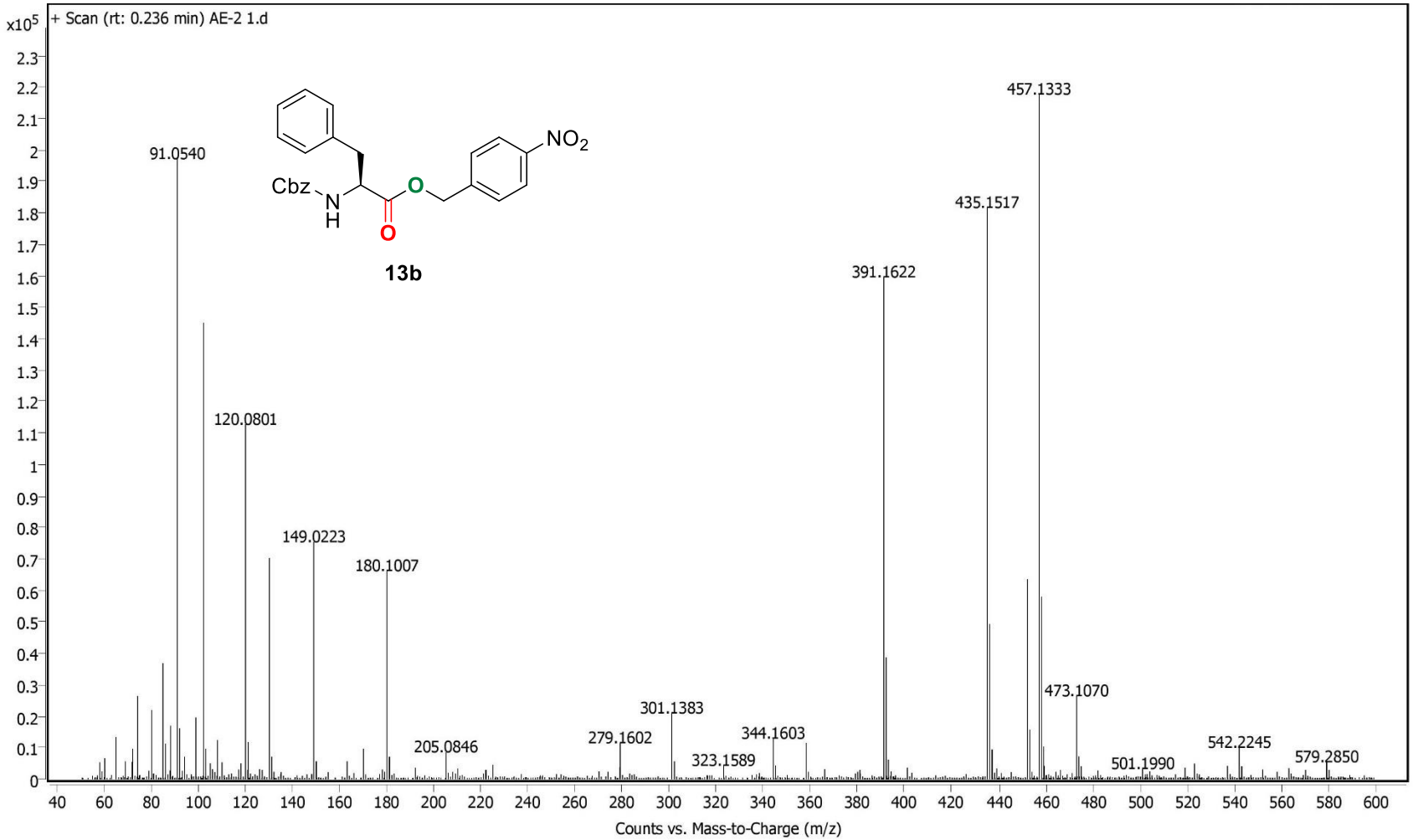


Figure S157. HRMS Spectrum of **13b**

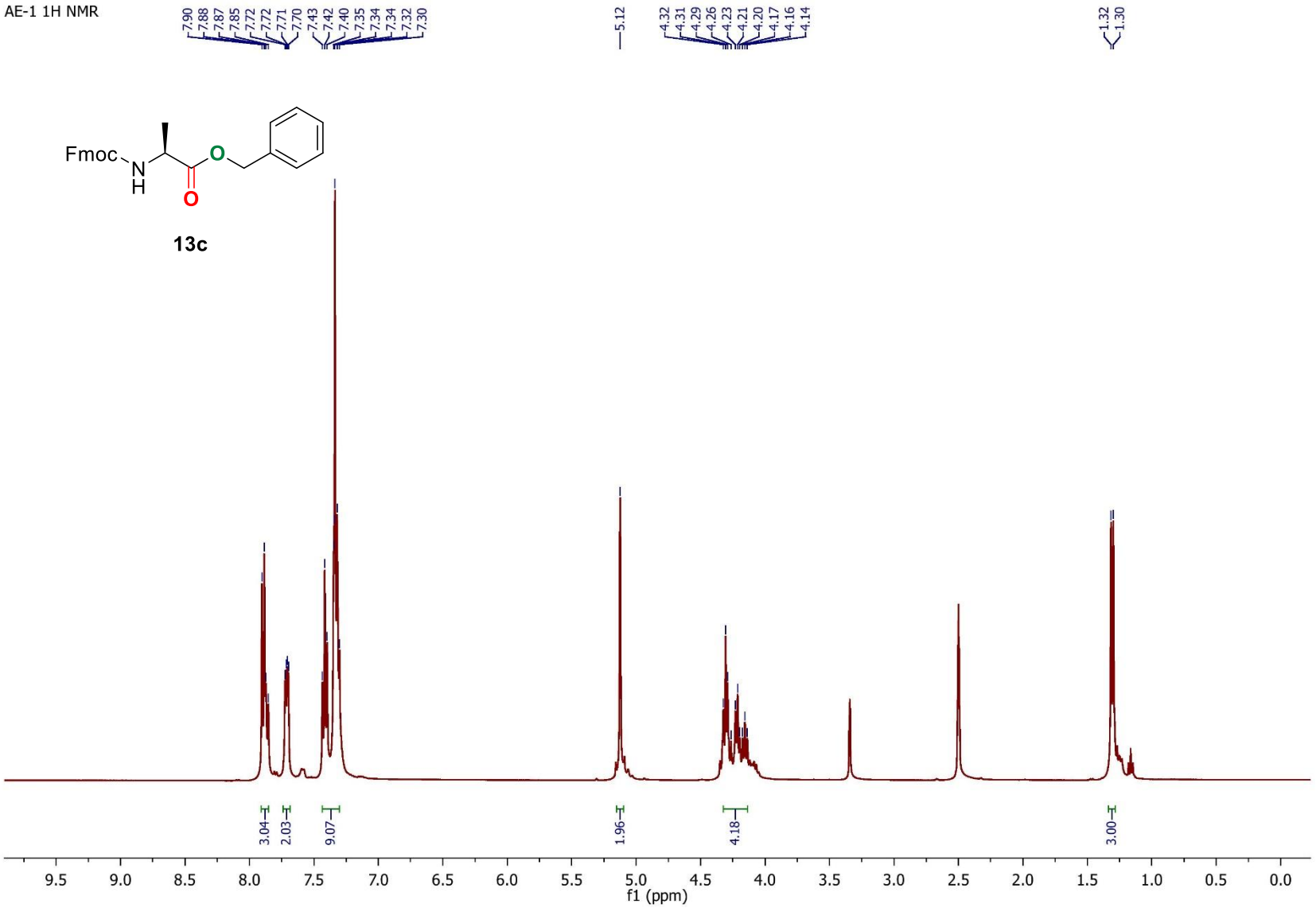


Figure S158. ^{1}H NMR Spectrum of **13c (400MHz, DMSO-d$_6$)**

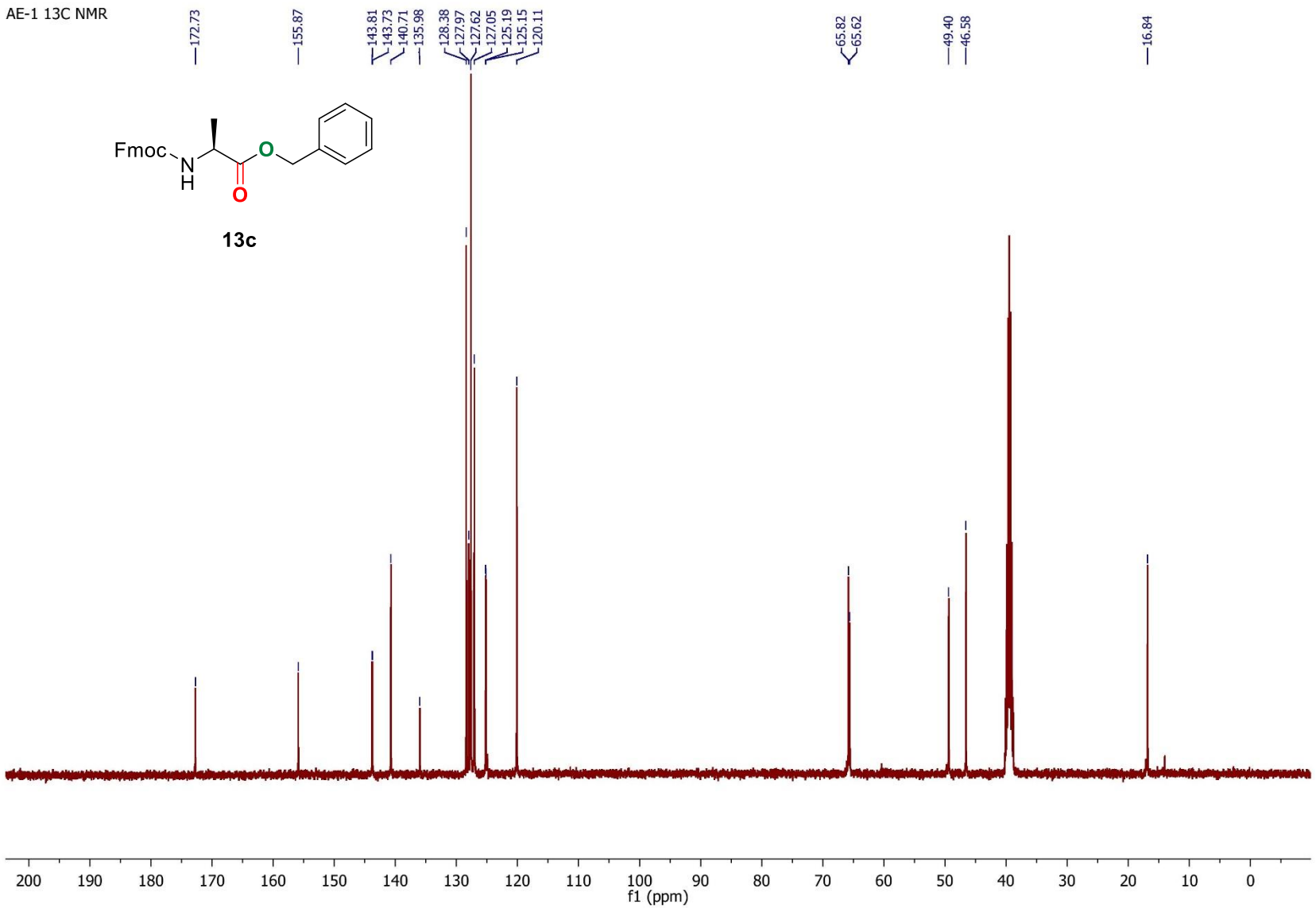


Figure S159. ^{13}C NMR Spectrum of **13c (101MHz, DMSO-d$_6$)**

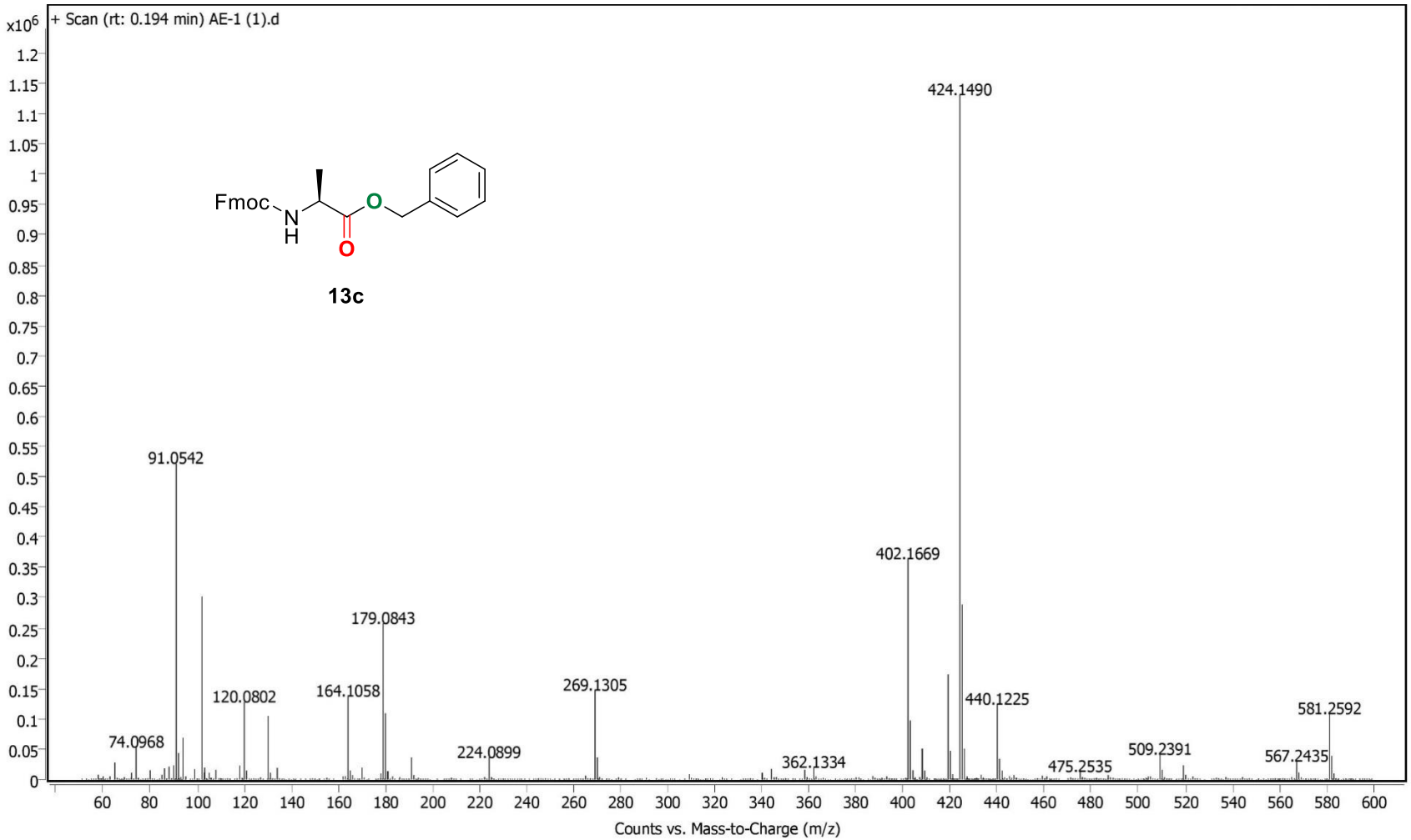


Figure S160. HRMS Spectrum of **13c**

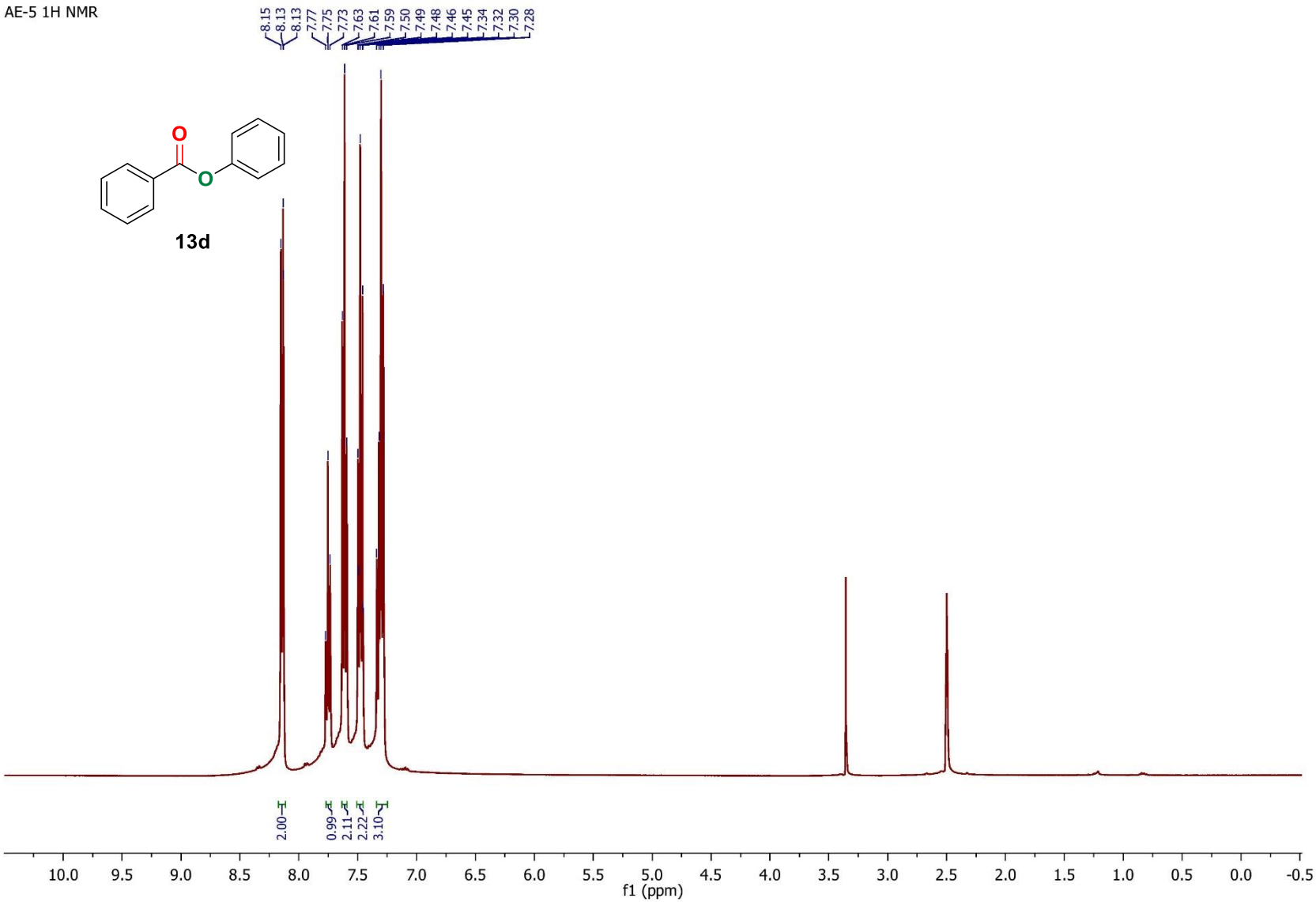


Figure S161. ^{1}H NMR Spectrum of **13d (400MHz, DMSO-d$_6$)**

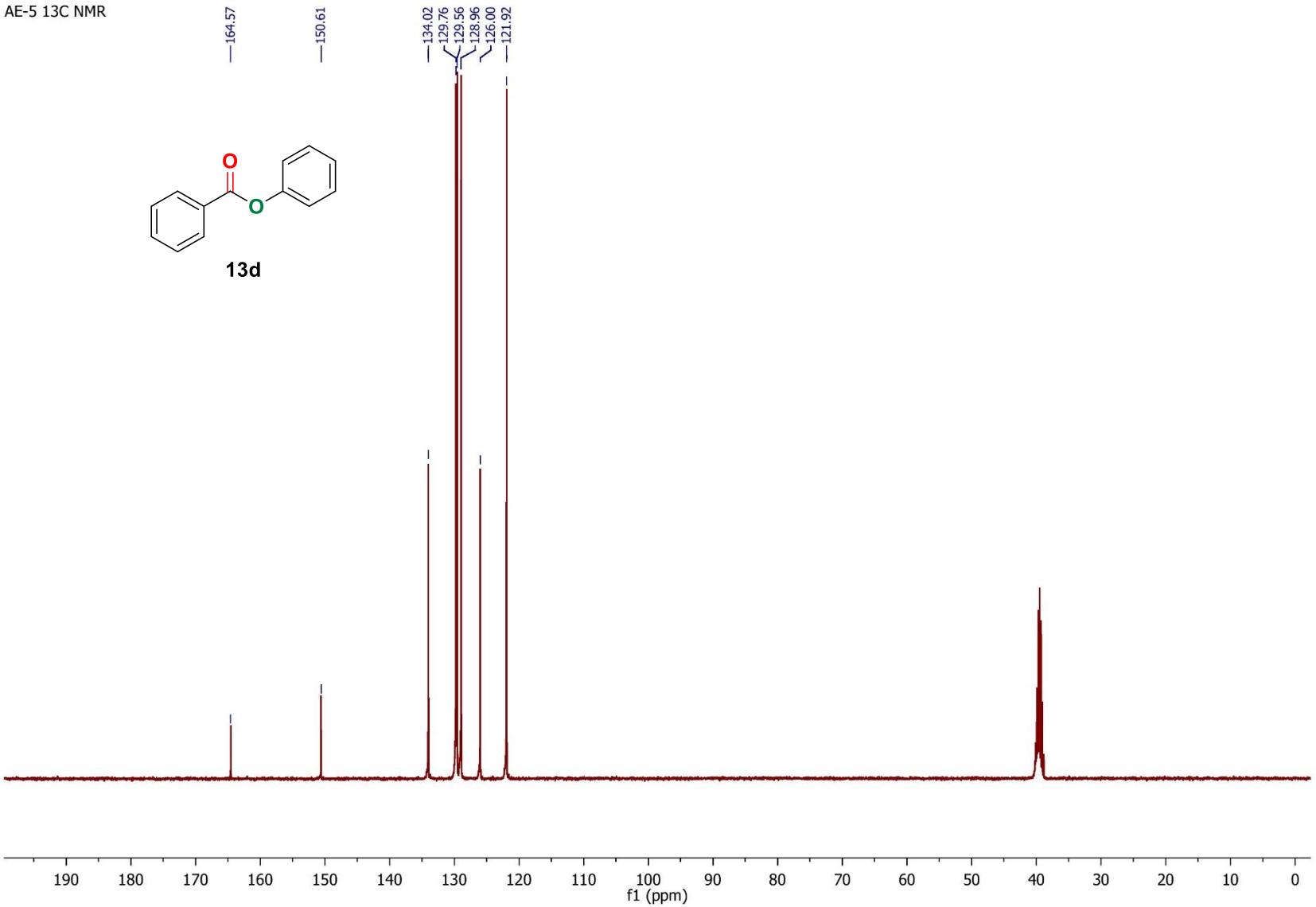


Figure S162. ^{13}C NMR Spectrum of **13d (101MHz, DMSO-d_6)**

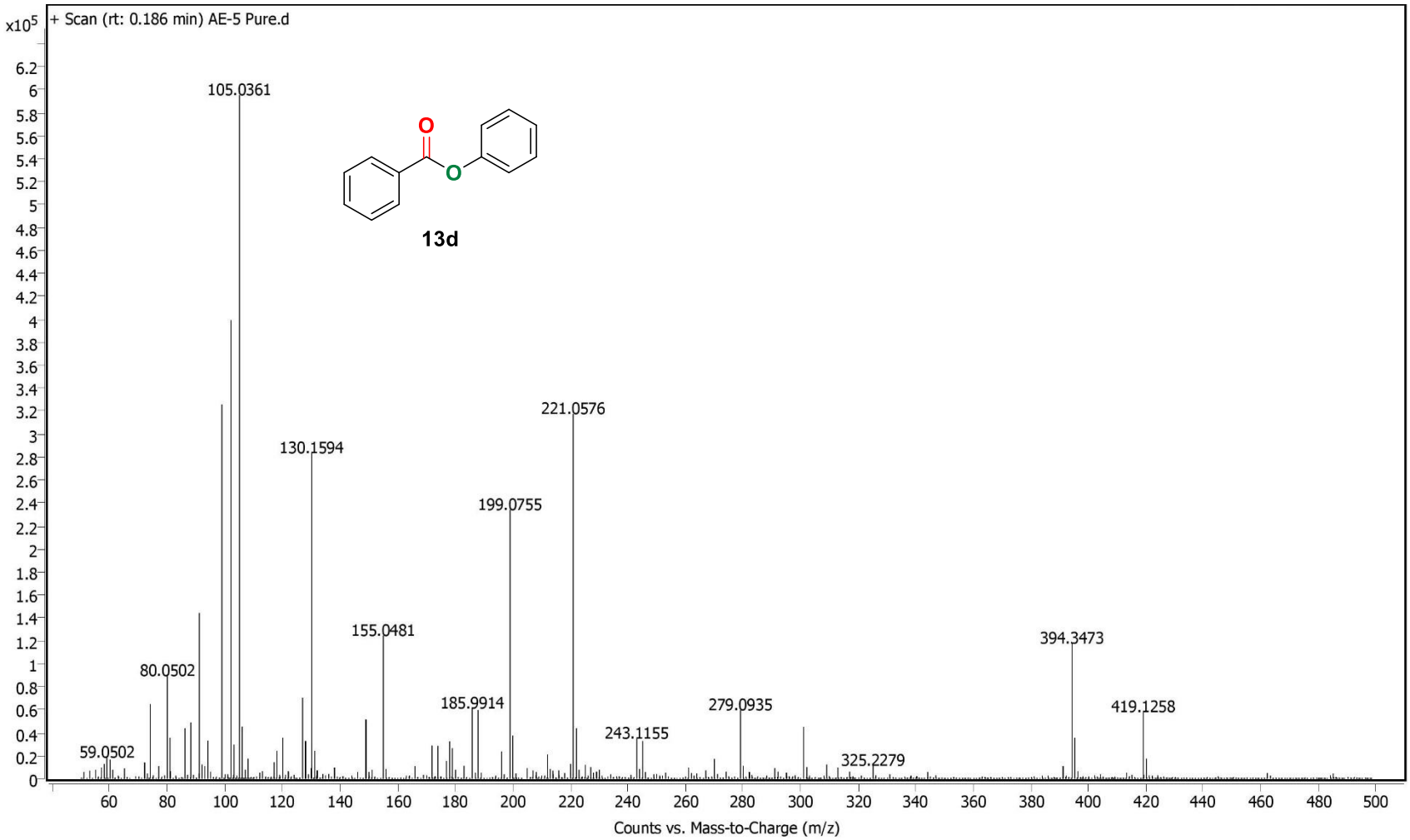


Figure S163. HRMS Spectrum of **13d**

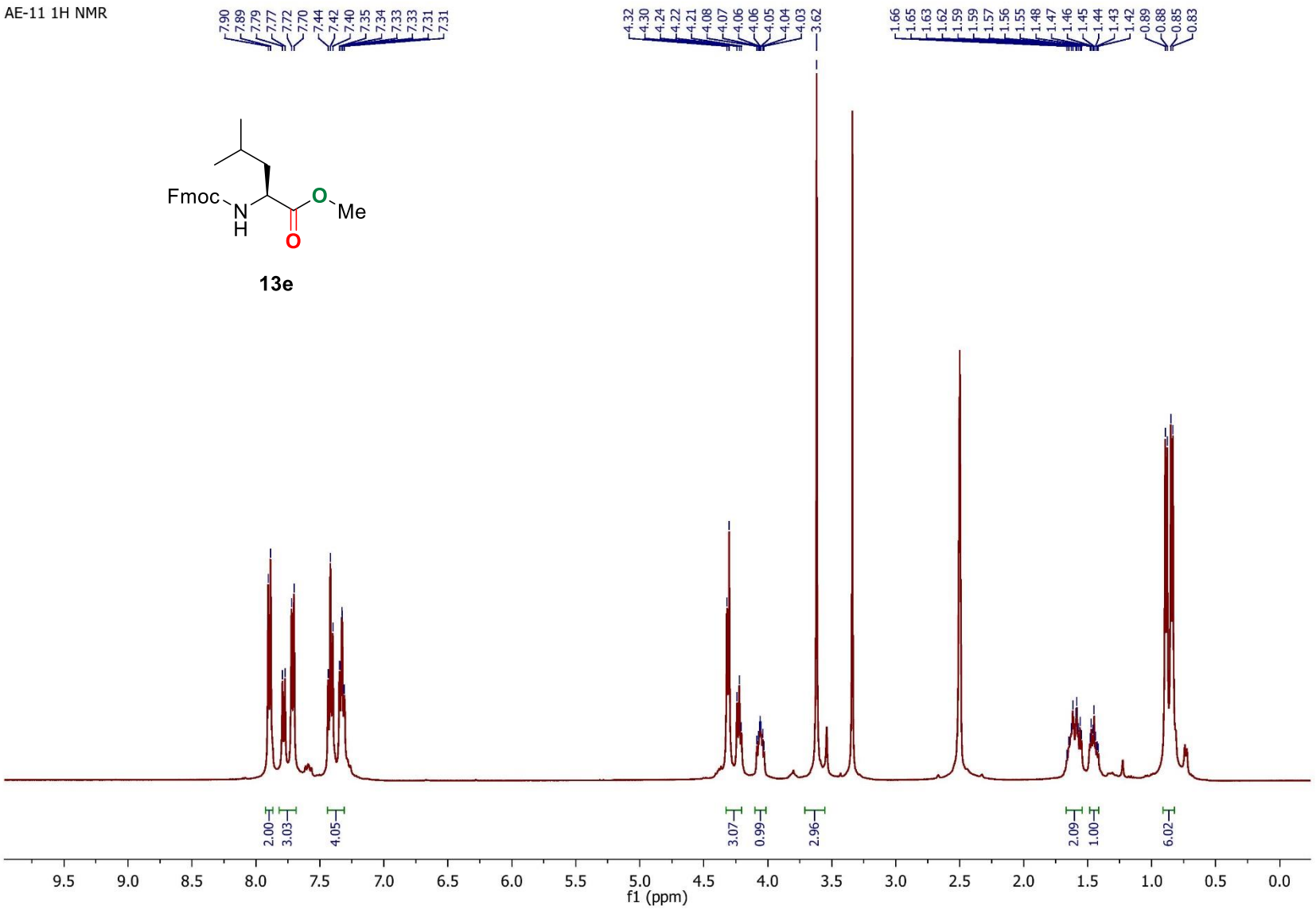


Figure S164. ^{1}H NMR Spectrum of **13e (400MHz, DMSO-d$_6$)**

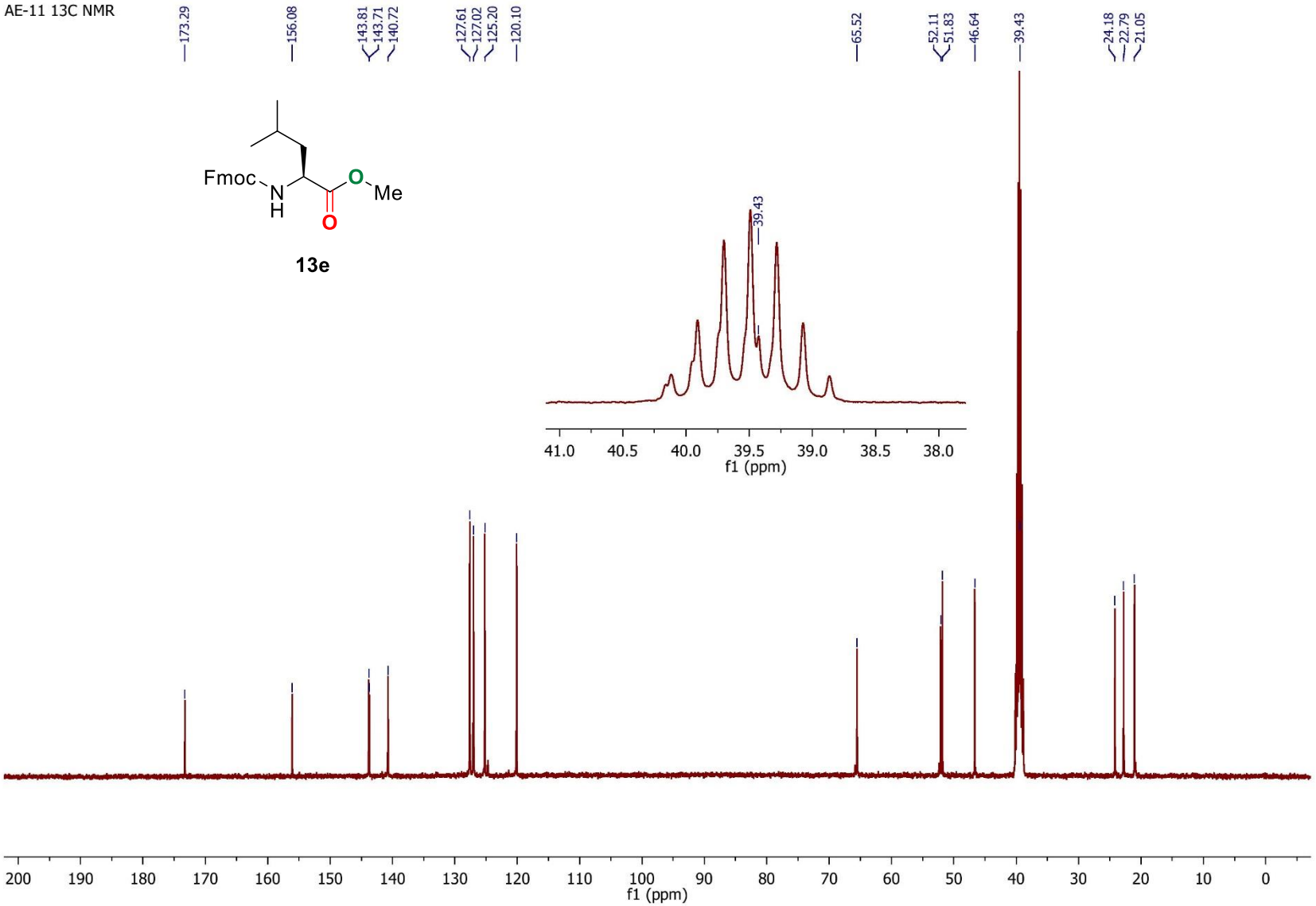


Figure S165. ^{13}C NMR Spectrum of **13e(101MHz, DMSO-d$_6$)**

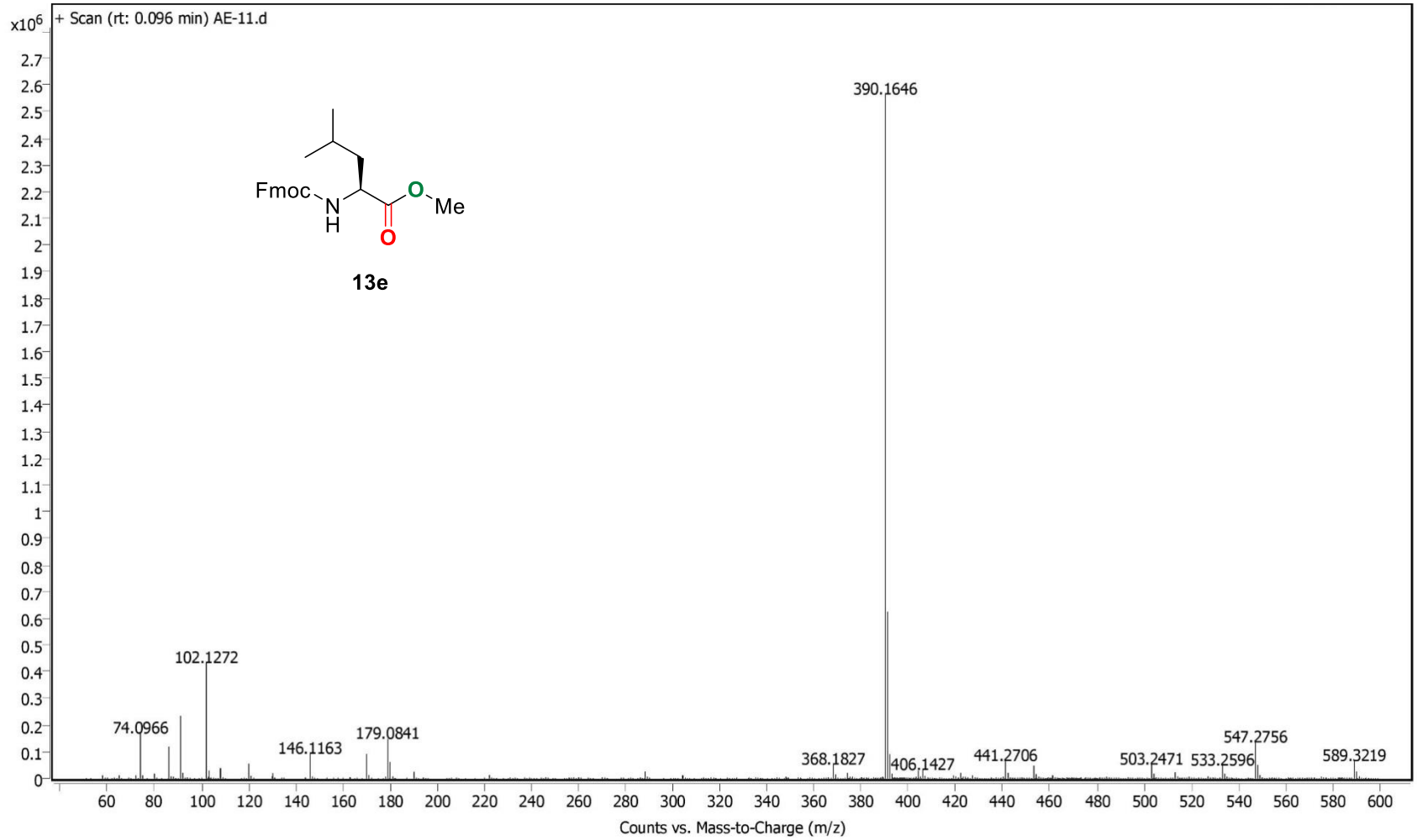


Figure S166. HRMS Spectrum of **13e**

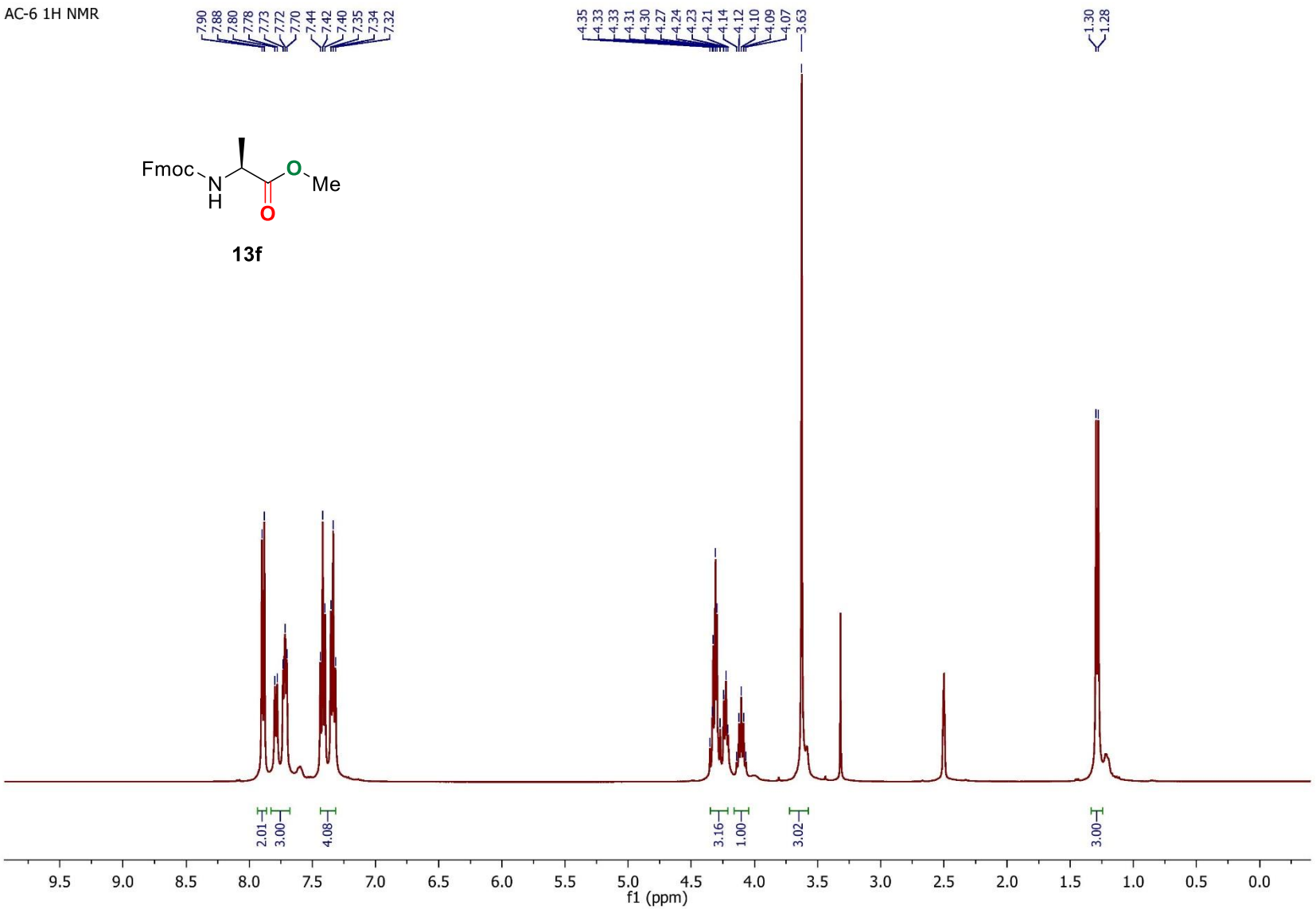


Figure S167. ^{1}H NMR Spectrum of **13f (400MHz, DMSO-d$_6$)**

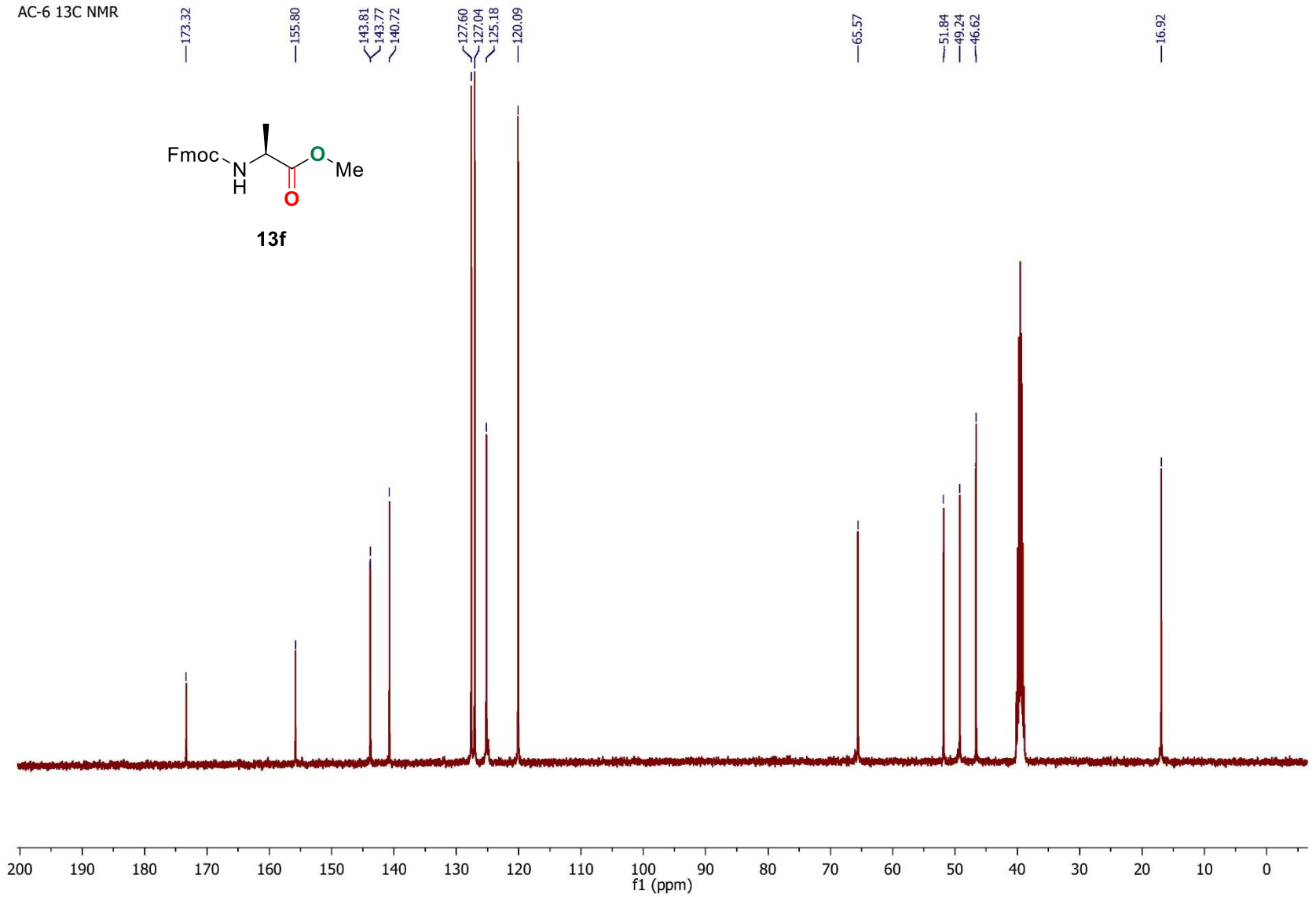


Figure S168. ^{13}C NMR Spectrum of **13f(101MHz, DMSO-d$_6$)**

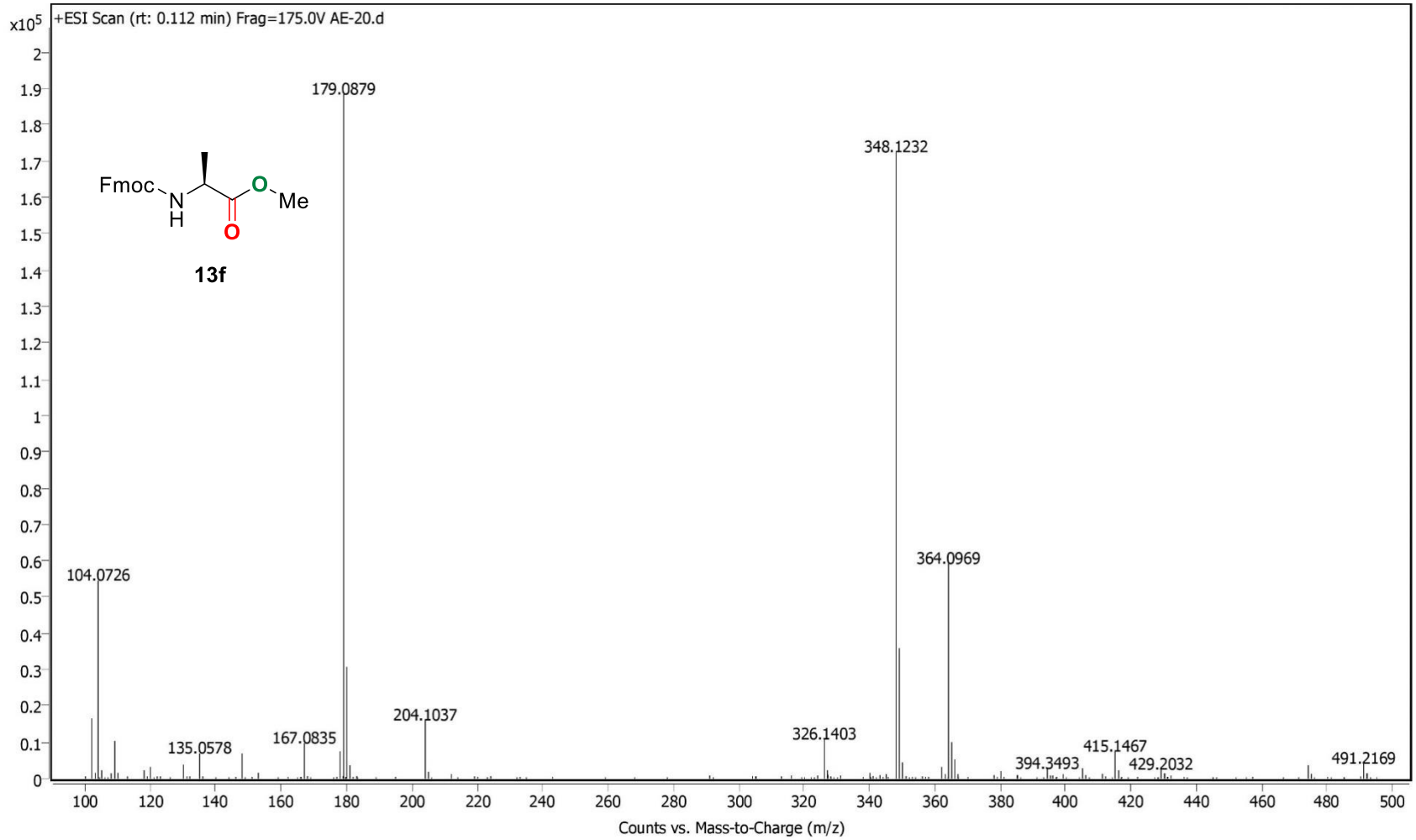


Figure S169 HRMS Spectrum of **13f**

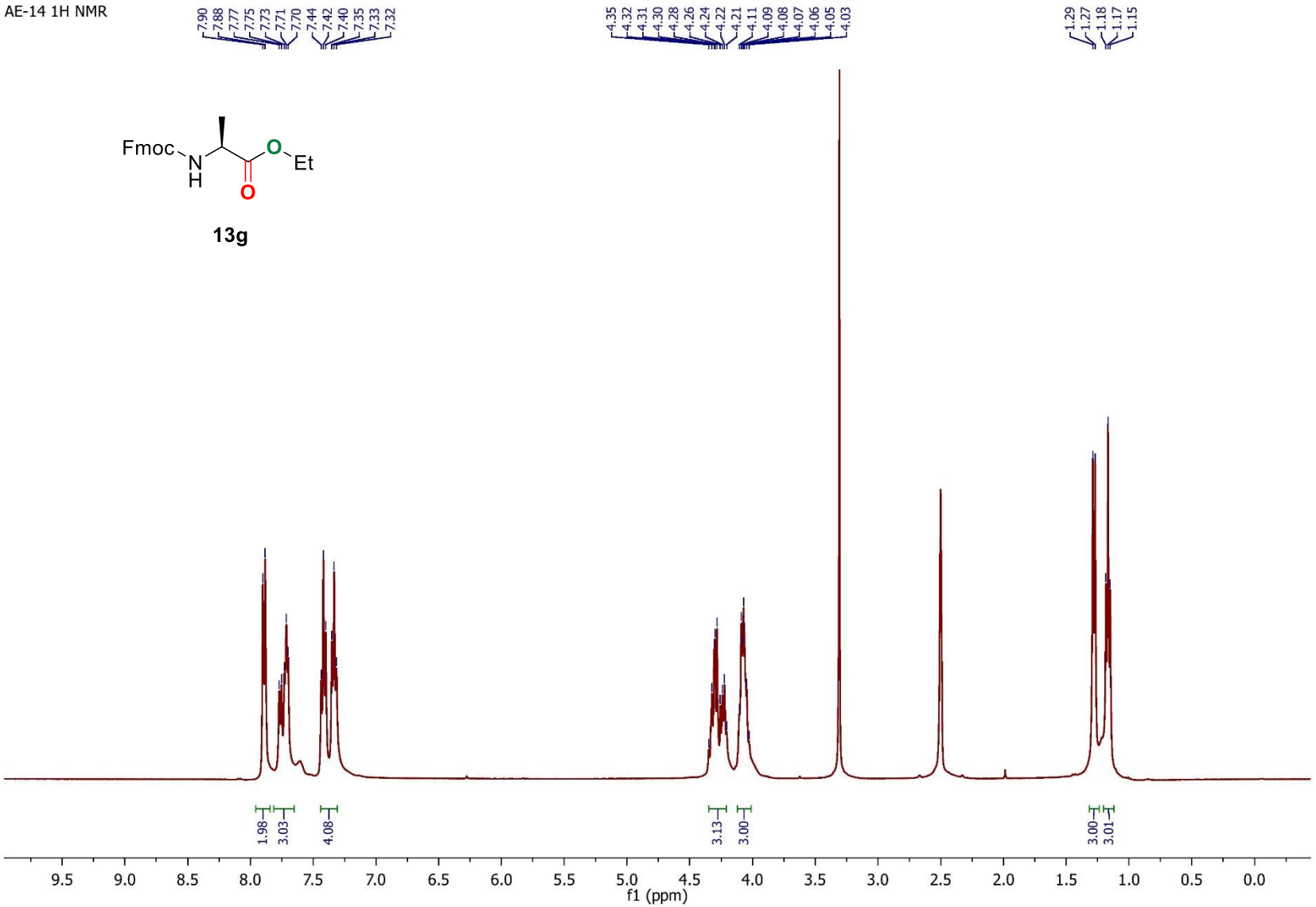


Figure S170. ^{1}H NMR Spectrum of **13g (400MHz, DMSO-d_6)**

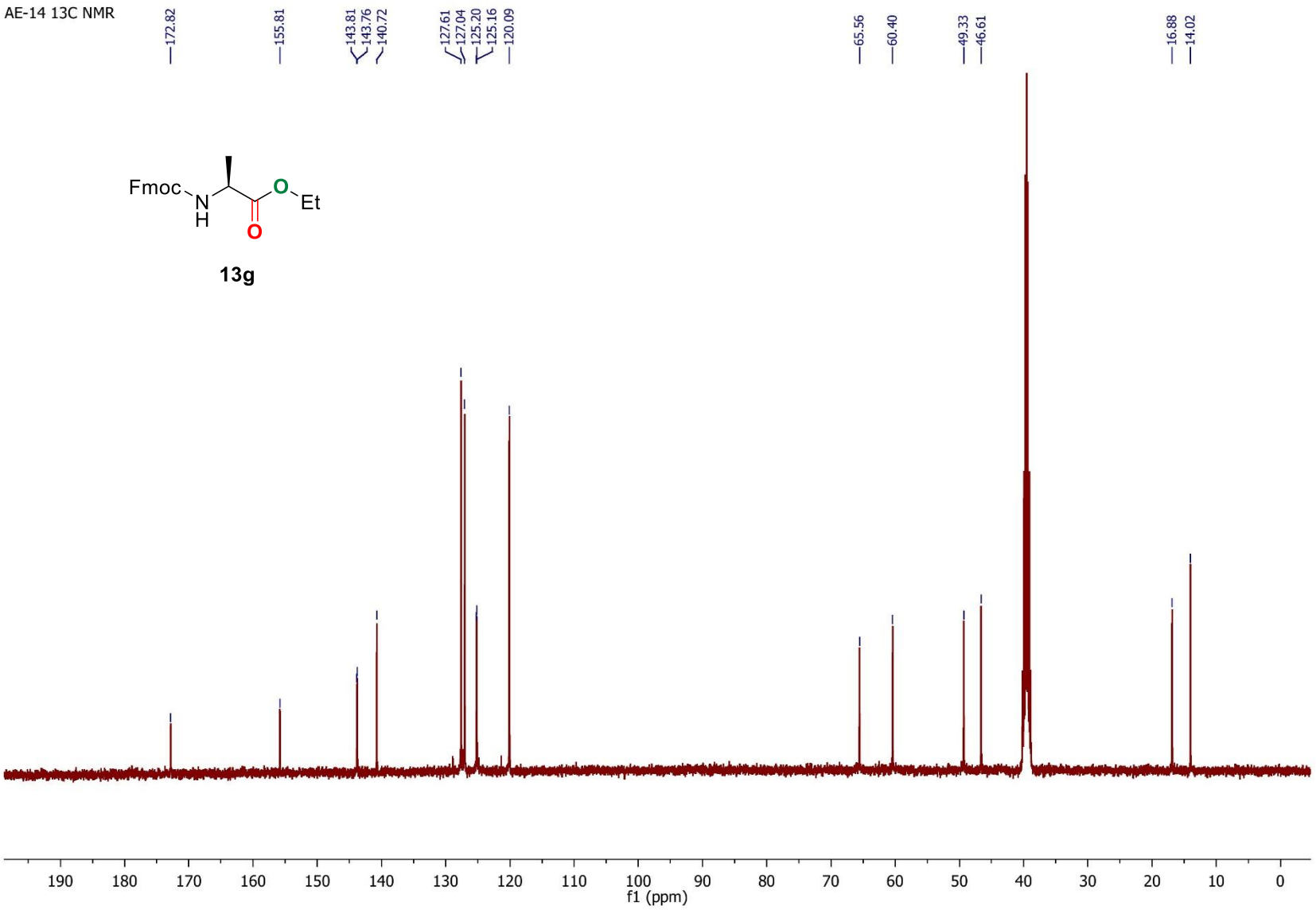


Figure S171. ^{13}C NMR Spectrum of **13g (101MHz, DMSO-d_6)**

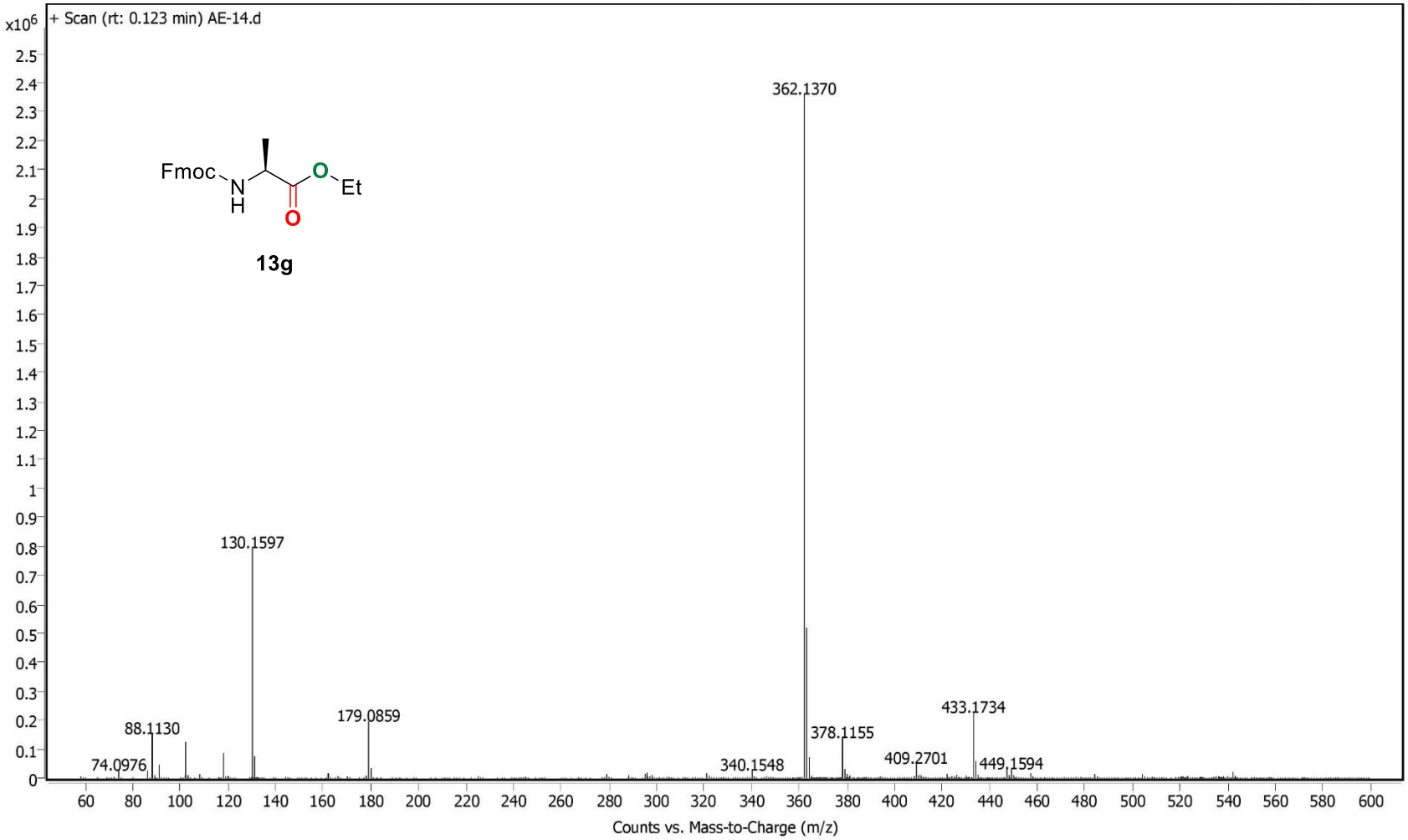


Figure S172. HRMS Spectrum of **13g**

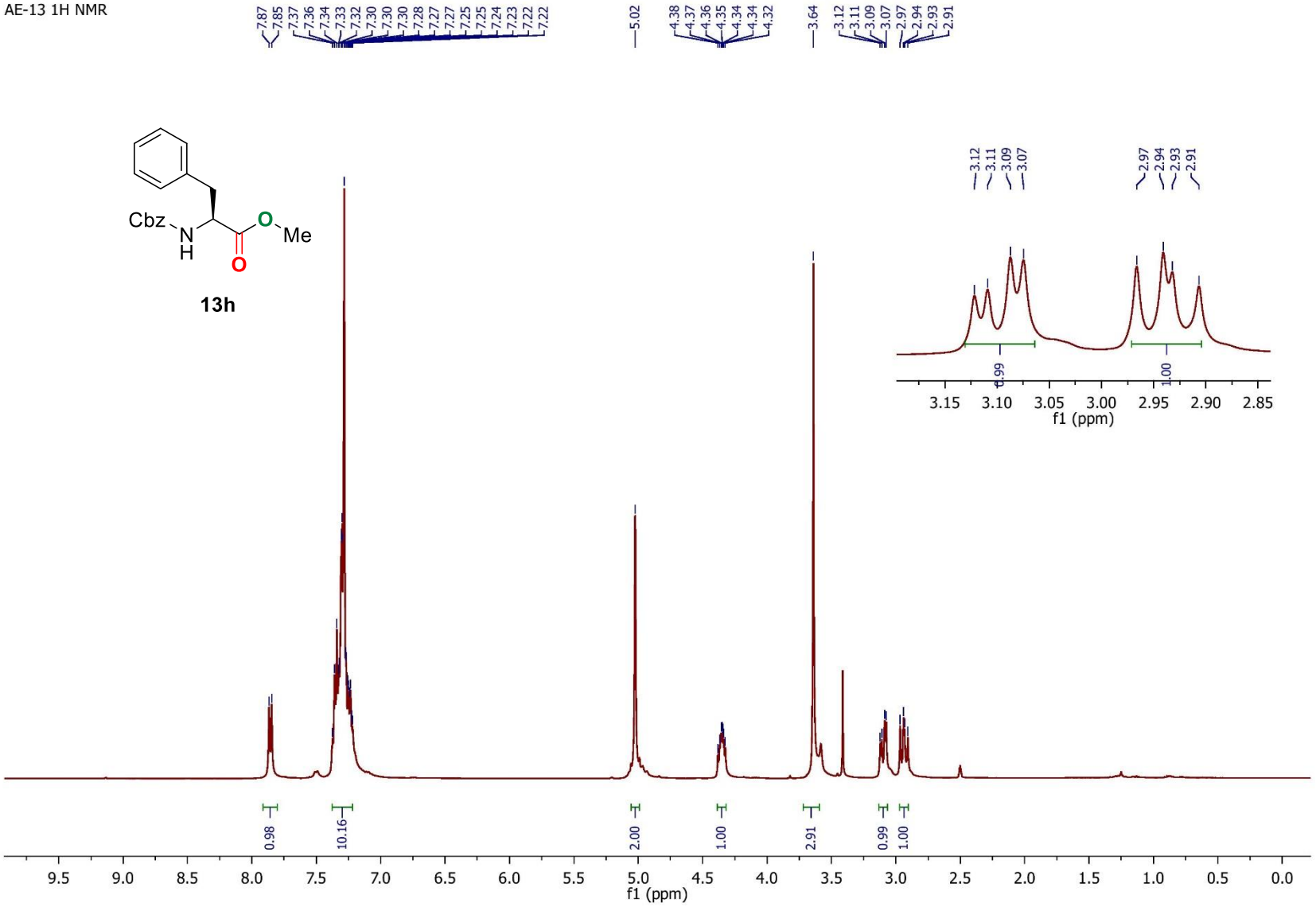


Figure S173. ^{1}H NMR Spectrum of **13h (400MHz, DMSO-d$_6$)**

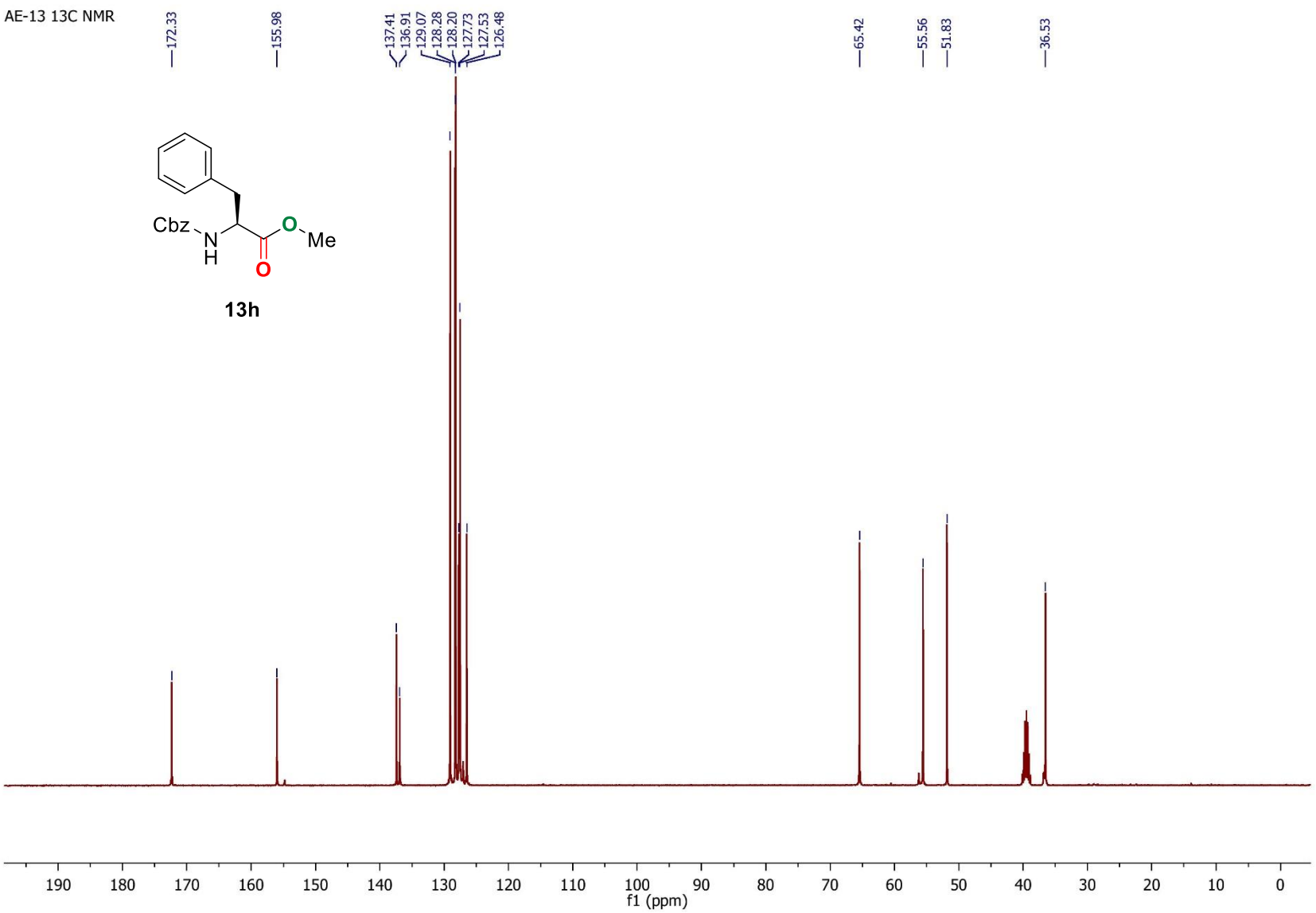


Figure S174. ^{13}C NMR Spectrum of **13h (101MHz, DMSO-d$_6$)**

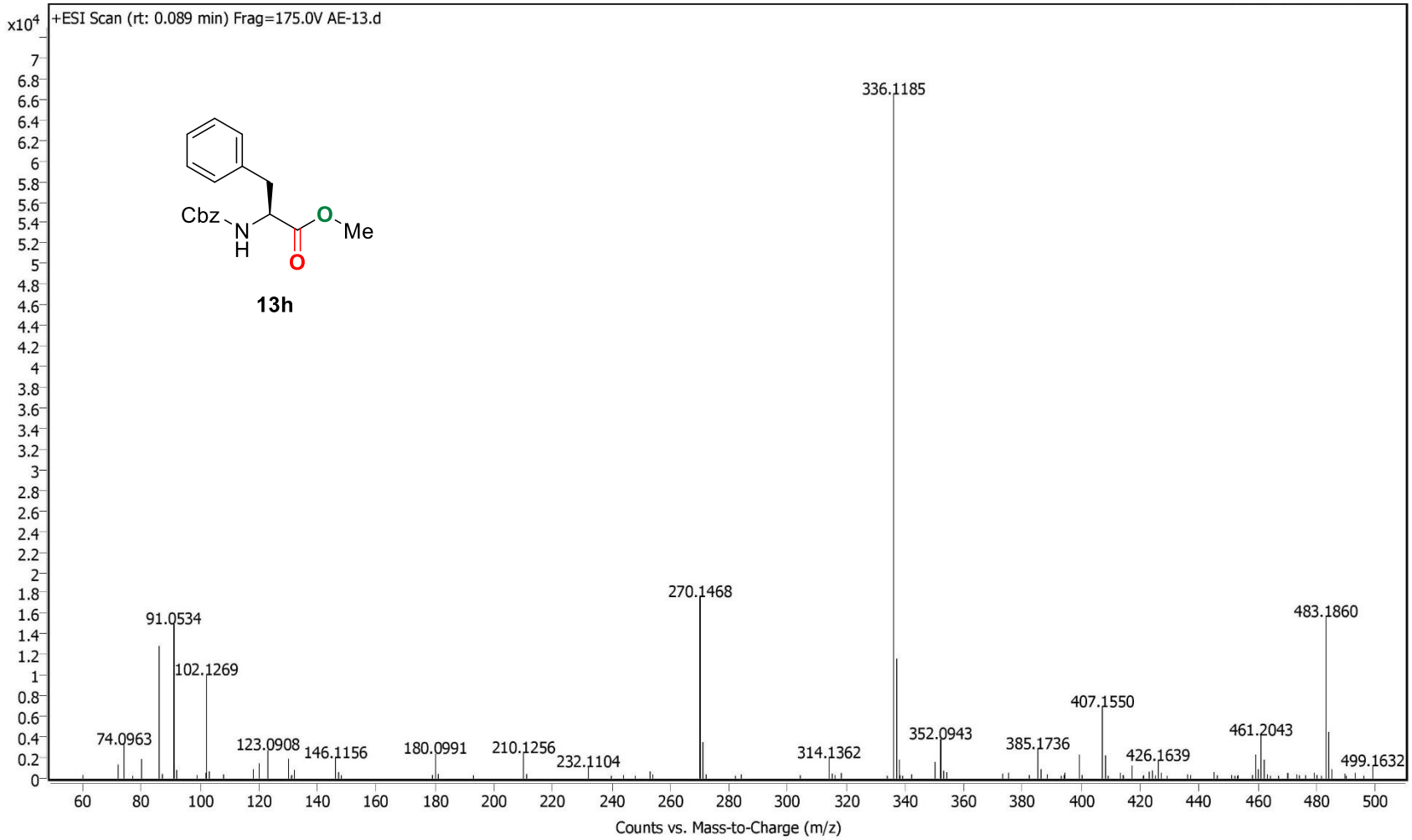


Figure S175 HRMS Spectrum of **13h**

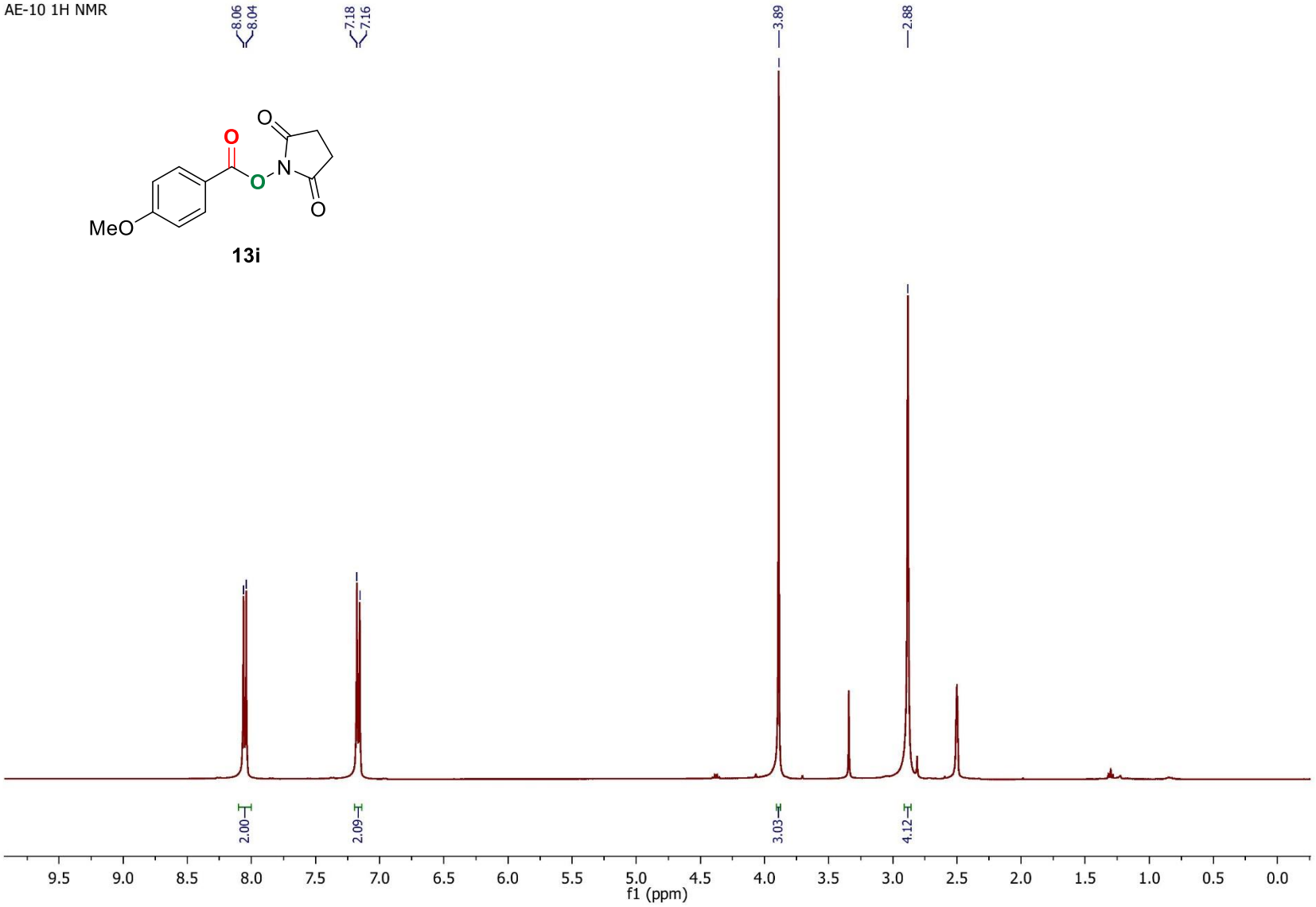


Figure S176. ^{1}H NMR Spectrum of **13i (400MHz, DMSO-d$_6$)**

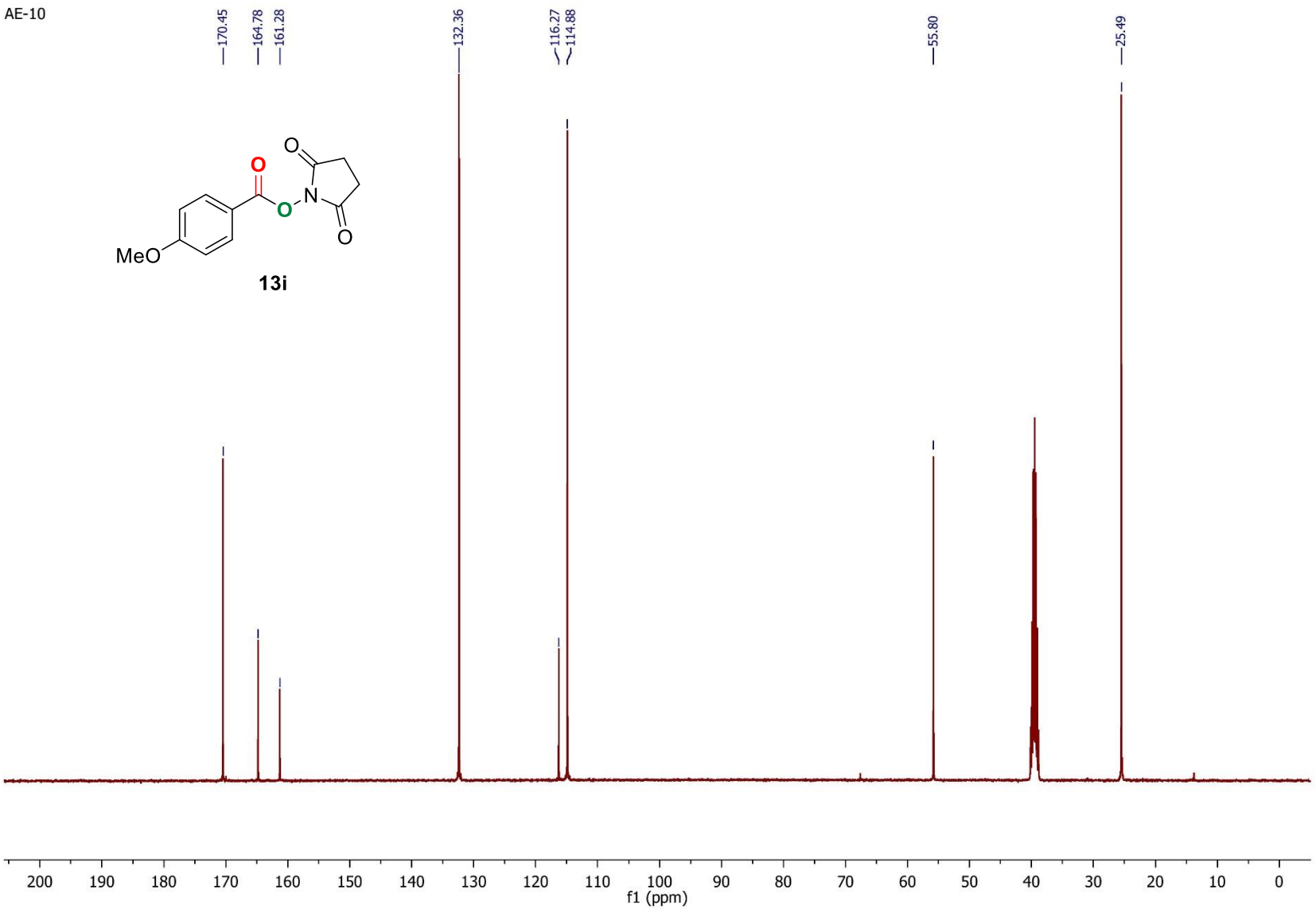


Figure S177. ^{13}C NMR Spectrum of **13i (101MHz, DMSO-d$_6$)**

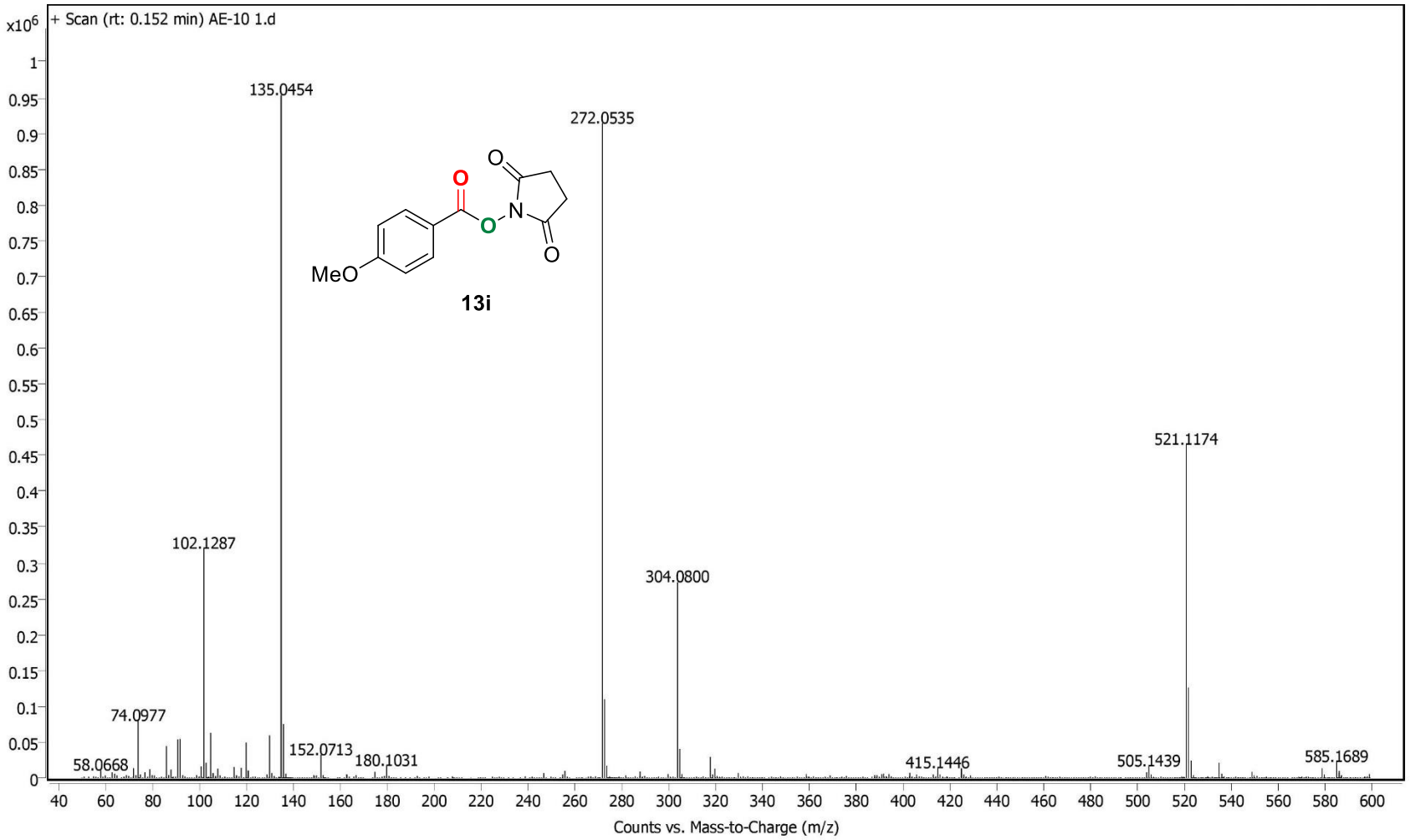
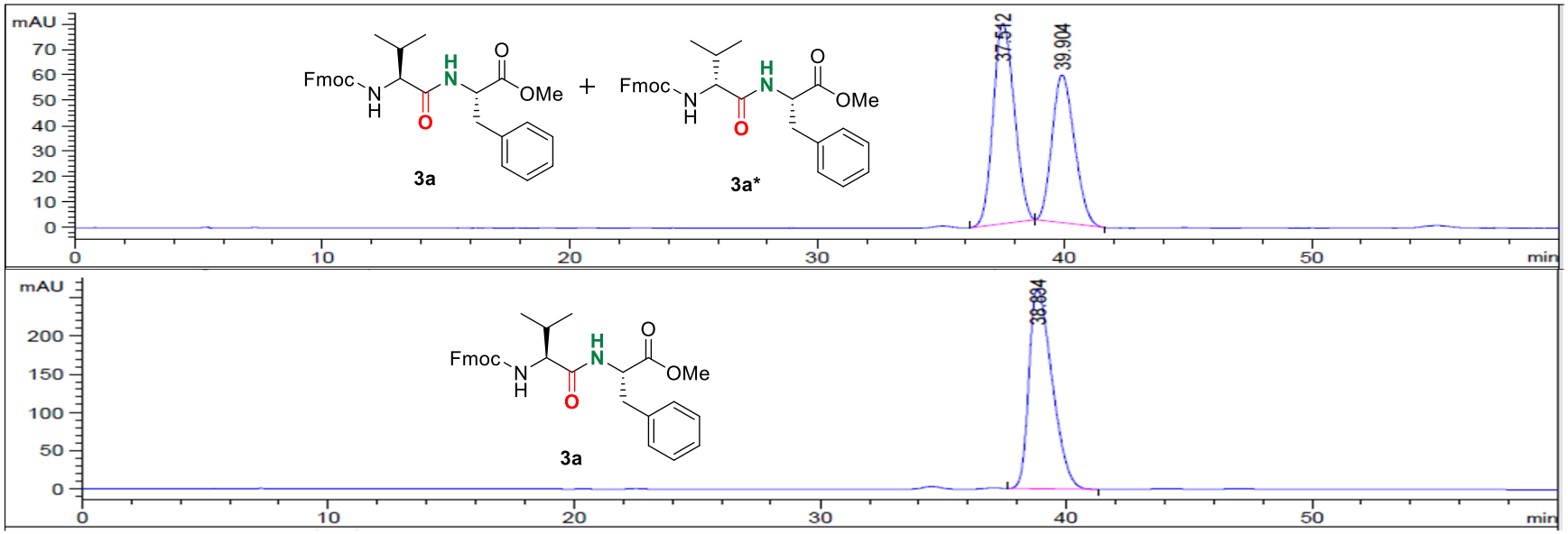


Figure S178. HRMS Spectrum of **13i**

HPLC studies for determining racemization of 3a



HPLC condition: water-acetonitrile (35-65%) in 60 min; VWD at λ = 254 nm; flow rate: 0.5 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

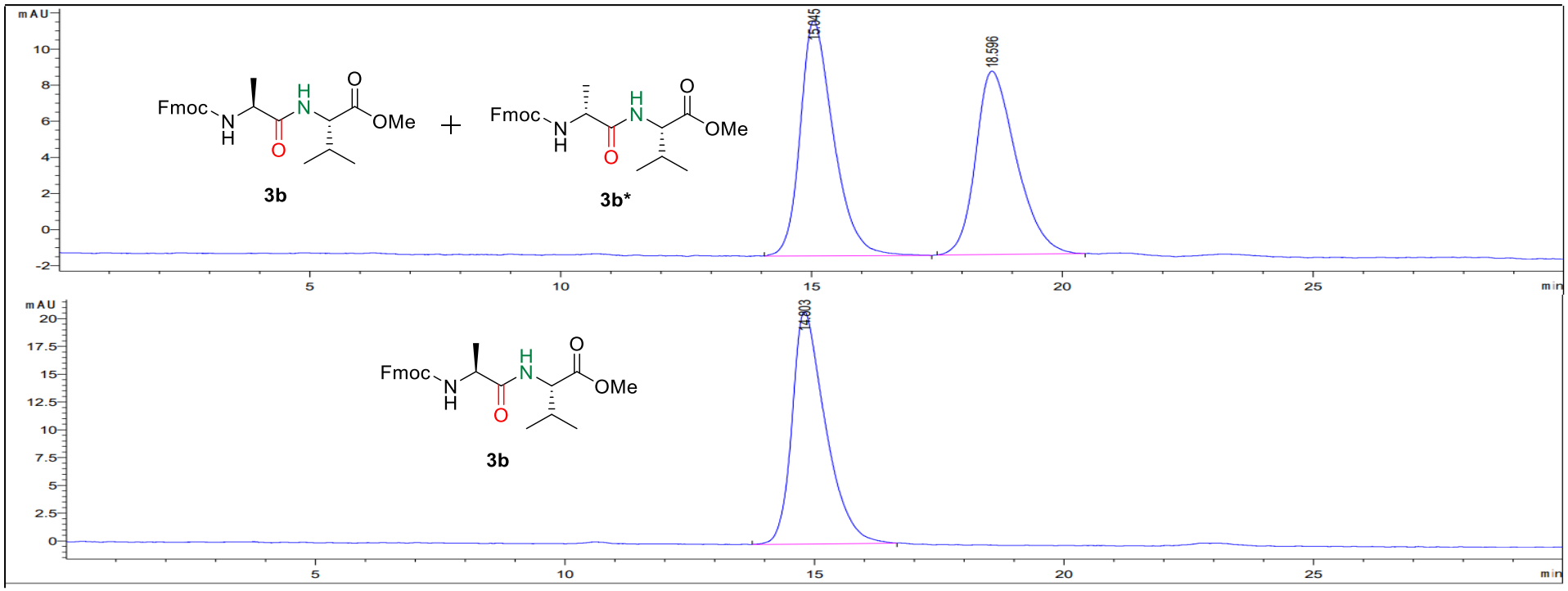
1) Mixed HPLC data of (L,L)-3a and (D,L) 3a*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	37.512	4681.70166	78.72181	56.1238
02	39.904	3660.03784	58.05646	43.8762

2) Pure HPLC data of (L,L)-3a

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	38.834	1.71320e4	262.20193	100.0000

HPLC studies for determining racemization of 3b



HPLC condition: water-acetonitrile (30-70%) in 30 min; VWD at λ = 254 nm; flow rate: 0.5 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

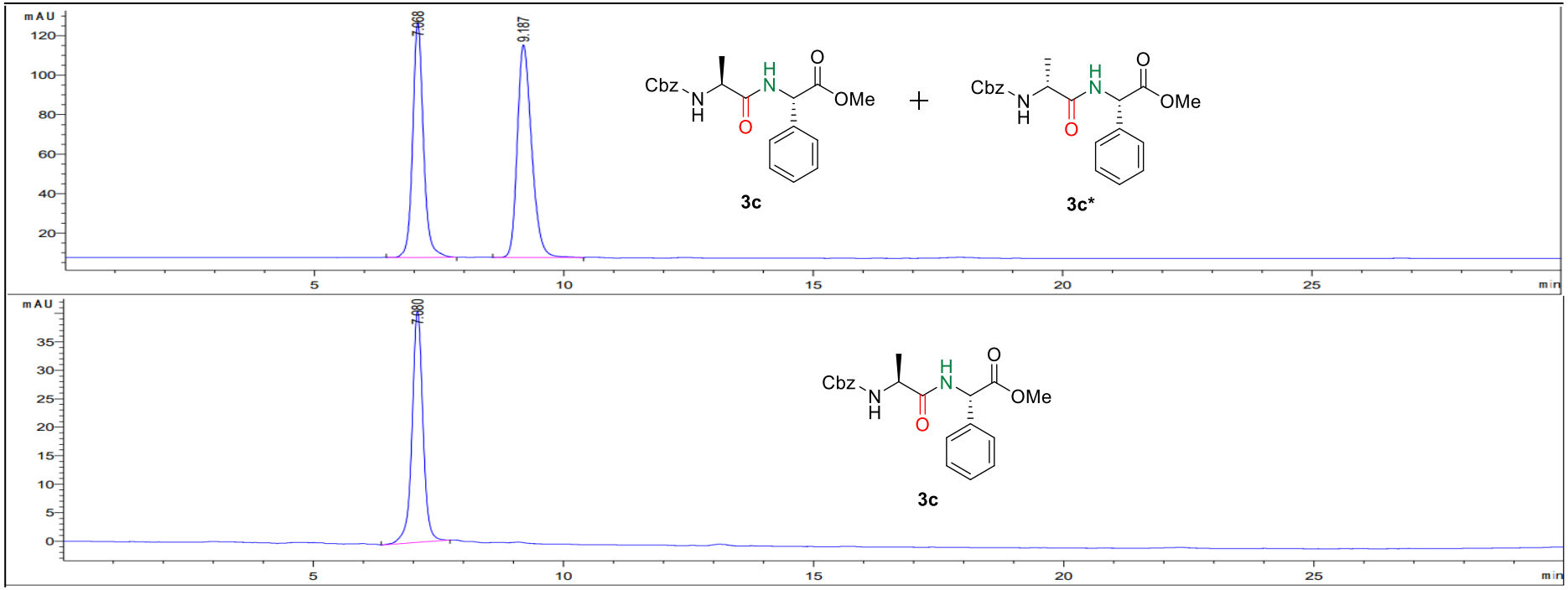
1) Mixed HPLC data of (L,L)-3b and (D,L) 3b*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	15.045	600.54443	13.01576	51.2951
02	18.596	570.21930	10.15413	48.7049

2) Pure HPLC data of (L,L)-3b

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	14.803	973.65771	20.89940	100.0000

HPLC studies for determining racemization of 3c



HPLC condition: water-acetonitrile (30-70%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

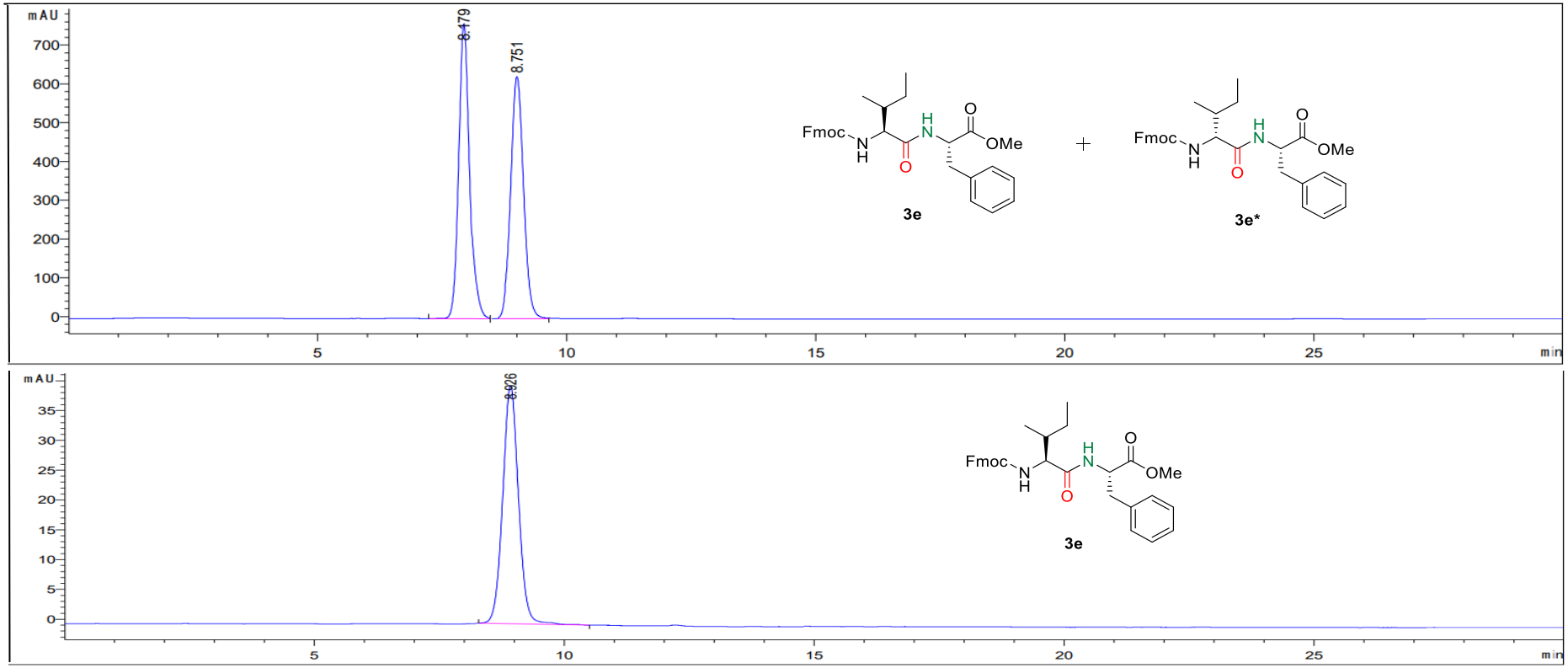
1) Mixed HPLC data of (L,L)-3c and (D,L) 3c*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.068	1779.08960	119.15787	45.3229
02	9.187	2146.27686	107.67322	54.6771

2) Pure HPLC data of (L,L)-3c

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.080	613.83362	40.67035	100.0000

HPLC studies for determining racemization of 3e



HPLC condition: water-methanol (30-70%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

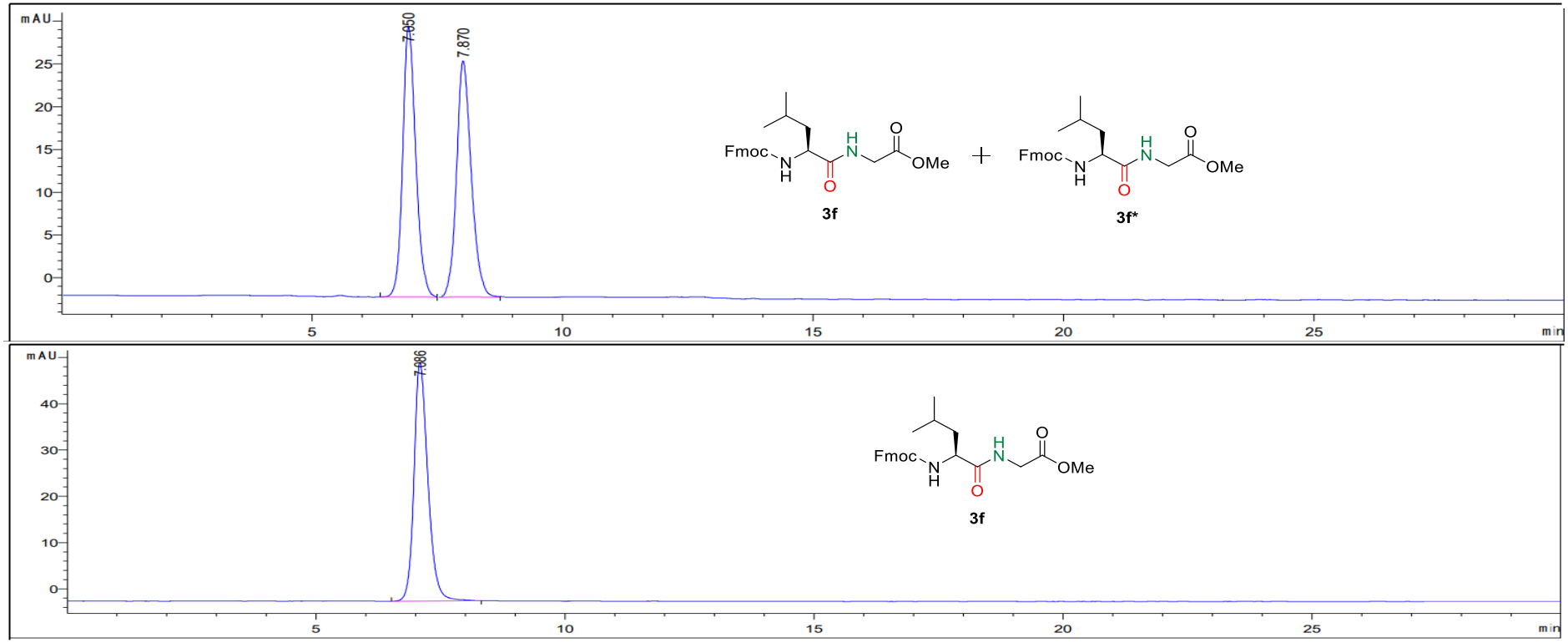
1) Mixed HPLC data of (L,L)-3e and (D,L) 3e*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.179	1.10687e4	760.18402	49.6071
02	8.751	1.12440e4	623.56458	50.3929

2) Pure HPLC data of (L,L)-3e

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.926	878.66614	39.93617	100.0000

HPLC studies for determining racemization of 3f



HPLC condition: water-acetonitrile (25-75%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

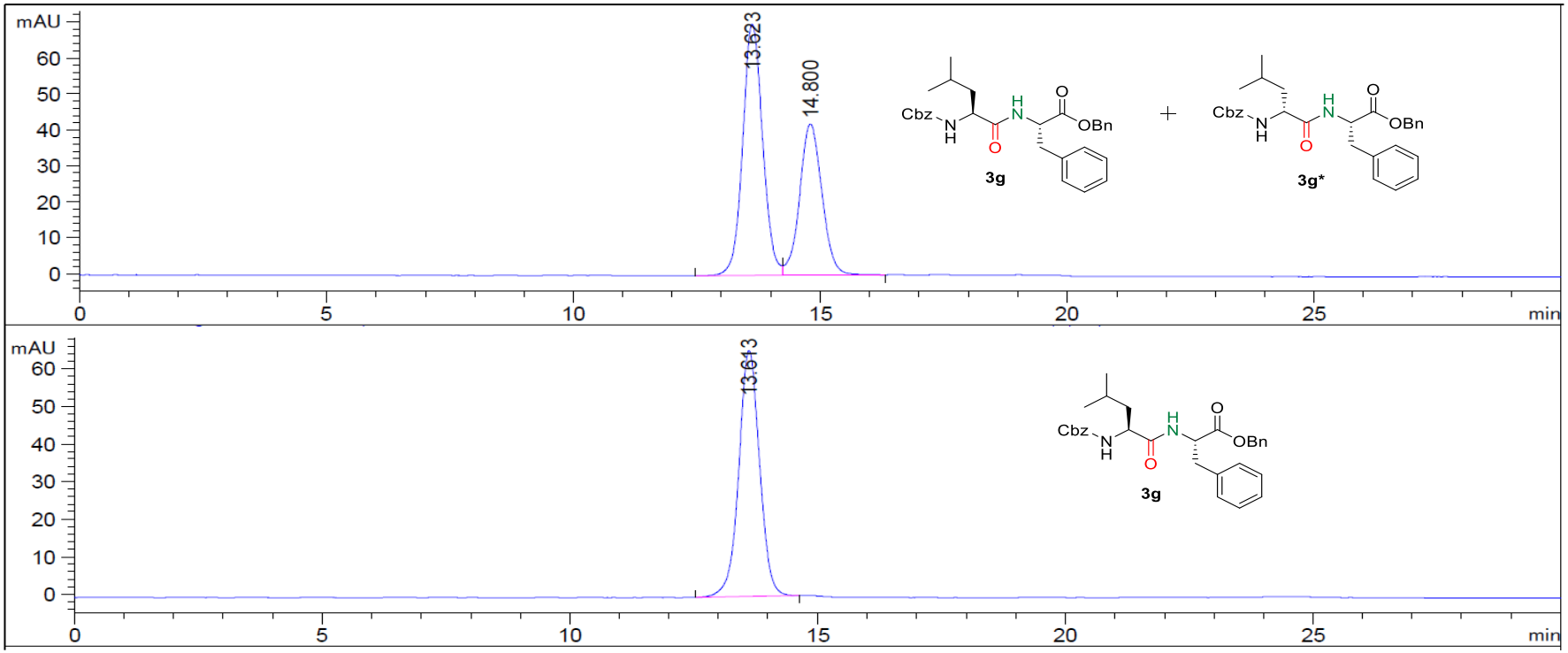
1) Mixed HPLC data of (L,L)-3f and (D,L) 3f*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.050	571.71155	31.61432	49.1314
02	7.870	591.92725	27.71265	50.8686

2) Pure HPLC data of (L,L)-3f

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.086	997.24335	51.54872	100.0000

HPLC studies for determining racemization of 3g



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

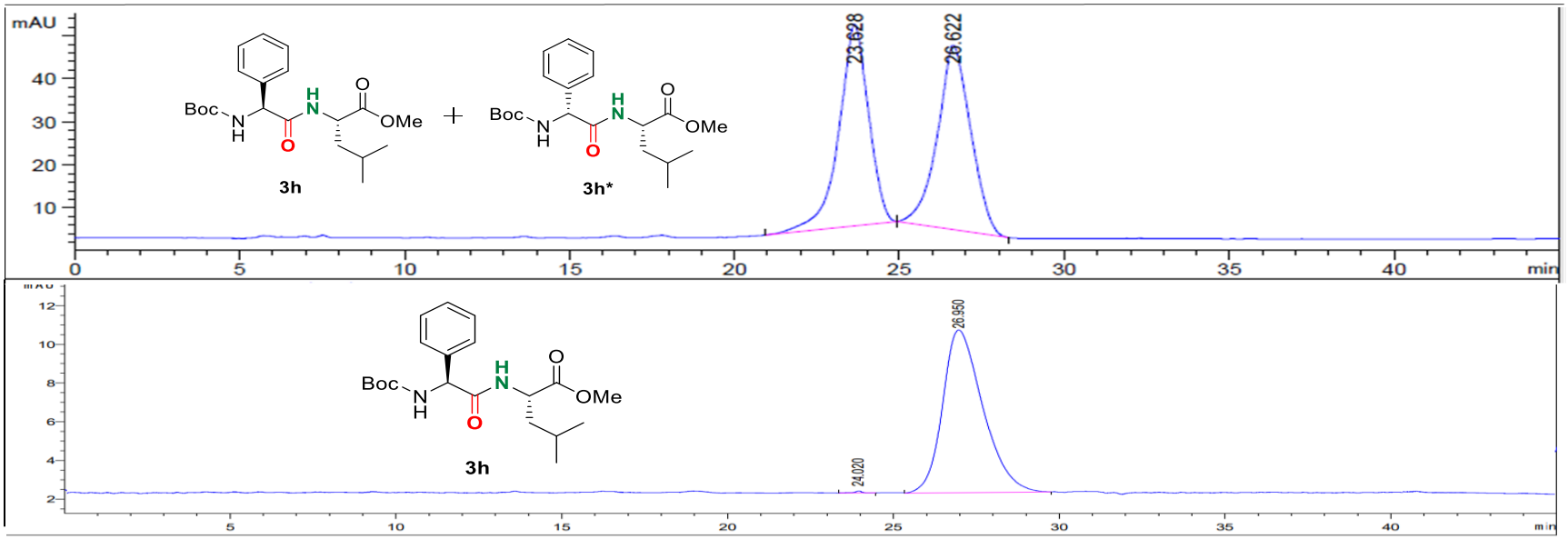
1) Mixed HPLC data of (L,L)-3g and (D,L) 3g*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	13.623	1964.21533	69.83543	59.7167
02	14.800	1325.00928	42.06074	40.2833

2) Pure HPLC data of (L,L)-3g

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	13.613	1910.98755	65.43951	100.0000

HPLC studies for determining racemization of 3h



HPLC condition: water-acetonitrile (45-55%) in 45 min; VWD at λ = 254 nm; flow rate: 0.5 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

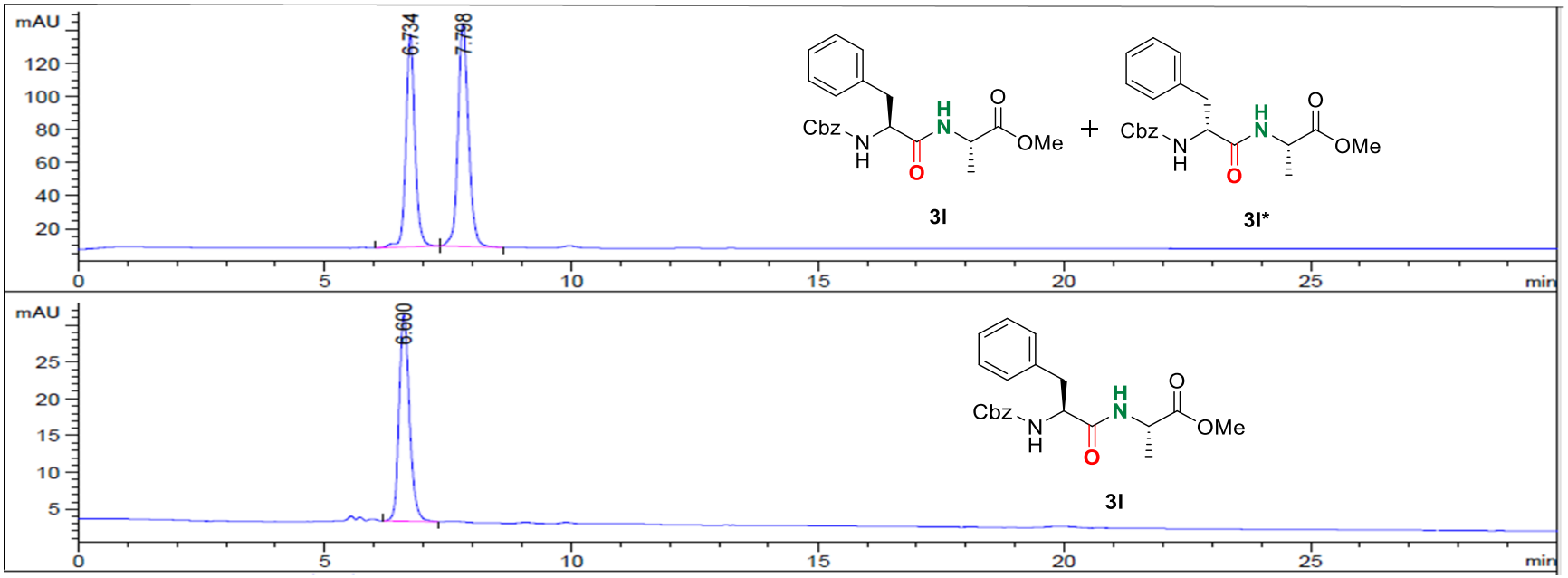
1) Mixed HPLC data of (L,L) 3h and (D,L) 3h*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	23.628	2936.18945	46.86104	49.4232
02	26.622	3004.72339	42.84006	50.5768

2) Pure HPLC data of (L,L) 3h

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	26.950	3071.90132	10.98769	99.1460
02	24.020	10.30883	2.34351e-1	0.8540

HPLC studies for determining racemization of 3l



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 0.5 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

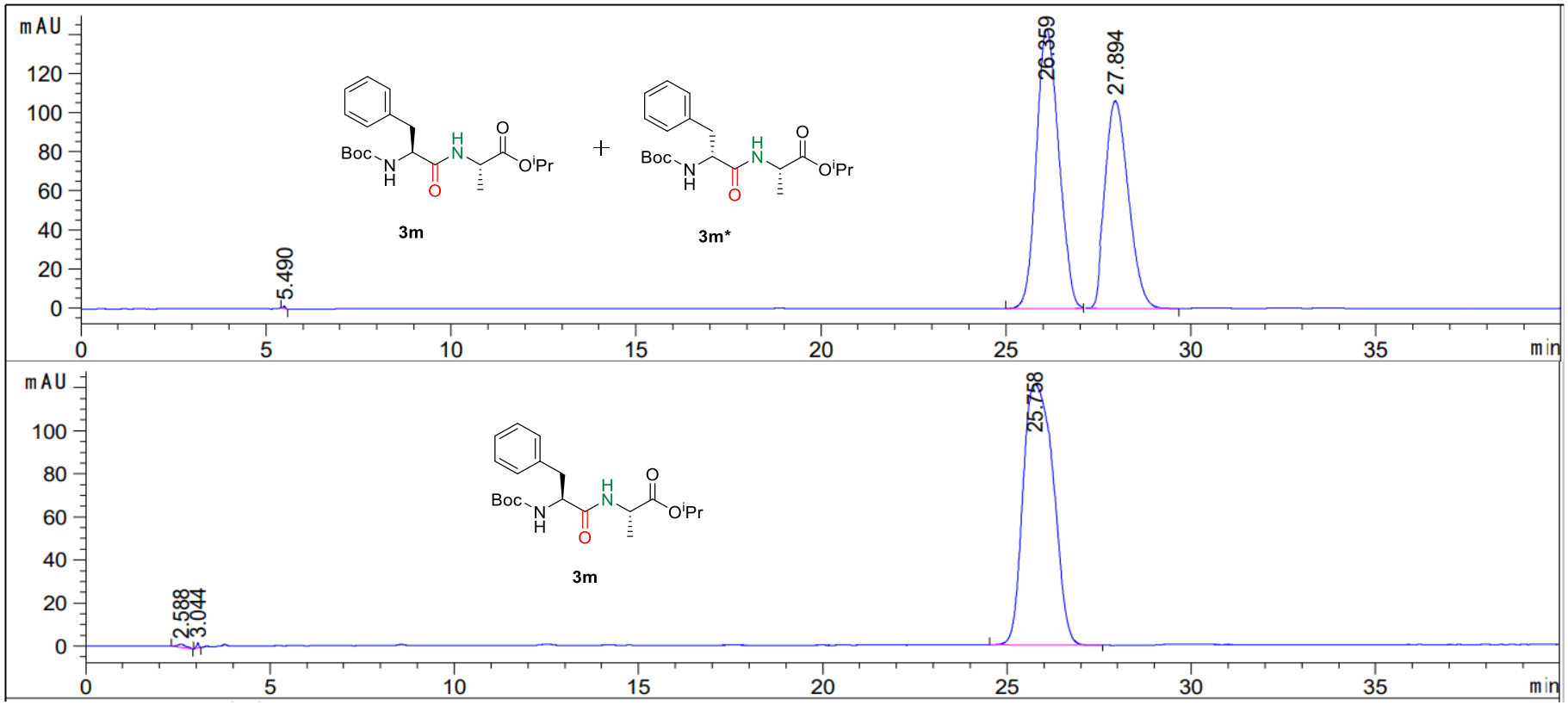
1) Mixed HPLC data of (L,L) 3l and (D,L) 3l*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	6.734	1643.57092	128.69798	45.1775
02	7.798	1994.46069	135.09608	54.8225

2) Pure HPLC data of (L,L) 3l

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	6.600	413.22910	28.17320	100.0000

HPLC studies for determining racemization of 3m



HPLC condition: water-acetonitrile (10-90%) in 40 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

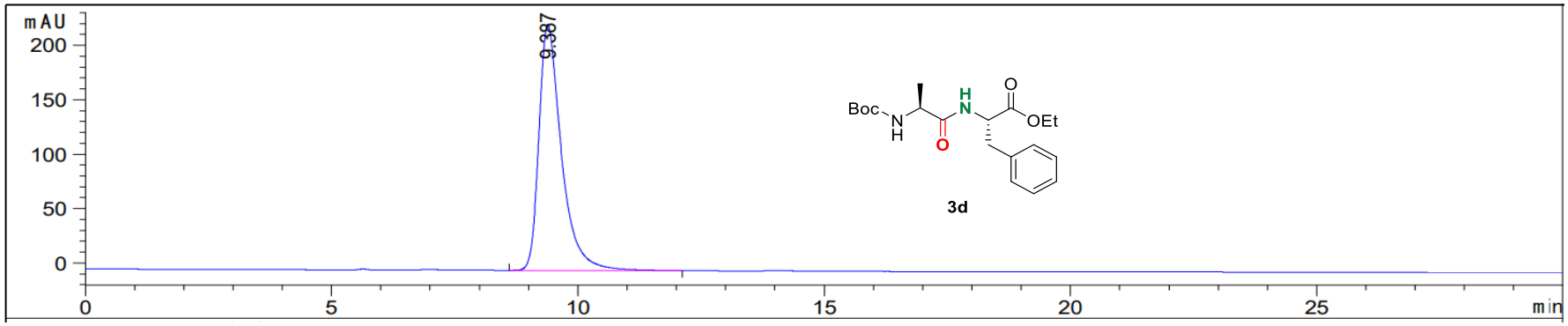
1) Mixed HPLC data of (L,L)-3m and (D,L) 3m*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	26.359	6084.63623	143.03291	55.5591
02	27.894	4867.00586	106.26966	44.4409

2) Pure HPLC data of (L,L)-3m

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	2.588	24.85943	1.46002	0.2623
02	3.044	11.20006	2.52789	0.1182
03	25.758	9443.19336	120.97589	99.6196

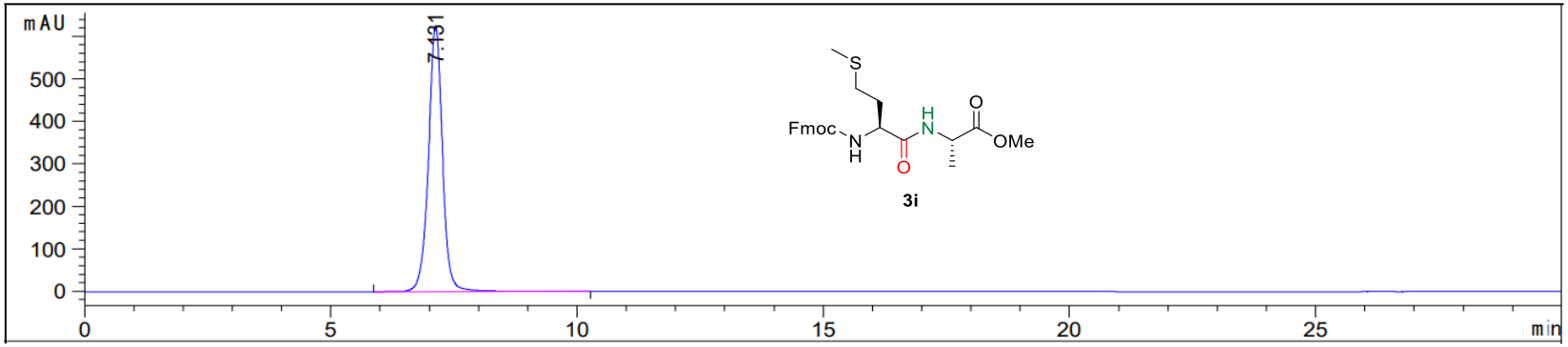
HPLC studies for determining purity of 3d



HPLC condition: water-acetonitrile (10-80%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	9.387	7186.17773	226.27376	100.0000

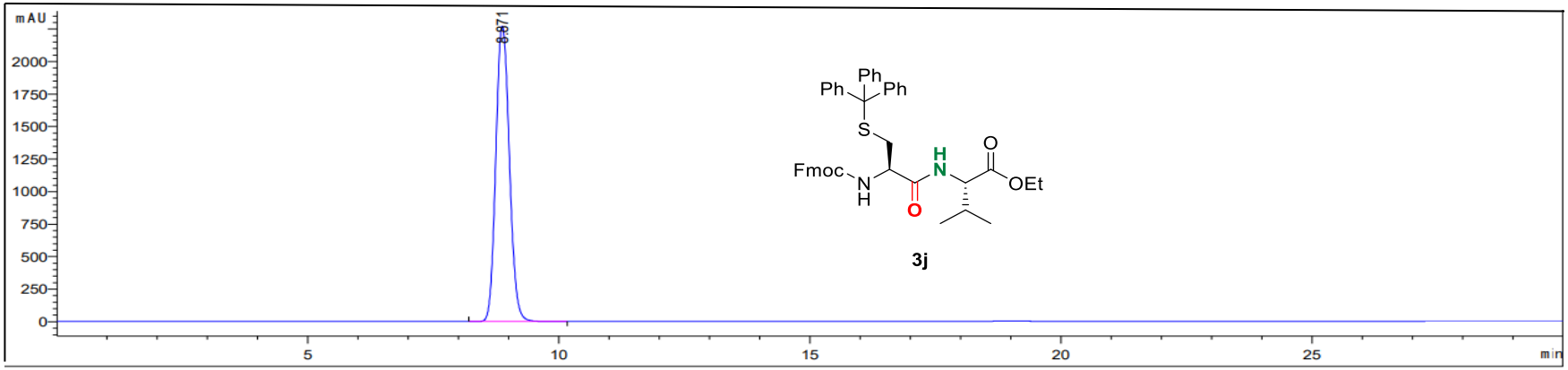
HPLC studies for determining purity of 3i



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.131	1.24626e4	626.05316	100.0000

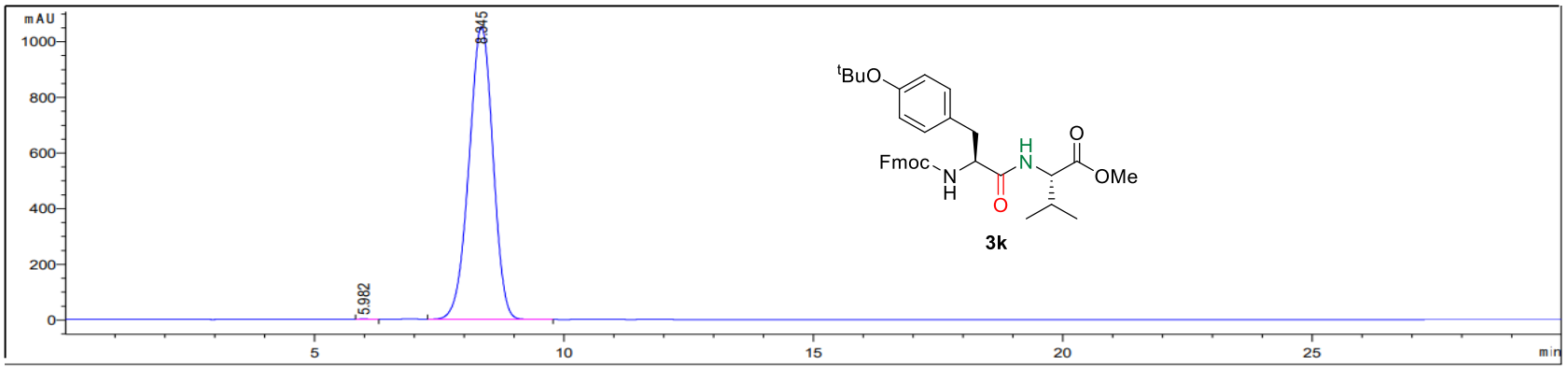
HPLC studies for determining purity of 3j



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.871	4.26956e4	2271.42090	100.0000

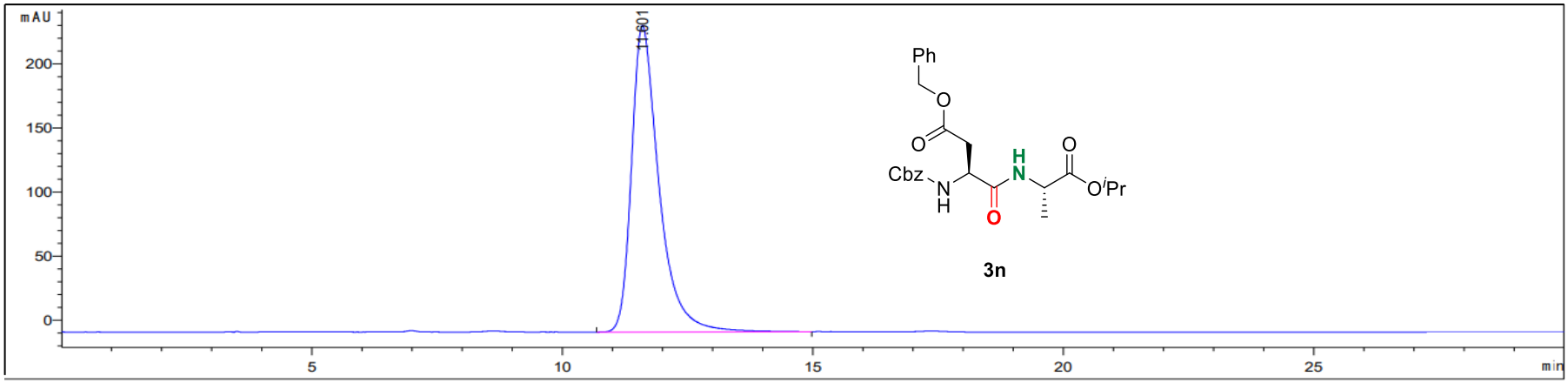
HPLC studies for determining purity of 3k



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	5.982	13.60264	1.26654	0.0387
02	8.345	3.51652e4	1052.47986	99.9613

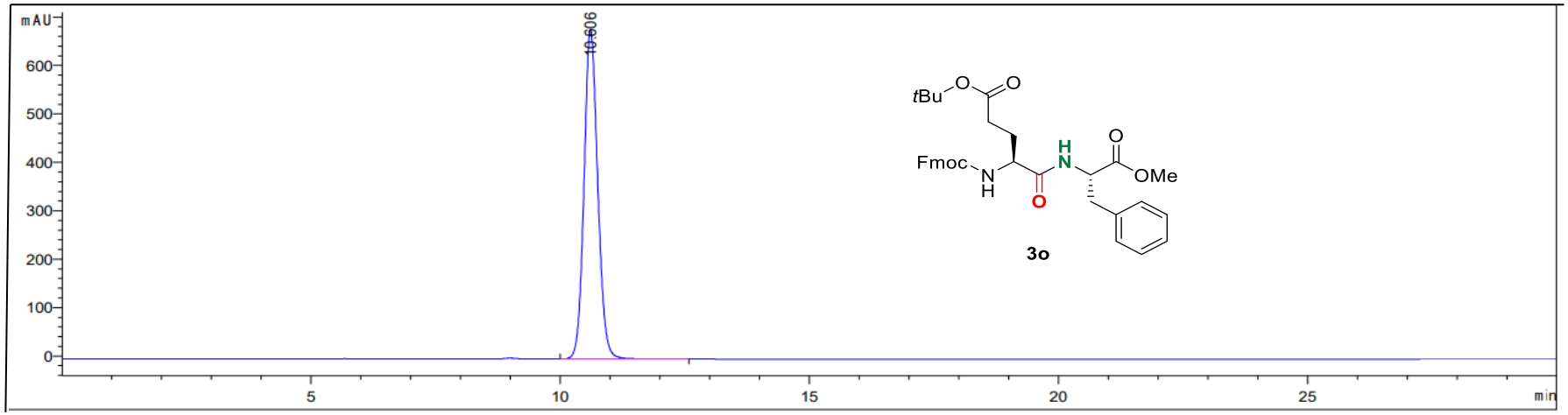
HPLC studies for determining purity of 3n



HPLC condition: water-methanol (10-80%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	11.601	9131.27148	239.25229	100.0000

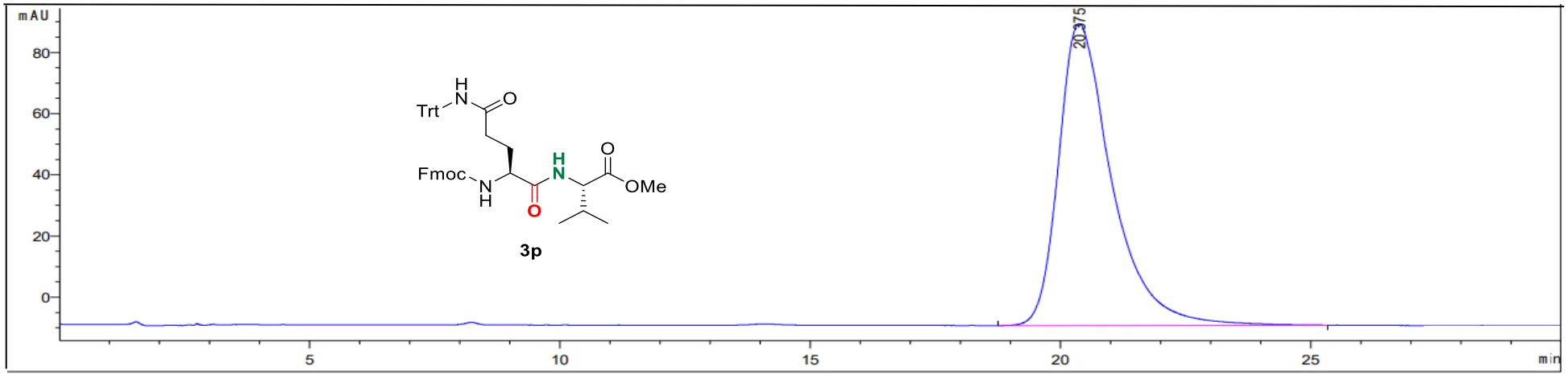
HPLC studies for determining purity of 3o



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	10.606	1.30119e4	681.39630	100.0000

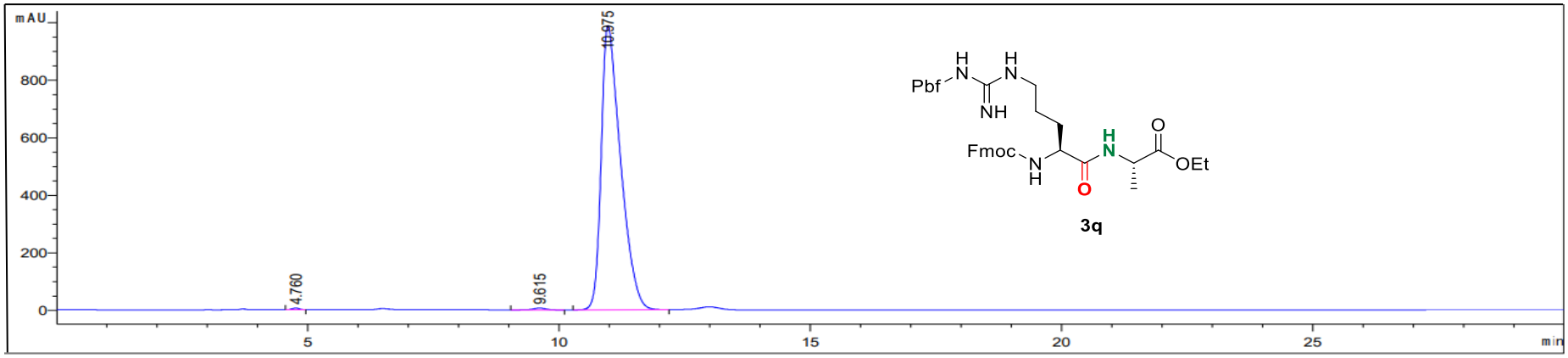
HPLC studies for determining purity of 3p



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	20.375	7294.27002	98.69247	100.0000

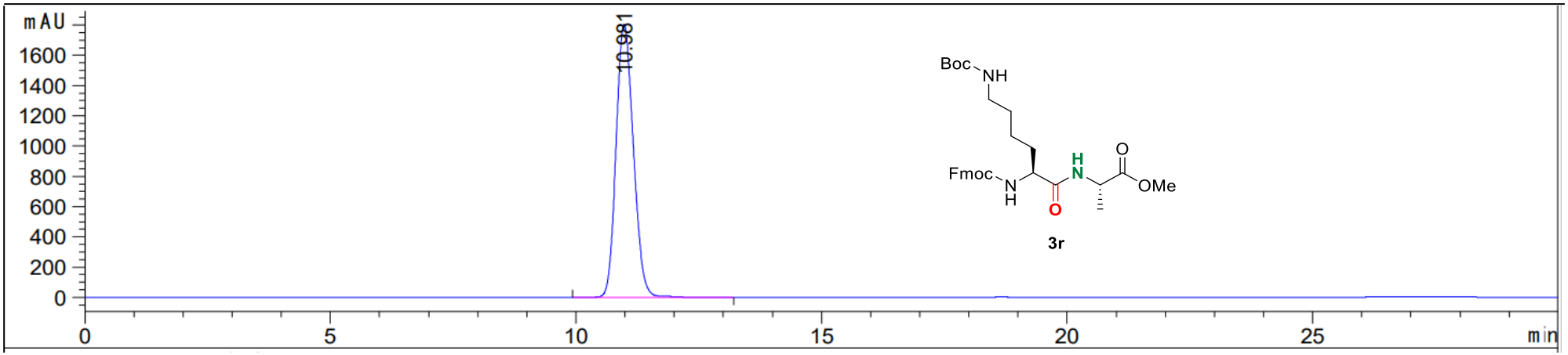
HPLC studies for determining purity of 3q



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	4.760	49.42589	5.50452	0.1857
02	9.615	107.03154	6.03026	0.4022
03	10.975	2.64578e4	988.27802	99.4121

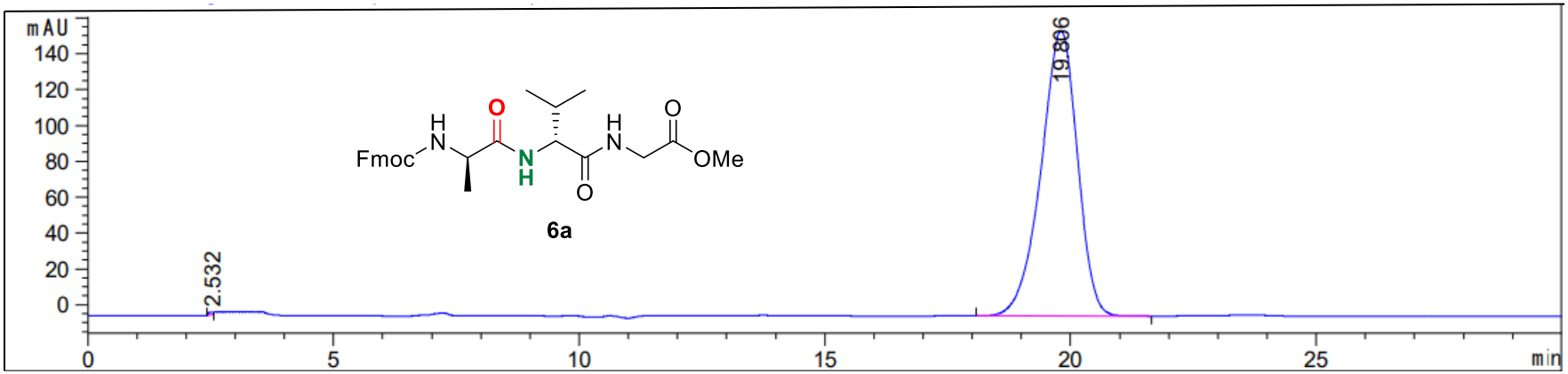
HPLC studies for determining purity of 3r



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	10.981	4.41475e4	1804.00330	100.0000

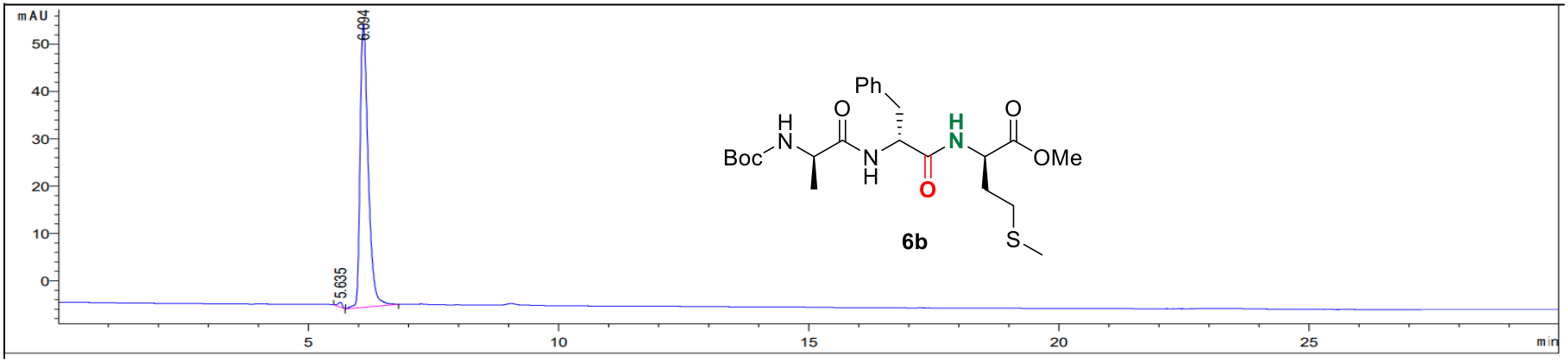
HPLC studies for determining purity of 6a



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	2.532	8.98613	1.41761	0.1095
02	19.806	8194.95605	159.09897	99.8905

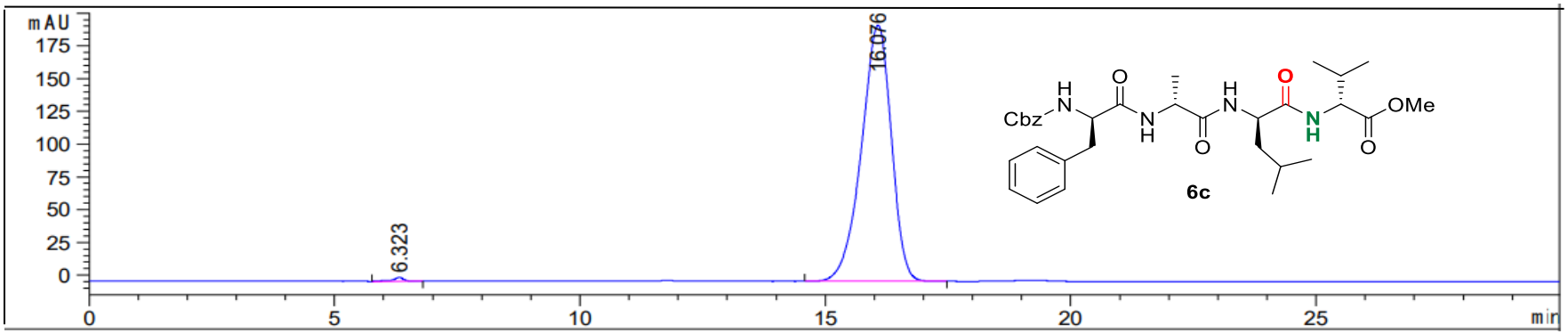
HPLC studies for determining purity of 6b



HPLC condition: water-acetonitrile (10-80%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	5.635	5.76925	1.02053	0.8540
02	6.094	669.78314	59.91338	99.1460

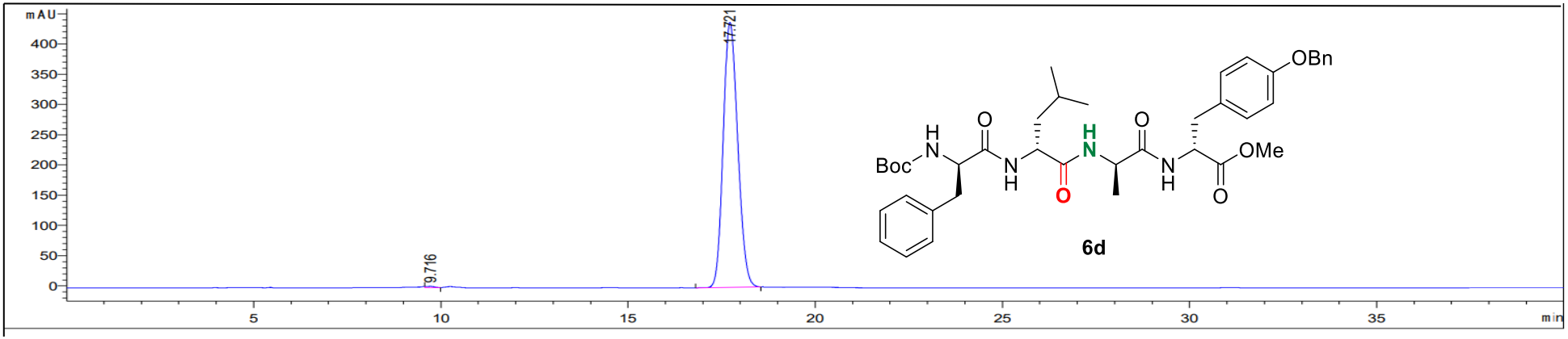
HPLC studies for determining purity of 6c



HPLC condition: water-methanol (10-95%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	6.323	46.68183	3.01123	0.5603
02	16.076	8285.20215	195.39769	99.4397

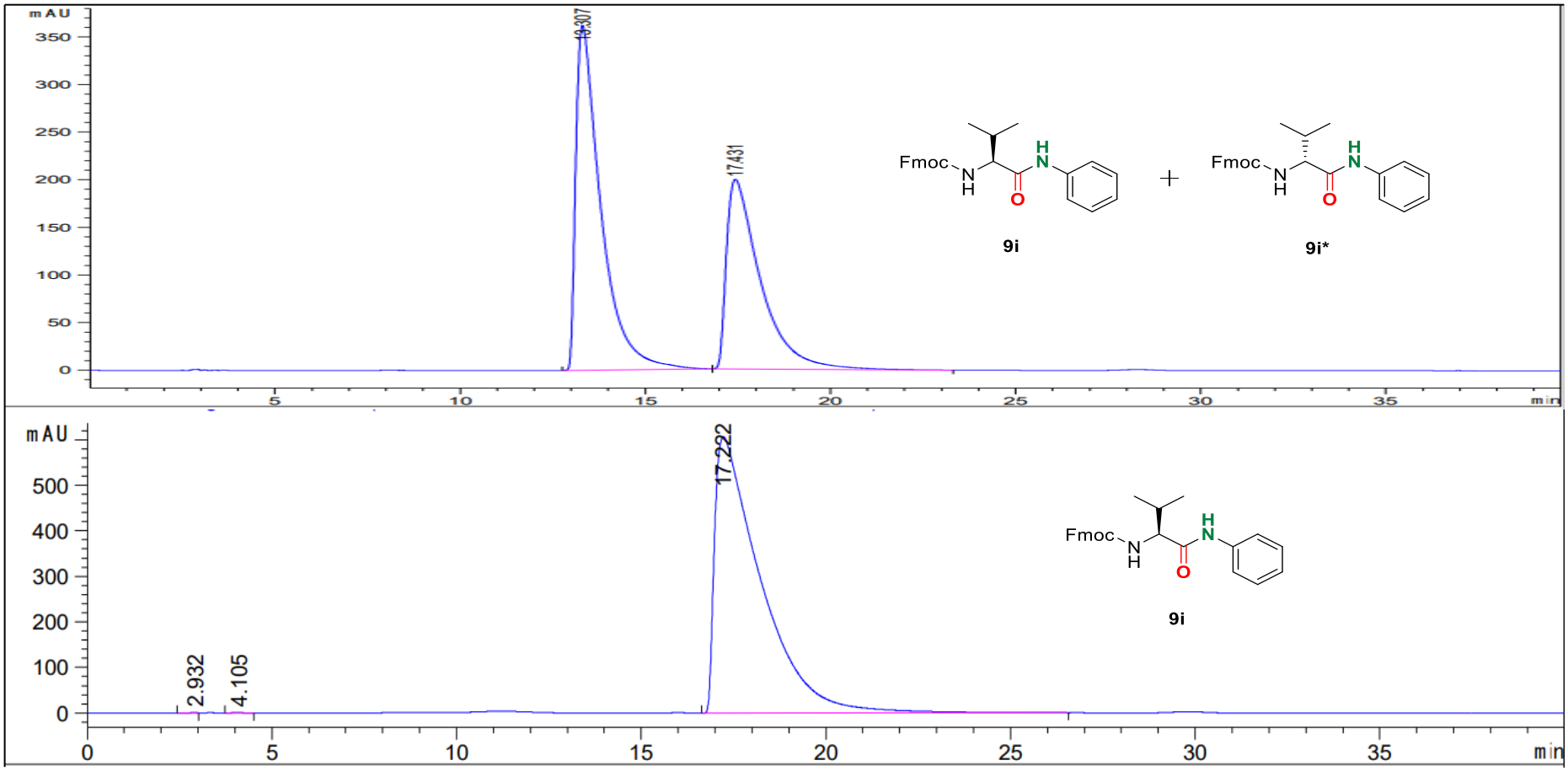
HPLC studies for determining purity of 6d



HPLC condition: water-methanol (10-90%) in 40 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	9.716	30.02806	3.01123	2.08486
02	17.721	1.17986e4	438.12491	99.7461

HPLC studies for determining racemization of 9i



HPLC condition: water-acetonitrile (20-80%) in 40 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

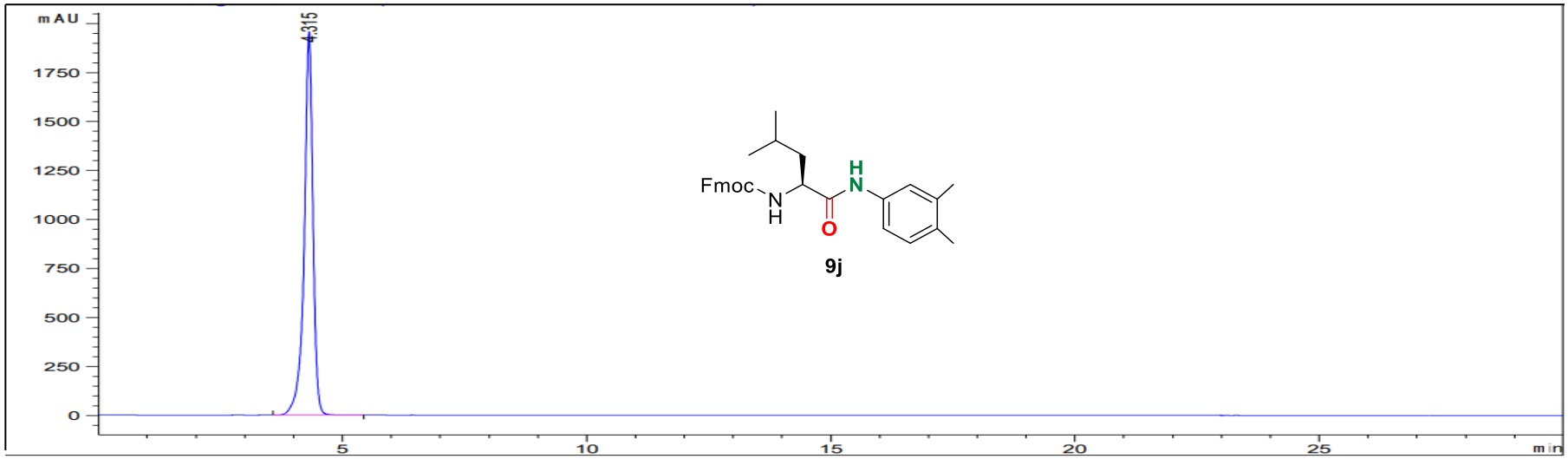
1) Mixed HPLC data of (L)-9i and (D) 9i*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	13.307	1.70683e4	361.95816	57.3414
02	17.431	1.26978e4	199.26224	42.6586

2) Pure HPLC data of (L)-9i

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	2.932	12.77854	1.15554	0.0243
02	4.105	15.76748	1.20070	0.0300
03	17.222	5.25043e4	606.95490	99.9457

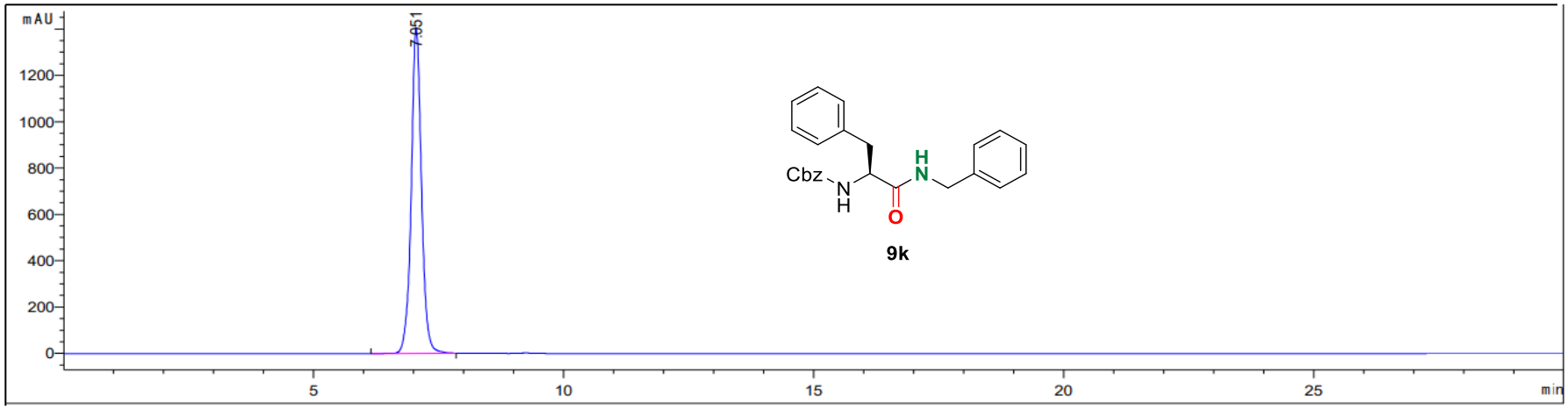
HPLC studies for determining purity of 9j



HPLC condition: water-methanol (10-80%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	4.315	2.46149e4	1954.96155	100.0000

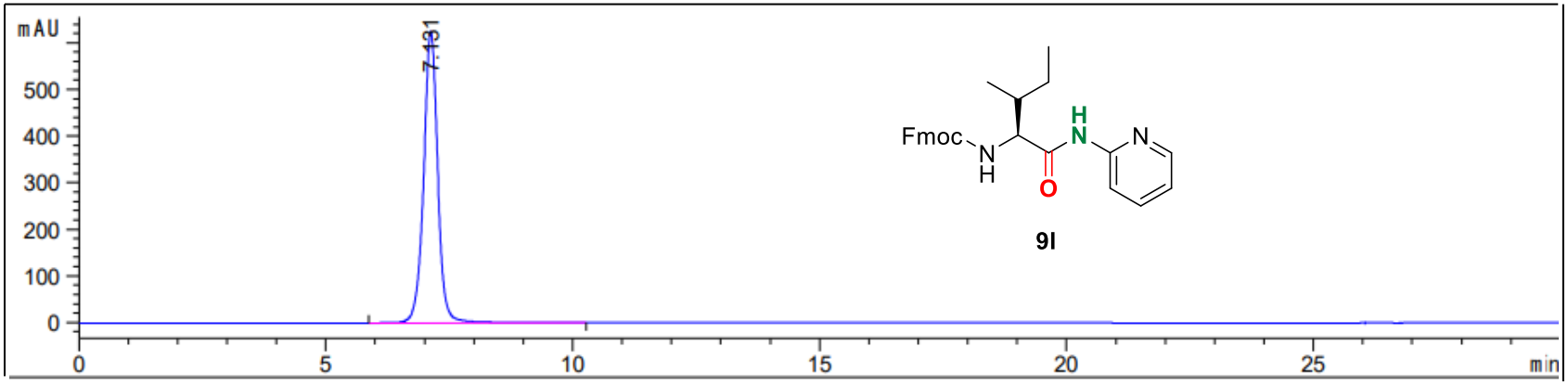
HPLC studies for determining purity of 9k



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.051	1.99362e4	1405.59753	100.0000

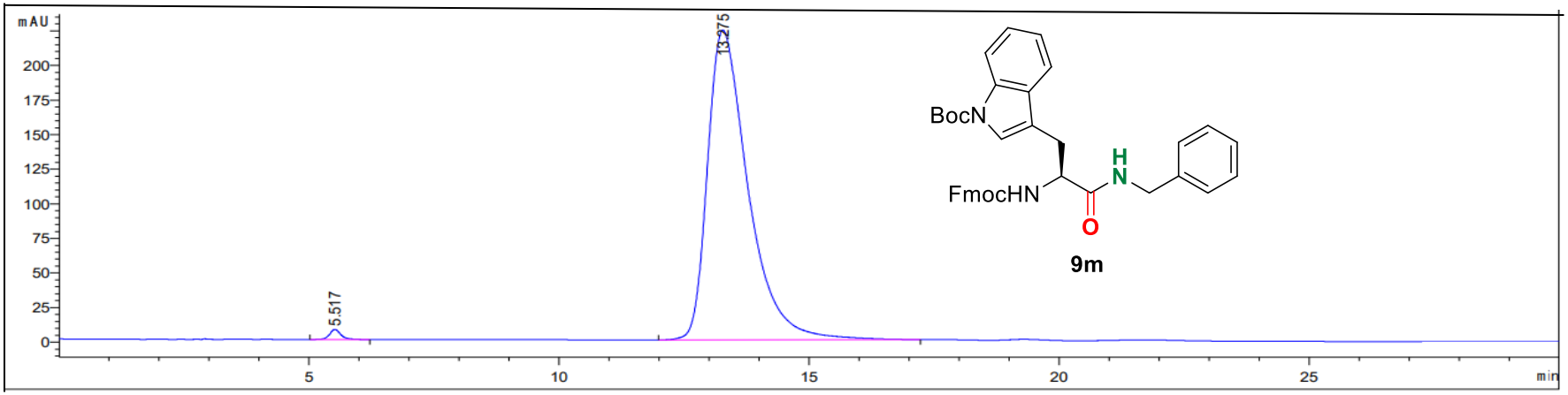
HPLC studies for determining purity of 9l



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	7.131	1.24626e4	626.05316	100.0000

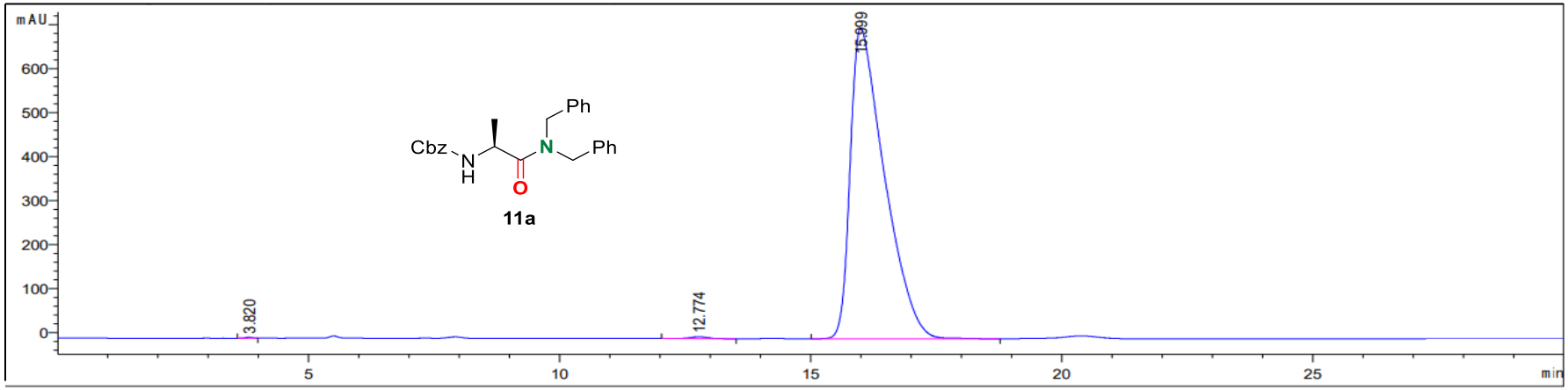
HPLC studies for determining purity of 9m



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	5.517	116.08534	7.31107	0.9083
02	13.275	1.26645e4	224.07771	99.0917

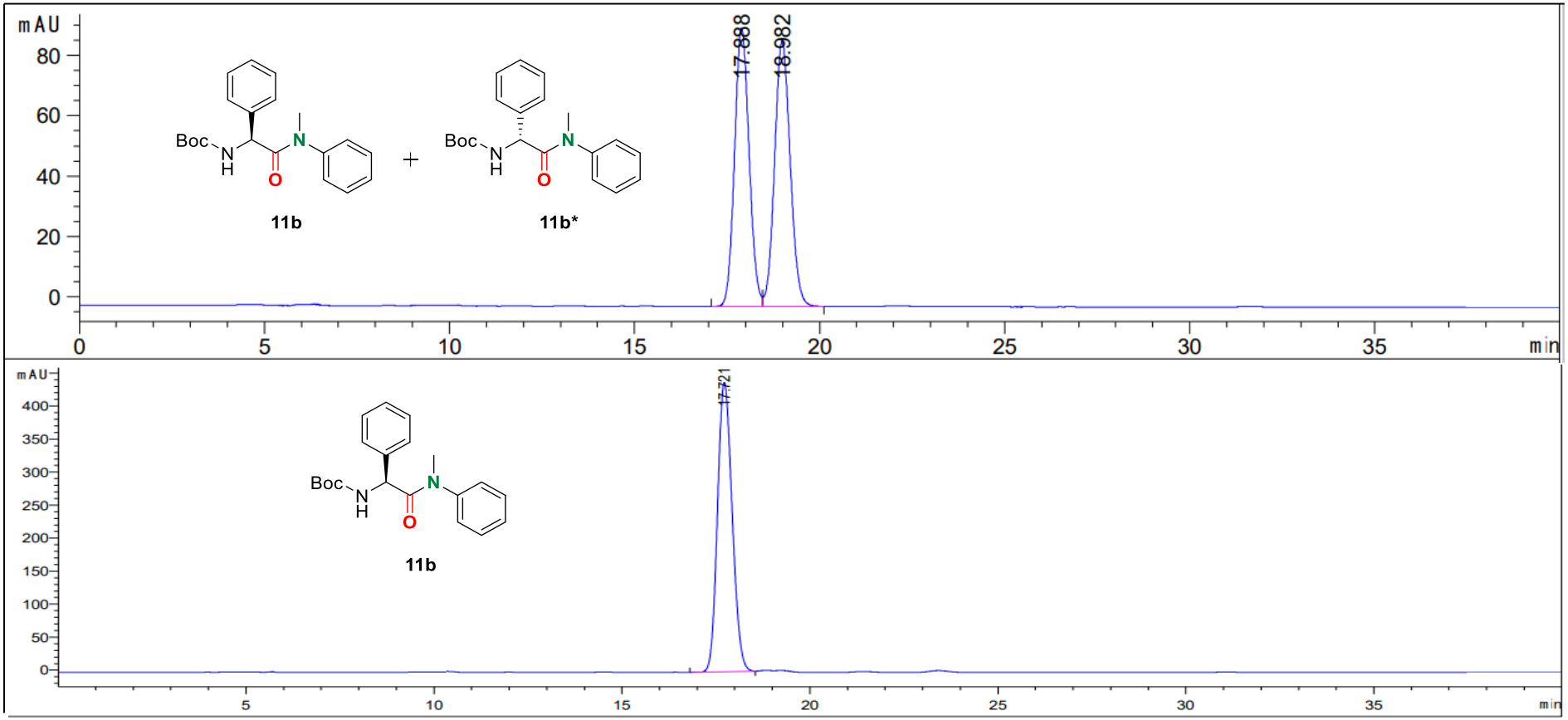
HPLC studies for determining purity of 11a



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	3.820	19.06471	2.39236	0.0568
02	12.774	109.43756	4.34640	0.3263
03	15.999	3.34085e4	705.88959	99.6168

HPLC studies for determining racemization of 11b



HPLC condition: water-acetonitrile (20-80%) in 40 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

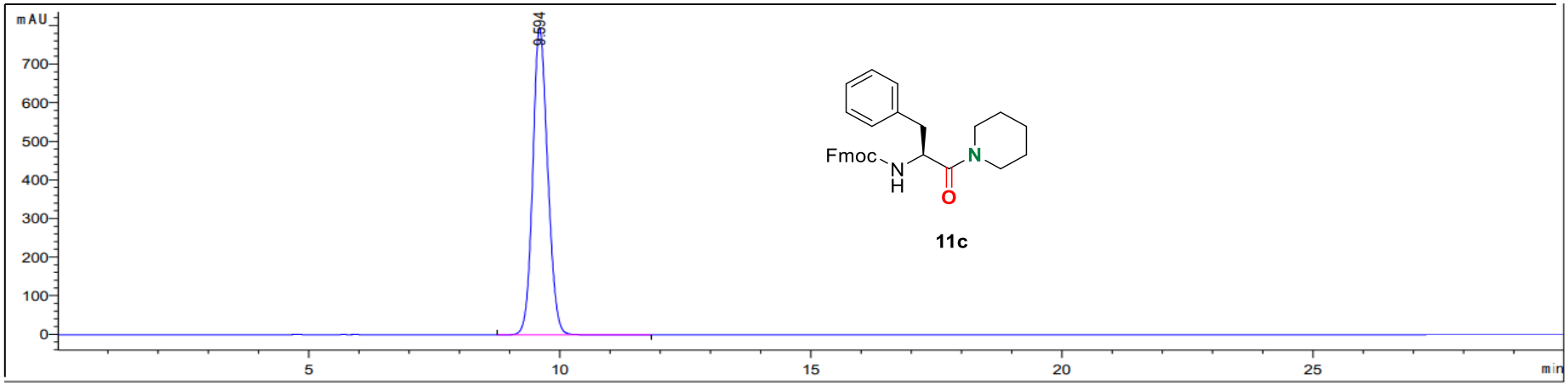
1) Mixed HPLC data of (L)-11b and (D) 11b*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	17.888	2525.66382	92.45739	49.4966
02	18.982	2577.03687	88.03035	50.5034

2) Pure HPLC data of (L)-11b

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	17.721	1.17986e4	438.12491	100.0000

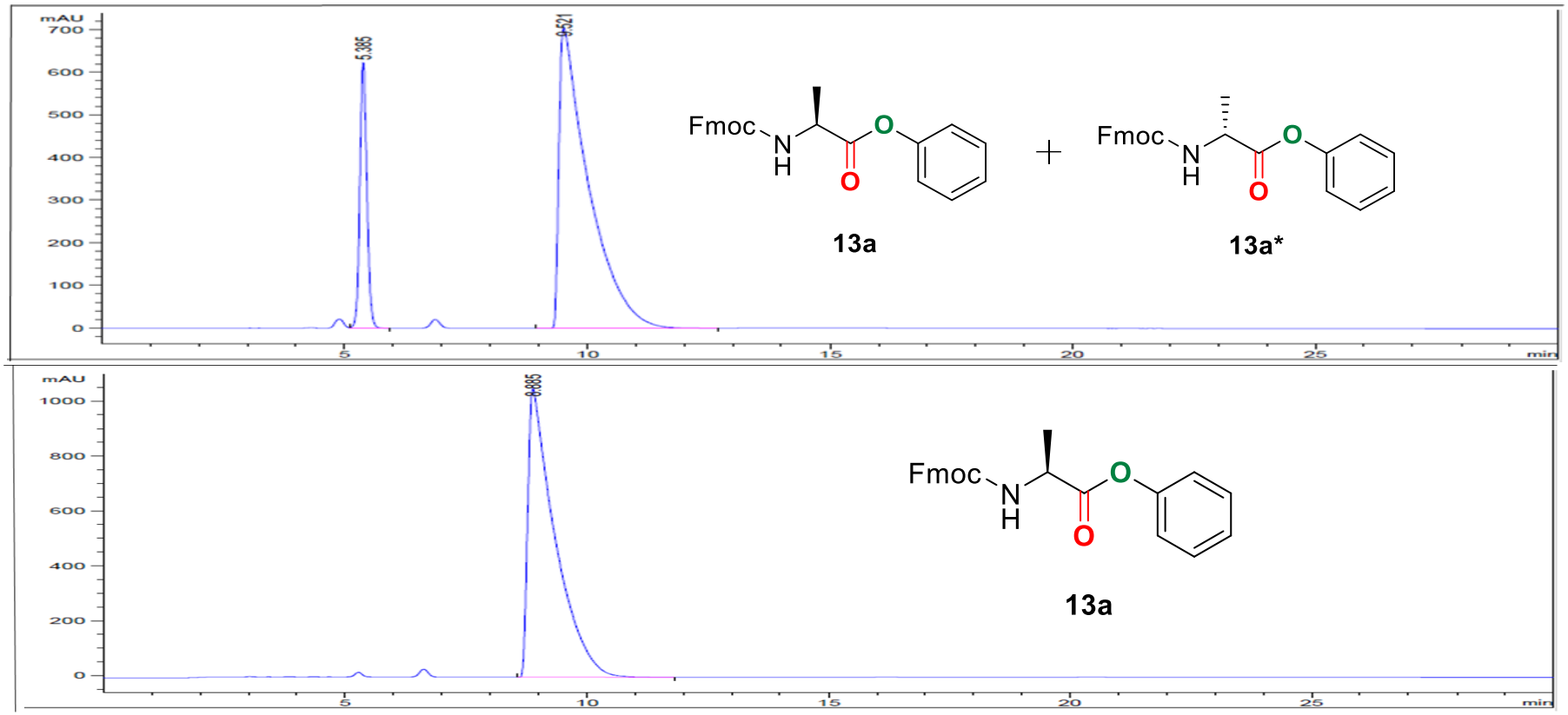
HPLC studies for determining purity of 11c



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	9.594	1.64776e4	796.59033	100.0000

HPLC studies for determining racemization of 13a



HPLC condition: water-acetonitrile (5-95%) in 30 min; VWD at λ = 254 nm; flow rate: 1.0 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

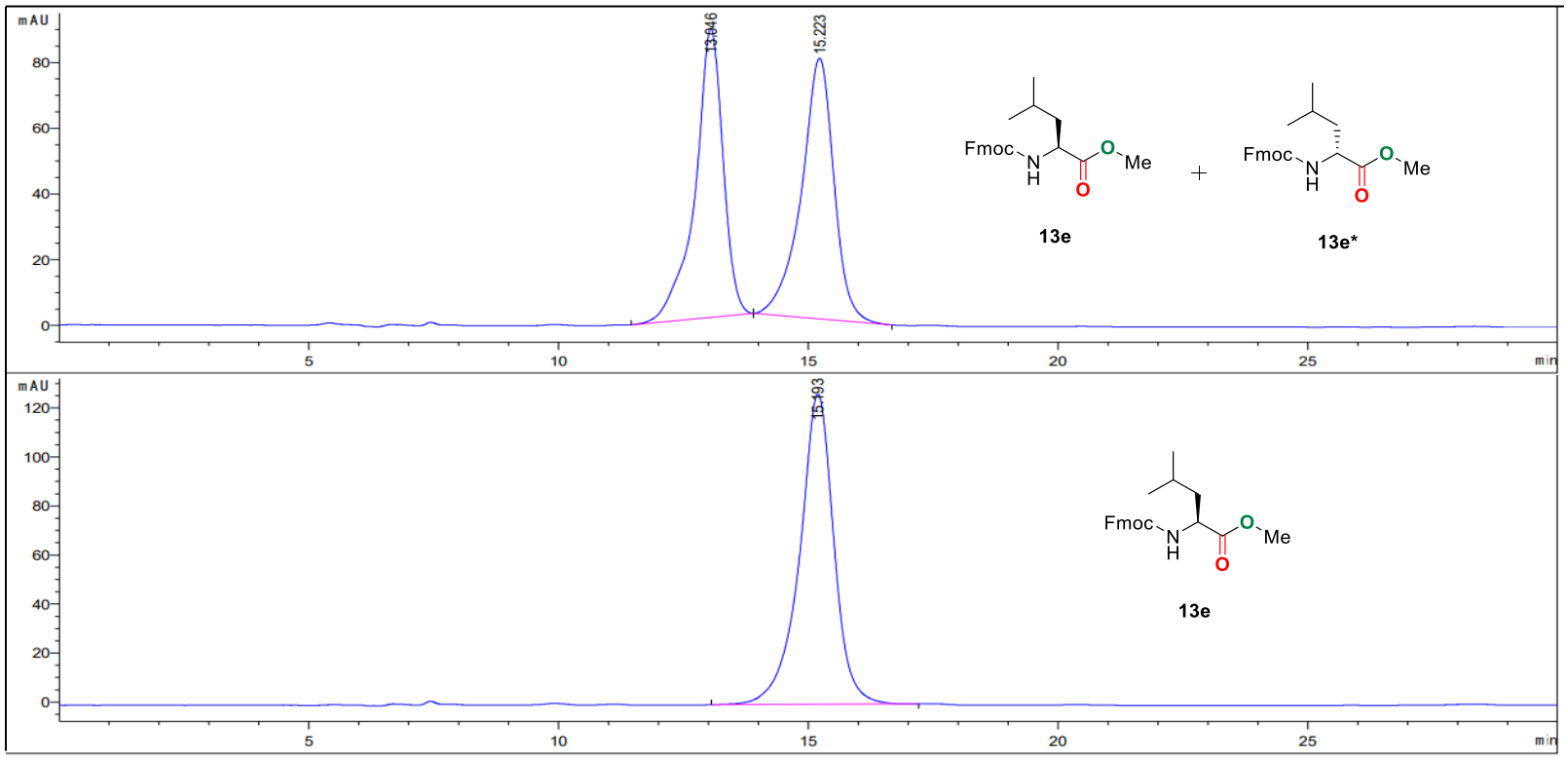
1) Mixed HPLC data of (L) 13a and (D) 13a*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	5.385	6370.93359	623.85791	17.6248
02	9.521	2.97765e4	704.49756	82.3752

2) Pure HPLC data of (L) 13a

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.885	4.08192e4	1052.43628	100.0000

HPLC studies for determining racemization of 13e



HPLC condition: water-methanol (20-80%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: phenomenex made Lux, pore size-5µ, Cellulose-1, diameter x length = 250 x 4.6 mm).

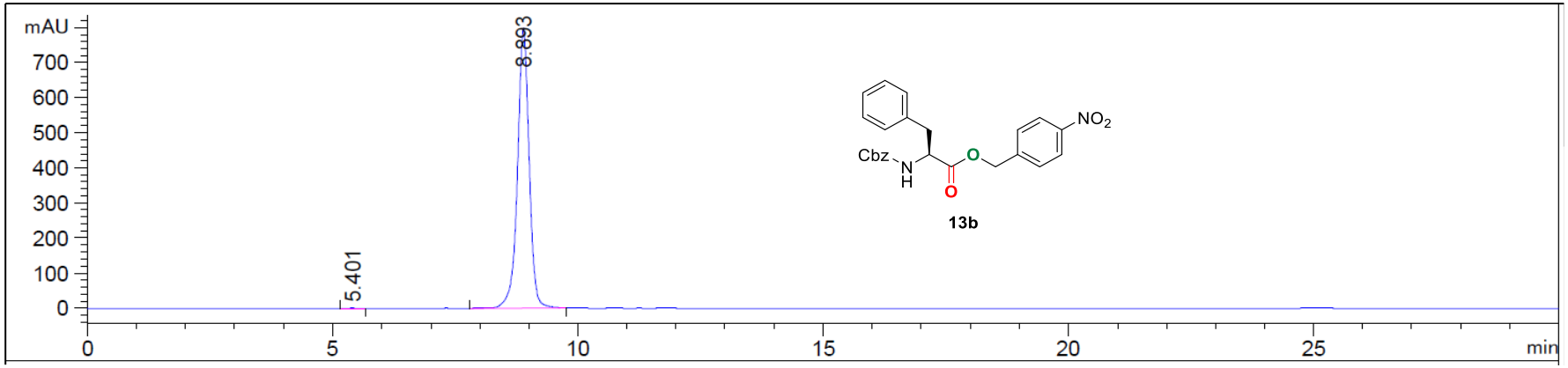
1) Mixed HPLC data of (L)-13b and (D) 13b*

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	13.046	3427.85913	87.93016	48.7894
02	15.223	3597.96167	79.31252	51.2106

2) Pure HPLC data of (L)-13b

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	15.193	6081.11279	126.53349	100.0000

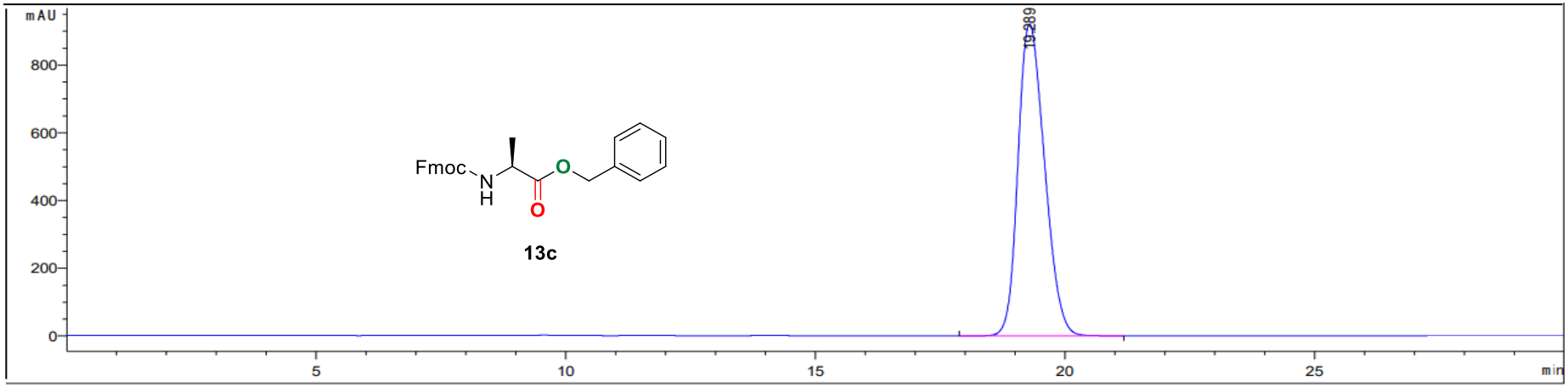
HPLC studies for determining purity of 13b



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	5.401	12.72812	1.02119	0.0961
02	8.893	1.32302e4	796.37695	99.9039

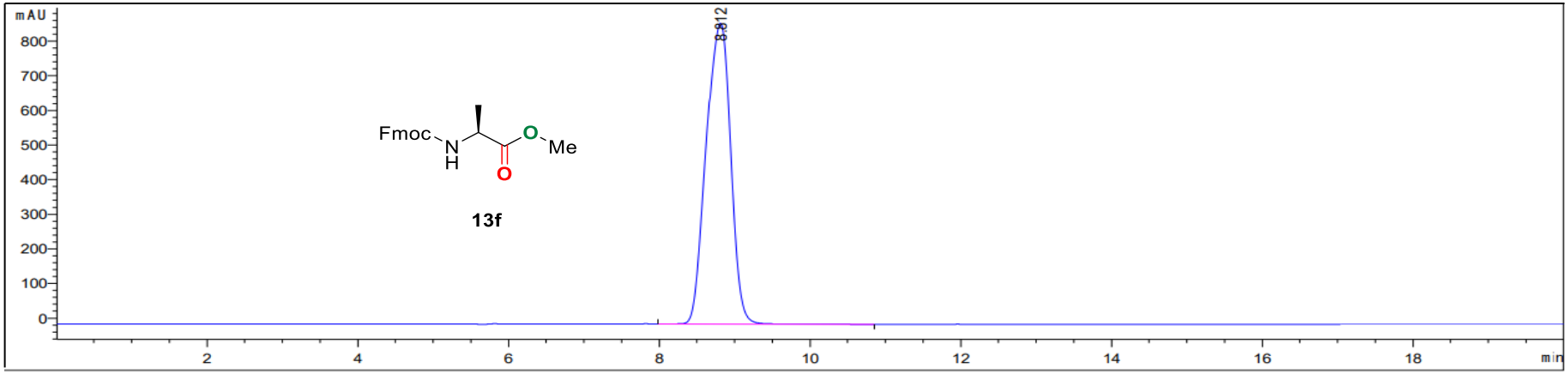
HPLC studies for determining purity of 13c



HPLC condition: water-acetonitrile (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	19.289	3.40364e4	921.13031	100.0000

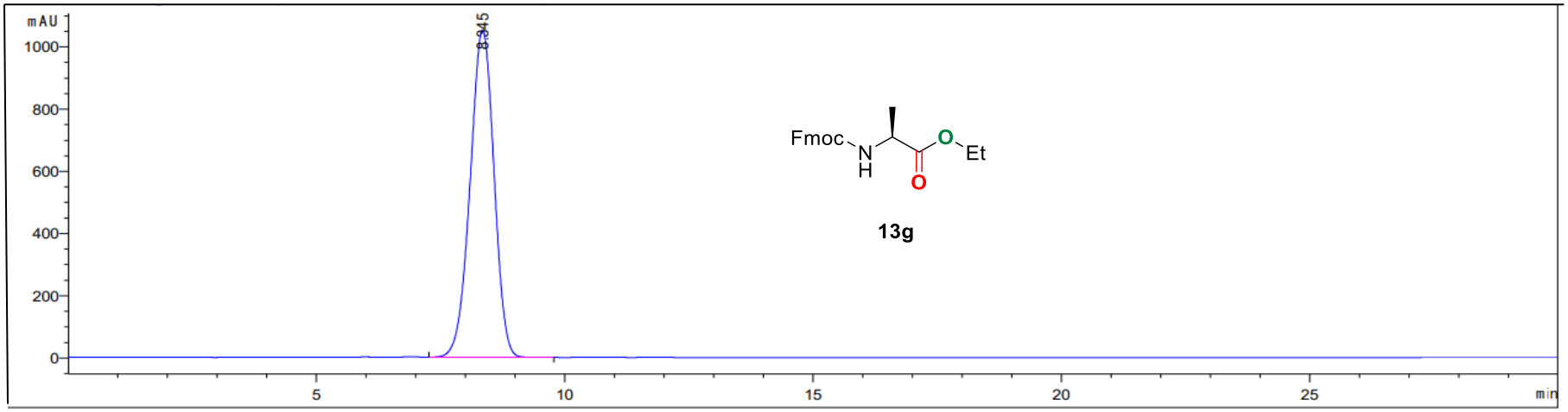
HPLC studies for determining purity of 13f



HPLC condition: water-methanol (10-90%) in 20 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.812	1.96162e4	869.33234	100.0000

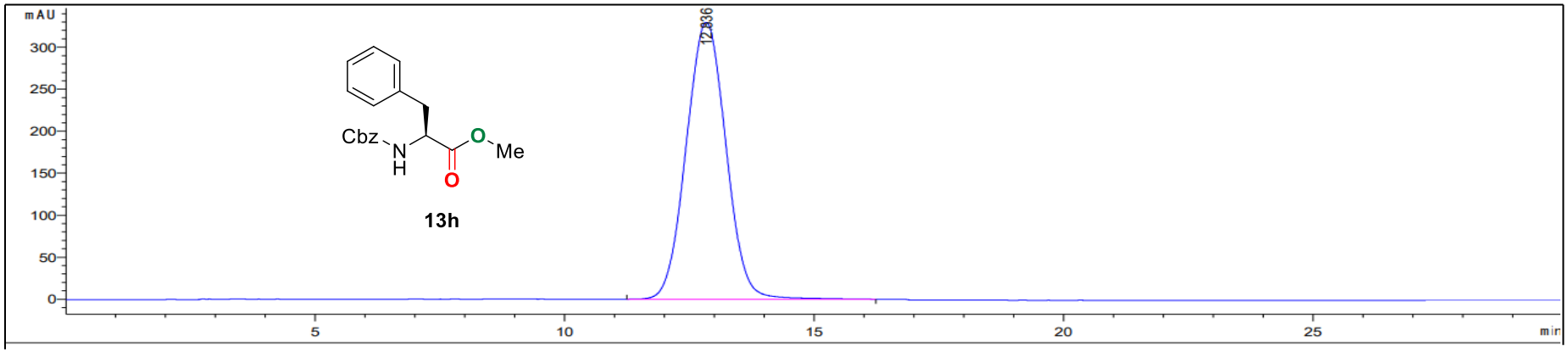
HPLC studies for determining purity 13g



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	8.345	3.51652e4	1052.47986	100.0000

HPLC studies for determining purity 13h



HPLC condition: water-methanol (10-90%) in 30 min; VWD at λ = 254 nm; flow rate: 1 mL/min; column: Eclipse XDB-C18, pore size-5µ, diameter x length = 4.6 x 150mm).

Peak	Ret Time [min]	Area	Height [mAU]	Area %
01	12.836	1.82512e4	329.72797	100.0000

Crystal Structure Analysis of (III) AITF (Code =TRY_a):

Crystals were grown from $CDCl_3$ solution by slow evaporation. A single crystal (0.18 × 0.11 × 0.16 mm) was mounted on loop with a small amount of the paraffin oil. The X-ray data were collected at 296K temperature on a Bruker APEX(II) DUO CCD diffractometer using Mo Kα radiation (λ = 0.71073Å), ω-scans (2θ = 56.72), for a total of 3763 independent reflections. Space group $P2_1/n$, a = 5.5295(13), b = 21.270(5), c = 12.923(3), α, γ = 90 and β = 98.235(8),V = 1504.2(6)Å^3, monoclinic, Z = 4 for chemical formula $C_{10}H_8N_2O_5F_6S_2$, with one molecule in asymmetric unit; ρcalcd = 1.829 gcm^{-3}, μ = 0.451 mm^{-1}, F (000) = 832, The structure was obtained by direct methods using SHELXS-97.[1] The final R value was 0.0727 (wR2 = 0.2050) 3763 observed reflections ($F_0 \geq 4\sigma$ ($|F_0|$)) and 216 variables, S = 1.047.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) TRY_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: TRY_a

```
Bond precision:   C-C = 0.0074 A          Wavelength=0.71073

Cell:             a=5.5295(13)     b=21.270(5)         c=12.923(3)
                  alpha=90         beta=98.235(8)      gamma=90
Temperature:      296 K

                 Calculated                Reported
Volume           1504.2(6)                 1504.2(6)
Space group      P 21/n                    P 21/n
Hall group       -P 2yn                    -P 2yn
Moiety formula   C10 H8 F6 N2 O5 S2        ?
Sum formula      C10 H8 F6 N2 O5 S2        C10 H8 F6 N2 O5 S2
Mr               414.30                    414.30
Dx,g cm-3        1.829                     1.830
Z                4                         4
Mu (mm-1)        0.451                     0.451
F000             832.0                     832.0
F000'            833.69
h,k,lmax         7,28,17                   7,28,17
Nref             3769                      3763
Tmin,Tmax
Tmin'

Correction method= Not given

Data completeness= 0.998          Theta(max)= 28.360

R(reflections)= 0.0727( 2610)                wR2(reflections)=
                                             0.2050( 3763)
S = 1.047                 Npar= 216
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT031_ALERT_4_B Refined Extinction Parameter Within Range of ...      1.632 Sigma
PLAT097_ALERT_2_B Large Reported Max.  (Positive) Residual Density       2.52 eA-3
PLAT230_ALERT_2_B Hirshfeld Test Diff for    C3       --C4       .        9.0 s.u.
PLAT230_ALERT_2_B Hirshfeld Test Diff for    C3       --C8       .        9.2 s.u.
```

Alert level C

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DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.144
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 .........      0.144 Report
PLAT052_ALERT_1_C Info on Absorption Correction Method   Not Given     Please Do !
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.52 Report
PLAT213_ALERT_2_C Atom N1              has ADP max/min Ratio .....        3.3 prolat
PLAT230_ALERT_2_C Hirshfeld Test Diff for    N1       --C2       .        7.0 s.u.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C3 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.7 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00743 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     16.063 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.582 Check
PLAT971_ALERT_2_C Check Calcd Resid. Dens.  2.17Ang From O1              2.39 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  1.00Ang From O1      .      -0.45 eA-3
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          2 Report
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of         C9 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C10 Check
PLAT434_ALERT_2_G Short Inter HL..HL Contact F2       ..F6       .       2.78 Ang.
                                  1/2+x,3/2-y,1/2+z  =      4_676 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .      Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          4 Note
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged      Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  4 ALERT level B = A potentially serious problem, consider carefully
 17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 10 ALERT level G = General information/check it is not something unexpected

  6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
```

```
  15 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_DIFMX02_TRY_a
;
PROBLEM: The maximum difference density is > 0.1*ZMAX*0.75
RESPONSE: ...
;
_vrf_RINTA01_TRY_a
;
PROBLEM: The value of Rint is greater than 0.12
RESPONSE: ...
;
_vrf_PLAT031_TRY_a
;
PROBLEM: Refined Extinction Parameter Within Range of ...      1.632 Sigma
RESPONSE: ...
;
_vrf_PLAT097_TRY_a
;
PROBLEM: Large Reported Max.  (Positive) Residual Density       2.52 eA-3
RESPONSE: ...
;
_vrf_PLAT230_TRY_a
;
PROBLEM: Hirshfeld Test Diff for    C3       --C4       .        9.0 s.u.
RESPONSE: ...
;
_vrf_PLAT020_TRY_a
;
PROBLEM: The Value of Rint is Greater Than 0.12 .........      0.144 Report
RESPONSE: ...
;
_vrf_PLAT052_TRY_a
;
PROBLEM: Info on Absorption Correction Method   Not Given     Please Do !
RESPONSE: ...
;
_vrf_PLAT053_TRY_a
;
PROBLEM: Minimum Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
_vrf_PLAT054_TRY_a
;
PROBLEM: Medium  Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
```

```
_vrf_PLAT055_TRY_a
;
PROBLEM: Maximum Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
_vrf_PLAT094_TRY_a
;
PROBLEM: Ratio of Maximum / Minimum Residual Density ....       2.52 Report
RESPONSE: ...
;
_vrf_PLAT213_TRY_a
;
PROBLEM: Atom N1              has ADP max/min Ratio .....        3.3 prolat
RESPONSE: ...
;
_vrf_PLAT241_TRY_a
;
PROBLEM: High   'MainMol' Ueq as Compared to Neighbors of         C3 Check
RESPONSE: ...
;
_vrf_PLAT250_TRY_a
;
PROBLEM: Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.7 Note
RESPONSE: ...
;
_vrf_PLAT340_TRY_a
;
PROBLEM: Low Bond Precision on  C-C Bonds ..............    0.00743 Ang.
RESPONSE: ...
;
_vrf_PLAT906_TRY_a
;
PROBLEM: Large K Value in the Analysis of Variance ......     16.063 Check
RESPONSE: ...
;
_vrf_PLAT971_TRY_a
;
PROBLEM: Check Calcd Resid. Dens.  2.17Ang From O1              2.39 eA-3
RESPONSE: ...
;
_vrf_PLAT976_TRY_a
;
PROBLEM: Check Calcd Resid. Dens.  1.00Ang From O1      .      -0.45 eA-3
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 12/09/2022; check.def file version of 09/08/2022

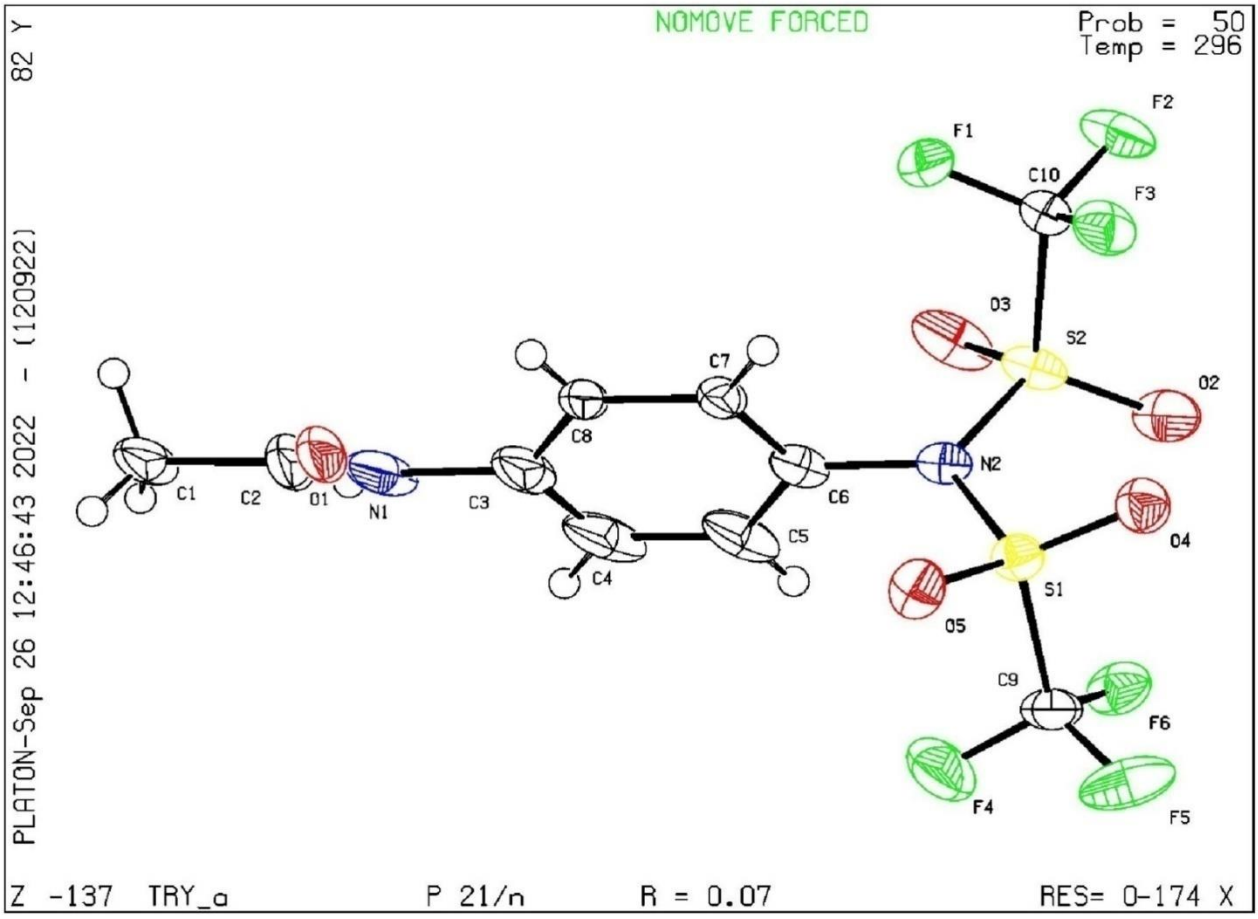

Figure S175. ORTEP diagram of **(III) AITF (CCDC = 2209512)**. Ellipsoids are drawn at 50% probability.

Crystal Structure Analysis of 9e (Code =TRY6_a):

Crystals were grown from MeOH solution by slow evaporation. A single crystal (0.16 × 0.10 × 0.12 mm) was mounted on loop with a small amount of the paraffin oil. The X-ray data were collected at 273K temperature on a Bruker APEX(II) DUO CCD diffractometer using Mo Kα radiation (λ = 0.71073Å), ω-scans (2θ = 56.646), for a total of 2376 independent reflections. Space group C2/c, a = 11.206(3), b = 9.424(3), c = 18.834(6), α, γ = 90 and β = 106.89(9),V = 3440(3)Å^3, monoclinic, Z = 8 for chemical formula C_{11} H_8 NO_2F, with one molecule in asymmetric unit; ρcalcd = 1.432 gcm^{-3}, μ = 0.112 mm^{-1}, F (000) = 848, The structure was obtained by direct methods using SHELXS-97.[1] The final R value was 0.0407 (wR2 = 0.0931) 1838 observed reflections ($F_0 \geq 4\sigma$ (|F_0|)) and 137 variables, S = 0.935

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) TRY6_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: TRY6_a

```
Bond precision:   C-C = 0.0020 A          Wavelength=0.71073

Cell:             a=11.206(3)     b=9.424(3)          c=18.834(6)
                  alpha=90        beta=106.890(9)     gamma=90
Temperature:      273 K

                 Calculated                Reported
Volume           1903.2(10)                1903.2(10)
Space group      C 2/c                     C 2/c
Hall group       -C 2yc                    -C 2yc
Moiety formula   C11 H8 F N O2             ?
Sum formula      C11 H8 F N O2             C11 H8 F N O2
Mr               205.18                    205.18
Dx,g cm-3        1.432                     1.432
Z                8                         8
Mu (mm-1)        0.112                     0.112
F000             848.0                     848.0
F000'            848.51
h,k,lmax         14,12,25                  14,12,25
Nref             2376                      1838
Tmin,Tmax
Tmin'

Correction method= Not given

Data completeness= 0.774          Theta(max)= 28.323

R(reflections)= 0.0407( 1288)                wR2(reflections)=
                                             0.0931( 1838)
S = 0.935                 Npar= 137
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level B

```
PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L=    0.600        489 Report
```

Alert level C

```
PLAT052_ALERT_1_C Info on Absorption Correction Method   Not Given     Please Do !
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.292 Check
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..          1 Check
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT019_ALERT_1_G _diffrn_measured_fraction_theta_full/*_max < 1.0      0.926 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        273 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        273 Check
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O3       .      106.0 Degree
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         50 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          4 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
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```

Validation response form

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```
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_vrf_PLAT911_TRY6_a
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600        489 Report
RESPONSE: ...
;
_vrf_PLAT052_TRY6_a
;
PROBLEM: Info on Absorption Correction Method   Not Given     Please Do !
```

```
RESPONSE: ...
;
_vrf_PLAT053_TRY6_a
;
PROBLEM: Minimum Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
_vrf_PLAT054_TRY6_a
;
PROBLEM: Medium  Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
_vrf_PLAT055_TRY6_a
;
PROBLEM: Maximum Crystal Dimension Missing (or Error) ...     Please Check
RESPONSE: ...
;
_vrf_PLAT906_TRY6_a
;
PROBLEM: Large K Value in the Analysis of Variance ......      2.292 Check
RESPONSE: ...
;
_vrf_PLAT934_TRY6_a
;
PROBLEM: Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..          1 Check
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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PLATON version of 12/09/2022; check.def file version of 09/08/2022

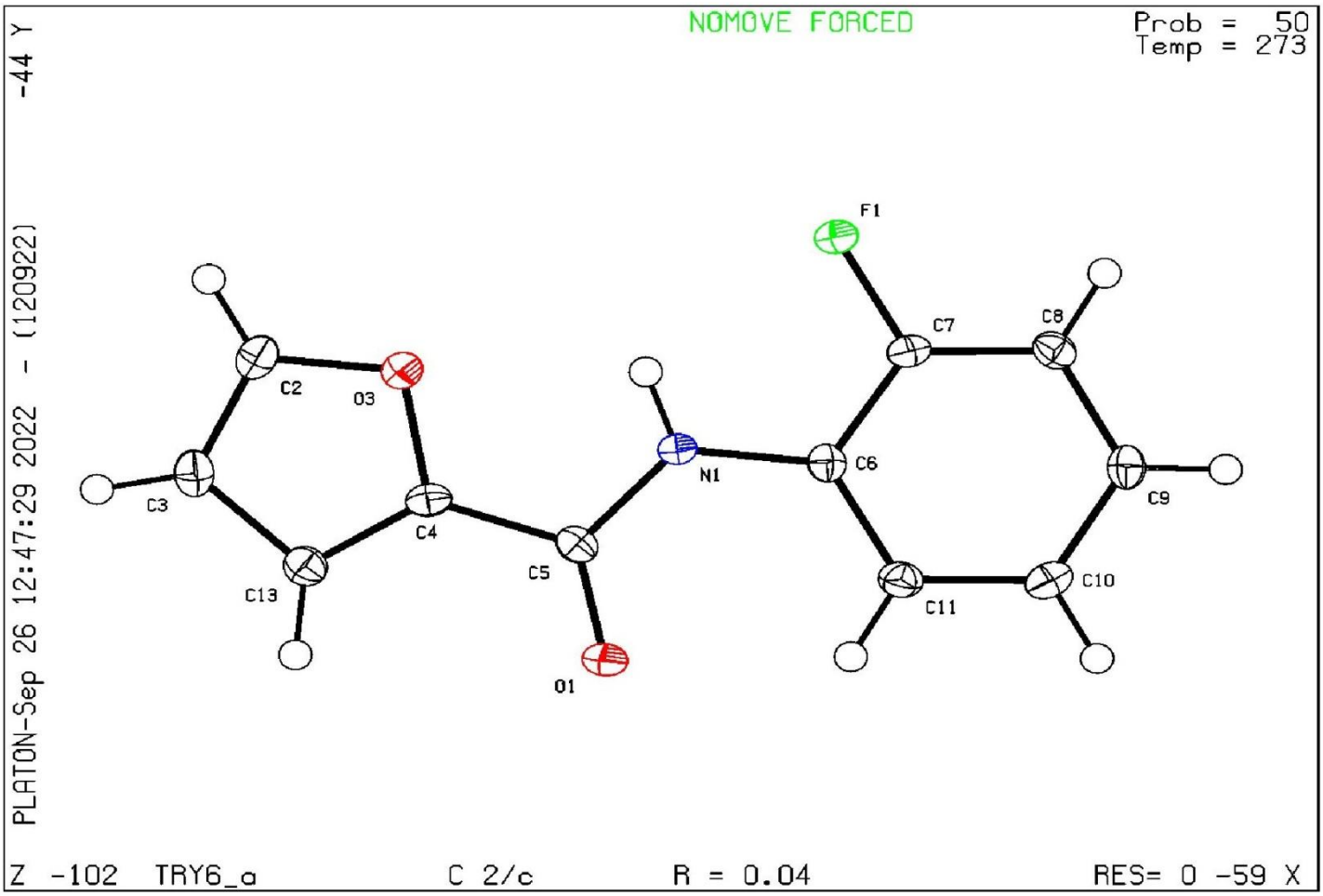

Figure S76. ORTEP diagram of **9e (CCDC = 2209513)**. Ellipsoids are drawn at 50% probability.

Reference:

1) Sheldrick, G. M. *Acta Crystallography. Sect A*. 1990, **46**, 467.

Differential scanning calorimetry (DSC) analysis of triflate surrogates

(A) DSC data was obtained on Perkin Elmer Differential scanning calorimeter 8000 **II** (5.050mg) was loaded into aluminum volatile pan and held at 25 ^{o}C for 10 min then 25 ^{o}C to 180 ^{o}C at 10 ^{o}C/min.

(B) DSC data was obtained on Perkin Elmer Differential scanning calorimeter 8000 **III** (4.150mg) was loaded into aluminum volatile pan and held at 25 ^{o}C for 10 min then 25 ^{o}C to 180 ^{o}C at 10 ^{o}C/min.

(C) DSC data was obtained on Perkin Elmer Differential scanning calorimeter 8000 **IV** (4.150mg) was loaded into aluminum volatile pan and held at 25 ^{o}C for 10 min then 25 ^{o}C to 180 ^{o}C at 10 ^{o}C/min.

(D) DSC data was obtained on Perkin Elmer Differential scanning calorimeter 8000 **V** (3.930mg) was loaded into aluminum volatile pan and held at 25 ^{o}C for 10 min then 25 ^{o}C to 180 ^{o}C at 10 ^{o}C/min.

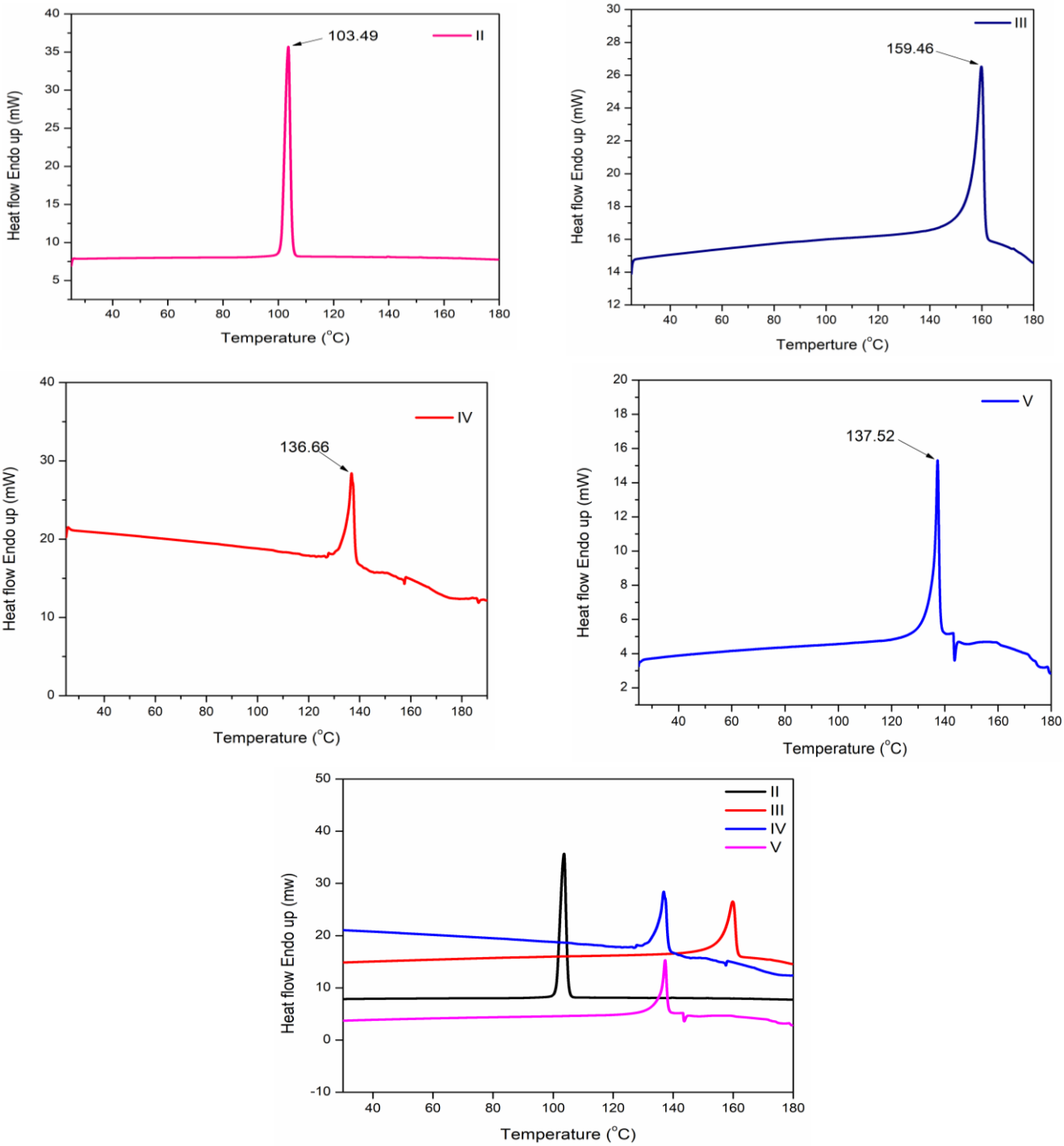

Figure S177. DSC data of triflate surrogates II-V