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Supporting Information

Redirection of the Transcription Factor SP1 to AT Rich Binding Sites by a Synthetic Adaptor Molecule

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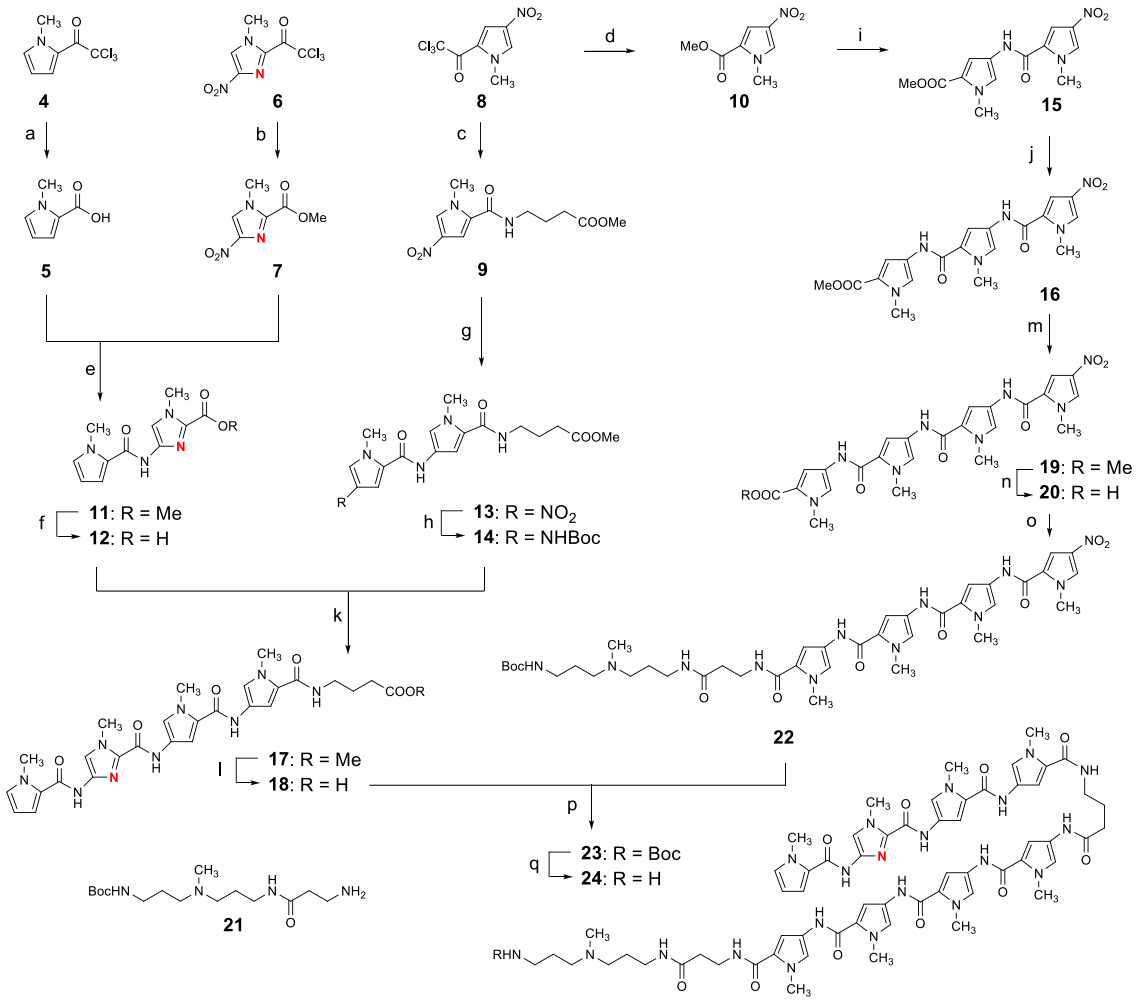
General

Oxygen and water sensitive reactions were conducted under argon. Column chromatography: silica gel, 60 Å pore size, 0.04-0.063 mm particle size (Macherey-Nagel). Melting points (uncorrected): MPM-H2 Schorpp Gerätetechnik. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C-NMR) were recorded with Bruker AV 250 (^{1}H: 250 MHz; ^{13}C: 62.9 MHz), Bruker AV 300 (^{1}H: 300 MHz; ^{13}C: 75.5 MHz) or Bruker AV 500 (^{1}H: 500 MHz; ^{13}C: 125.8 MHz) spectrometers. Chemical shifts for protons are reported in parts per million (δ scale) and internally referenced to the proton resonances of the solvent ($CDCl_3$: δ 7.26, d_6-DMSO: δ 2.50). Chemical shifts for carbon are reported in parts per million (δ scale) and referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16, d_6-DMSO: δ 39.52). Data are represented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet), coupling constants in Hz, and integration. Mass spectra: ESI-MS spectra were obtained on a Fisons VG Plattform II, LC-ESI spectra on a Surveyor MSQ instrument (ThermoFisher). HRMS spectra were recorded on a MALDI LTQ Orbitrap mass spectrometer (ThermoFisher). Mass spectra of oligonucleotides and conjugates (ESI/TOF): micrOTOF-Q II (Bruker) with Agilent 1200 Series HPLC and MultoKrom 5-C18 column. The concentrations of oligonucleotides was determined on a NanoDrop 2000c spectrometer (ThermoFisher).

Liquid phase synthesis of polyamide 24



Scheme S1. a) NaOH, MeOH, 79%; b) DMAP, MeOH, 85 %; c) methyl 4-aminobutanoate hydrochloride, DIPEA, DCM, 95 %; d) DMAP, MeOH, 89 %; e) **7**, H_2, Pd/C, EtOAc, then **5**, HOBt, DIC, DIPEA, DMF, 79%; f) NaOH, MeOH, 86%; g) **9**, H_2, Pd/C, EtOAc, then **8**, DIPEA, DCM, 81%; h) H_2, Pd/C, Boc_2O, MeOH, 100%; i) **10**, H_2, Pd/C, EtOAc, then **8**, DIPEA, DCM, 86%; j) **15**, H_2, Pd/C, EtOAc, then **8**, DIPEA, DCM, 79%; k) **14**, AcCl, MeOH, then **12**, HBTU, DIPEA, DMF, 85%; l) LiOH, MeOH, H_2O, 85%; m) **16**, H_2, Pd/C, Boc_2O, MeOH, then TFA, DCM, then **8**, DIPEA, DCM, 71%; n) NaOH, EtOH, 89%; o) **20** + **21**, DIC, HOBt, DIPEA, DMF, 80%; p) **22**, H_2, Pd/C, DMF, then **18**, HBTU, DIPEA, 62%; q) TFA, DCM, 100%. Synthesis of linker **21** see below.

1-Methyl-1H-pyrrole-2-carboxylic acid 5 (RN: 6973-60-0)

Compound **4** (3.20 g, 14.1 mmol, 1.0 eq) was suspended in MeOH (9.5 mL). 2 M NaOH (35 mL, 70 mmol, 5.0 eq) was added, and the mixture was stirred for 23 h at room temperature (rt). The resulting solution was acidified with 1 M HCl, and filtrated. The filtrate was extracted with EtOAc and the combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain **5** as a brown solid (1.44 g, 11.5 mmol, 79 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 12.14 (s, 1H, OH), 7.03 (t, J = 2.0 Hz, 1H, C^5-H), 6.78 (dd, J = 3.9, 1.8 Hz, 1H, C^3-H), 6.05 (dd, J = 3.9, 2.5 Hz, 1H, C^4-H), 3.83 (s, 3H, N-CH_3) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 162.0 (C=O), 129.8 (C^5), 122.5 (C^2), 117.3 (C^3), 107.3 (C^4), 36.3 (N-CH_3) ppm.

Methyl 1-methyl-4-nitro-1*H*-imidazole-2-carboxylate 7 (RN: 169770-25-6)

Compound **6** (4.00 g, 14.7 mmol, 1.0 eq) and DMAP (90 mg, 7.3 mmol, 0.05 eq) were suspended in MeOH (28 mL) and stirred for 8 h at rt. The suspension was filtered, and the crude product **7** was washed with MeOH. The filtrate was evaporated, and residue was suspended in MeOH. The mixture was filtered to obtain further **7** as a colorless solid. Yield: 2.32 g, 12.5 mmol, 85 %. R_f = 0.38 (cyclohexane/EtOAc 1:2). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.86 (s, 1H), 4.11 (s, 3H), 3.95 (s, 3H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 158.7, 146.1, 134.8, 124.6, 53.1, 37.2 ppm. MS (ESI): m/z calcd. for $C_6H_8N_3O_4$ ($[M+H]^+$): 186.1; found 186.2. HRMS (MALDI): m/z calcd. for $C_6H_8N_3O_4$ ($[M+H]^+$): 186.05093; found 186.05090.

Methyl 4-(1-methyl-4-nitro-1*H*-pyrrole-2-carboxamido)butanoate 9 (RN: 491647-49-5)

Compound **8** (1.50 g, 5.56 mmol, 1.0 eq) and methyl 4-aminobutanoate hydrochloride (940 mg, 6.13 mmol, 1.1 eq) were suspended in dry DCM (10 mL) and DIPEA (1.9 mL, 8.3 mmol, 1.5 eq) was added. The resulting solution was stirred for 27 h at rt. Subsequently the solvent was removed and the crude product was purified by column chromatography (cyclohexane/EtOAc 1:1). **9** was obtained as a colorless solid (1.42 g, 5.39 mmol, 95 %). R_f = 0.30 (cyclohexane/EtOAc 1:1). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.40 (t, J = 5.5 Hz, 1H), 8.12 (d, J = 1.9 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 3.89 (s, 3H), 3.58 (s, 3H), 3.20 (q, J = 6.8 Hz, 2H), 2.36 (t, J = 7.4 Hz, 2H), 1.74 (p, J = 7.1 Hz, 2H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 173.1, 159.9, 133.8, 127.9, 126.4, 107.3, 51.3, 37.9, 37.4, 30.7, 24.4 ppm. HRMS (MALDI): m/z calcd. for $C_{11}H_{16}N_3O_5$ ($[M+H]^+$): 270.10845; found 270.10854.

Methyl 1-methyl-4-nitro-1*H*-pyrrole-2-carboxylate 10 (RN: 13138-76-6)

Compound **8** (2.00 g 7.38 mmol) was suspended in MeOH (15 mL). DMAP (90 mg, 0.74 mmol) was added and the mixture was stirred for 2 h. The suspension was filtered, and the residue of **10** was washed with methanol. The filtrate was evaporated. The residue was resuspended in methanol and filtered to obtain additional **10** as a colorless solid (1.21 g, 6.57 mmol, 89 %). Mp. 119 – 120 °C (Ref. 120 – 122 °C).[1] ^{1}H-NMR (300 MHz, DMSO-d_6) δ = 8.28 (d, J = 1.7 Hz, 1H, C^5-H), 7.32 (d, J = 2.1 Hz, 1H, C^3-H), 3.93 (s, 3H, N-CH_3), 3.80 (s, 3H, $COOCH_3$) ppm. ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 159.9, 134.2, 129.5, 122.7, 111.6, 51.9, 37.5 ppm.

Pyrrole-imidazole dimer 11

Compound **7** (1.00 g, 5.40 mmol, 1.0 eq) was suspended in dry EtOAc (20 mL) and Pd/C (100 mg, 10 % on active charcoal) was added. The suspension was stirred in a H_2-atmosphere for 2h. The mixture was filtered through celite and the solvent was removed under reduced pressure.

Compound **5** (810 mg, 6.48 mol, 1.2 eq), HOBt (1.00 mg, 6.48 mmol, 1.2 eq, 12 % H_2O) and DIC (1.36 mL, 10.8 mmol, 2.0 eq) were dissolved in dry DMF (10 mL). The mixture was stirred for 3 h at rt. Subsequently the solution was filtered, and the filtrate was added to the freshly prepared amine. After the addition of DIPEA (1.84 mL, 10.8 mmol, 2.0 eq) the solution was heated to 60 °C for 3 h. Thereafter

it was stirred for 16 h at RT and for 5 h at 60 °C. Afterwards the solution was added to a mixture of H_2O/sat. $NaHCO_3$ (4:1) and then extracted with DCM. The combined organic layers were dried over Mg_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane/EtOAc 1:4). **11** was obtained as a colorless solid (1.12 g, 4.27 mmol, 79 %). R_f = 0.55 (cyclohexane /EtOAc 1:4). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.58 (s, 1H), 7.67 (s, 1H), 7.17 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.04 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 159.0, 158.7, 137.9, 130.7, 128.9, 124.4, 115.3, 114.0, 107.0, 51.7, 36.5, 35.4 ppm. MS (ESI): *m*/*z* calcd. for $C_{12}H_{15}N_4O_3$ ($[M+H]^+$): 263.1; found 263.1. HRMS (MALDI): *m*/*z* calcd. for $C_{12}H_{15}N_4O_3$ ($[M+H]^+$): 263.11387; found 263.11403.

Pyrrole-imidazole dimer 12 (RN: 537049-66-4)

Compound **11** (246 mg, 936 µmol, 1.0 eq) was suspended in MeOH (10 mL). A solution of NaOH (44 mg, 1.1 mmol 1.2 eq) in 10 mL of water was added and the solution was boiled under reflux for 3 h. The solution was cooled to rt and extracted twice with dichloromethane. The aqueous phase was acidified with 37% HCl until a colorless solid precipitated. The suspension was filtered and the precipitate of **12** was washed with water and dried in vacuum (199 mg, 86%). ^{1}H-NMR (300 MHz, DMSO-d_6) δ = 10.55 (s, 1H), 7.61 (s, 1H), 7.16 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.03 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H) ppm (the COOH signal was not observable due to fast exchange). ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 160.1, 158.7, 137.5, 131.7, 128.9, 124.5, 114.9, 114.0, 107.0, 36.5, 35.5 ppm. MS (ESI): *m*/*z* calcd. for $C_{11}H_{13}N_4O_3$ ($[M+H]^+$): 249.1; found 249.2. HRMS (MALDI): *m*/*z* calcd. for $C_{11}H_{13}N_4O_3$ ($[M+H]^+$): 249.09822; found 249.09863.

Pyrrole-pyrrole dimer 13 (RN: 746653-28-1)

Compound **9** (400 mg, 1.49 mmol, 1.0 eq) was solved in EtOAc (10 mL) and Pd/C (50 mg, 10% on active charcoal) was added. The mixture was stirred in a H_2 atmosphere for 18 h. The catalyst was removed by filtration through celite and the solvent was removed under reduced pressure. The residue was solved in DCM (10 mL) and **8** (480 mg, 1.78 mmol) as well as DIPEA (500 µL, 3.00 mmol) was added. The solution was stirred for two days at rt. The resulting suspension was filtered, and the residue was washed with DCM. **13** was obtained as a yellow solid (470 mg, 1.20 mmol, 81 %). ^{1}H-NMR (300 MHz, DMSO-d_6) δ = 10.23 (s, 1H), 8.16 (d, *J* = 1.4 Hz, 1H), 8.08 (t, *J* = 5.6 Hz, 1H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.20 (d, *J* = 1.3 Hz, 1H), 6.85 (d, *J* = 1.4 Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 3.58 (s, 3H), 3.18 (q, *J* = 6.4 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.81 – 1.67 (m, 2H) ppm. ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 173.3, 161.3, 156.9, 133.9, 128.3, 126.4, 123.3, 121.4, 118.1, 107.6, 104.1, 51.3, 37.8, 37.6, 36.1, 30.9, 24.7 ppm. MS (ESI): *m*/*z* calcd. for $C_{17}H_{20}N_5O_6$ ($[M-H]^-$): 390.1; found 390.1. HRMS (MALDI): *m*/*z* calcd. for $C_{17}H_{22}N_5O_6$ ($[M+H]^+$): 392.15646; found 392.15498.

Pyrrole-pyrrole dimer 14 (corresponding ethyl ester: RN: 940931-11-3)

Compound **13** (2.00 g, 5.11 mmol, 1.0 eq), Boc_2O (2.23 g, 10.2 mmol, 2.0 eq) and Pd/C (200 mg, 10 % on active charcoal) were suspended in dry MeOH (40 mL) and stirred in a steel autoclave at 45 °C and 45 bar H_2-pressure for 19 h. The catalyst was removed by filtration through celite. The solvent was evaporated under reduced pressure to obtain **14** as a colorless foam (2.36 g, 100 %). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 9.81 (s, 1H), 9.09 (s, 1H), 8.02 (t, *J* = 5.7 Hz, 1H), 7.15 (d, *J* = 1.7 Hz, 1H), 6.88 (s *br*, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 6.81 (s *br*, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.58 (s, 3H), 3.18 (q, *J* = 6.7 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.77 – 1.70 (p, *J* = 7.2 Hz, 2H), 1.45 (s, 9H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 173.2, 161.4, 158.4, 152.9, 122.9, 122.8, 122.3, 122.1, 117.8, 117.0, 104.2, 103.8, 78.3, 51.3, 37.7, 36.1, 35.9, 30.8, 28.2, 24.7 ppm. MS (ESI): *m*/*z* calcd. for $C_{22}H_{30}N_5O_6$ ($[M-H]^-$): 460.2; found 460.3. HRMS (MALDI): *m*/*z* calcd. for $C_{22}H_{32}N_5O_6$ ($[M+H]^+$): 462.23471; found 462.23335.

Pyrrole-pyrrole dimer 15 (RN: 69910-20-9)

Compound **10** (4.38 g, 23.8 mmol) was suspended in EtOAc (100 mL) and Pd/C (0.40 g, 10% on active charcoal) was added. The mixture was stirred in a H_2-atmosphere for 19.5 h. Pd/C was removed by filtration through celite, the solvent was evaporated under reduced pressure and the residue dried in vacuum. Afterwards the crude amine was dissolved in 40 mL of DCM and compound **8** (7.08 g, 26.1 mmol) followed by DIPEA (6.0 mL, 35 mmol) were added. The solution was stirred for 4.5 h at rt. The precipitated yellow solid was filtered and washed with DCM to obtain **15** as a yellow solid (6.26 g, 20.4 mmol, 86 %). Mp. 250 °C (decomp.; ref. 262 °C).[1] ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.26 (s, 1H), 8.19 (d, J = 1.8 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 1.9 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 160.8, 156.9, 133.8, 128.3, 126.1, 122.2, 120.9, 118.9, 108.3, 107.7, 51.1, 37.5, 36.3 ppm. MS (ESI): *m*/*z* calcd. for $C_{13}H_{15}N_3O_5$ ([M+H]$^+$): 307.1; found 307.1. HRMS (MALDI): *m*/*z* calcd. for $C_{13}H_{14}N_3O_5$ ([M$^\bullet$]$^+$): 306.09587; found 306.09606.

Pyrrole-pyrrole-pyrrole trimer 16 (RN: 69910-21-0)

Compound **15** (2.00 g, 6.53 mmol, 1.0 eq) was added to a suspension of Pd/C (300 mg, 10% on active charcoal) in EtOAc (40 mL). The suspension was stirred in a steel autoclave under H_2 (40 bar) for 3 h at 45 °C and Pd/C was removed by filtration through celite. The solvent was evaporated under reduced pressure and the residue dried in vacuum. Afterwards the crude amine was dissolved in DCM (10 mL) and added to a solution of compound **8** (1.95 g, 7.18 mmol, 1.1 eq) in DCM (30 mL). DIPEA (1.7 mL, 10 mmol, 1.5 eq) was added and the solution was stirred for 22 h at rt. The precipitated yellow solid was filtered and washed with DCM to obtain **16** as a yellow solid (2.21 g, 5.16 mmol, 79 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.29 (s, 1H), 9.98 (s, 1H), 8.18 (d, J = 1.7 Hz, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 1.8 Hz, 1H), 7.26 (d, J = 1.7 Hz, 1H), 7.06 (d, J = 1.8 Hz, 1H), 6.91 (d, J = 1.9 Hz, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 160.8, 158.4, 157.0, 133.8, 128.3, 126.3, 122.9, 122.8, 121.5, 120.8, 118.8, 118.6, 108.4, 107.6, 104.6, 51.0, 37.5, 36.2, 36.2 ppm. MS (ESI): *m*/*z* calcd. for $C_{19}H_{21}N_6O_6$ ([M+H]$^+$): 429.2; found 429.0. HRMS (MALDI): *m*/*z* calcd. for $C_{19}H_{21}N_6O_6$ ([M+H]$^+$): 429.15171; found 429.15153.

Py-Im-Py-Py-γ-OMe 17

MeOH (3 mL) was cooled to 0 °C and AcCl (1 mL) was added. The solution was stirred for 20 min at this temperature and compound **14** (100 mg, 217 µmol, 1.0 eq) in MeOH (2 mL) was added. The mixture was stirred for 20 min at 0 °C and 60 min at rt. Afterwards the solvent was removed under reduced pressure. The hydrochloride, compound **12** (65 mg, 260 µmol, 1.2 eq) and HBTU (107 mg, 282 mol, 1.3 eq) were dissolved in DMF (5 mL). After that, DIPEA (111 µL, 650 mmol, 3.0 eq) was added and the mixture was stirred for 19 h at rt. Afterwards it was added to an aqueous solution of Na_2CO_3 in water (20%), extracted with DCM and dried over $MgSO_4$. The crude product was purified by column chromatography (cyclohexane/EtOAc/MeOH 2:9:1). **17** was obtained as a pale brown solid (109 mg, 184 µmol, 85 %). R_f = 0.39 (cyclohexane/ EtOAc /MeOH 2:9:1). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.24 (s, 1H), 9.98 (s, 1H), 9.90 (s, 1H), 8.04 (t, J = 5.6 Hz, 1H), 7.55 (s, 1H), 7.28 (d, J = 1.5 Hz, 1H), 7.19 (d, J = 1.5 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.00 – 6.97 (m, 1H), 6.88 (d, J = 1.6 Hz, 1H), 6.06 (dd, J = 3.8, 2.6 Hz, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.59 (s, 3H), 3.18 (q, J = 6.5 Hz, 2H), 2.34 (t, J = 7.4 Hz, 2H), 1.78 – 1.70 (m, 2H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ= 173.2, 161.3, 158.8 158.4, 155.8, 136.2, 134.1, 128.9, 124.6, 123.1, 122.9, 122.0, 121.2, 118.5, 117.9, 114.5, 113.8, 107.0, 105.1, 104.3, 51.3, 37.7, 36.5, 36.2, 36.0, 34.9, 30.8, 24.7 ppm. MS (ESI): *m*/*z* calcd. for $C_{28}H_{34}N_9O_6$ ([M+H]$^+$): 592.3; found 592.3 HRMS (MALDI): *m*/*z* calcd. for $C_{28}H_{33}N_9NaO_6$ ([M+Na]$^+$): 614.24460; found 614.24463.

Py-Im-Py-Py-γ-OH 18

Compound **17** (153 mg, 259 µmol, 1.0 eq) was suspended in MeOH/H_2O. Subsequently, LiOH*H_2O (54.0 mg, 1.29 mmol) was added at 0 °C and the solution was allowed to warm to rt over night The product was absorbed on silica and purified by column chromatography (DCM/MeOH 5:1). **18** was obtained as a colorless solid (127 mg, 221 µmol, 85 %). R_f = 0.72 (DCM/MeOH 5:1). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 12.04 (s *br*, 1H), 10.24 (s, 1H), 9.97 (s, 1H), 9.90 (s, 1H), 8.03 (t, *J* = 5.7 Hz, 1H), 7.55 (s, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.00 – 6.97 (m, 1H), 6.88 (d, *J* = 1.8 Hz, 1H), 6.06 (dd, *J* = 3.9, 2.5 Hz, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.18 (q, *J* = 6.5 Hz, 2H), 2.22 (t, *J* = 7.3 Hz, 2H), 1.71 (p, *J* = 7.2 Hz, 2H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 174.3, 161.3, 158.8, 158.4, 155.8, 136.2, 134.1, 128.9, 124.6, 123.2, 123.0, 122.0, 121.2, 118.5, 117.9, 114.5, 113.8, 107.0, 104.7, 104.3, 37.9, 36.4, 36.2, 36.0, 34.9, 31.1, 24.8 ppm. MS (ESI): *m*/*z* calcd. for $C_{27}H_{30}N_9O_6$ ([M-H]$^-$): 576.2; found 576.2. HRMS (MALDI): *m*/*z* calcd. for $C_{27}H_{32}N_9O_6$ ([M+H]$^+$): 578.24701; found 578.24758.

O_2N-Py-Py-Py-Py-OMe 19 (RN: 134985-79-8)

Compound **16** (200 mg, 467 µmol, 1.0 eq), Boc_2O (204 mg, 934 µmol, 2.0 eq) and Pd/C (20 mg, 10% on active charcoal) were suspended in MeOH (5 mL), and stirred in a steel autoclave under 40 bar H_2-pressure for 18 h at 45 °C. The catalyst was removed by filtration through celite and solvent was evaporated. Afterwards DCM (3 mL) and TFA (2 mL) were added. The solution was stirred at room temperature for 30 min to remove the protecting group. The solvent was then evaporated. The TFA-salt was suspended in DCM (5 mL) and compound **8** (254 mg, 934 µmol, 2.0 eq) was added. Then DIPEA (238 µL, 1.40 mmol, 3.0 eq) was added and the resulting solution was stirred for 49 h at rt. The precipitated solid was filtered, washed with DCM, and dried in vacuum to obtain **19** as a pale yellow solid (182 mg, 331 µmol, 71 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.30 (s, 1H), 10.00 (s, 1H), 9.94 (s, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.06 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 161.0, 158.6, 158.5, 157.1, 133.9, 128.4, 126.4, 123.1, 123.1, 122.7, 122.3, 121.5, 120.9, 118.8, 118.8, 118.7, 108.5, 107.6, 105.0, 104.7, 51.1, 37.6, 36.3, 36.3, 36.2 ppm. MS (ESI): *m*/*z* calcd. for $C_{25}H_{25}N_8O_7$ ([M-H]$^-$): 549.2; found 549.2. HRMS (MALDI): *m*/*z* calcd. for $C_{25}H_{26}N_8O_7$ ([M$^•$]$^+$): 550.19190; found 550.19124.

O_2N-Py-Py-Py-Py-OH 20 (RN: 134985-80-1)

Compound **19** (104 mg, 189 µmol, 1.0 eq) und NaOH (22.6 mg, 567 µmol, 3.0 eq) were suspended in EtOH (1.32 mL) and H_2O (0.95 mL) and refluxed for 1 h. The solution was cooled to rt and acidified with conc. HCl. The precipitated solid was filtered, washed with H_2O, and dried in vacuum. **20** was obtained as an orange solid (90 mg, 168 µmol, 89 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 12.15 (s *br*, 1H), 10.30 (s, 1H), 10.00 (s, 1H), 9.91 (s, 1H), 8.19 (d, *J* = 1.7 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.07 (d, *J* = 1.7 Hz, 1H), 7.05 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 1.9 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 162.0, 158.5, 158.4, 156.9, 133.8, 128.3, 126.3, 123.0, 122.7, 122.6, 122.2, 121.4, 120.3, 119.5, 118.7, 118.6, 108.4, 107.6, 104.8, 104.5, 37.5, 36.2, 36.2, 36.1 ppm. MS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_8O_7$ ([M-H]$^-$): 535.2; found 535.1. HRMS (MALDI): *m*/*z* calcd. for $C_{24}H_{24}N_8NaO_7$ ([M+Na]$^+$): 559.16602; found 559.16564.

O_2N-Py-Py-Py-Py-*β*-linker-Boc 22

Compound **20** (100 mg, 186 µmol, 1.0 eq) was dissolved in dry DMF (5 mL) and HOBt (28.5 mg, 186 µmol, 1 eq), linker **21** (70.8 mg, 223 µmol, 1.2 eq) as well as DIPEA (63.0 µl, 223 µmol, 2.0 eq) were added. Subsequently the solution was warmed to 60 °C and DIC (57.0 µl, 371 µmol, 2.0 eq) was added. The mixture was stirred for 3 h at 60 °C and for 18.5 h at rt. After that, the solvent was evaporated under reduced pressure and the crude product was purified twice by column chromatography (1. DCM/MeOH 9:1 + 1 % Et_3N, 2. DCM/MeOH 9:1 + 1 % NH_3). **22** was obtained as a yellow foam (124 mg, 148 µmol, 80 %). R_f = 0.34 (DCM/MeOH 9:1 + 1 % Et_3N). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.30 (s, 1H), 10.00 (s, 1H), 9.91 (s, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 8.01 (t, *J* = 5.6 Hz, 1H), 7.89 (t, *J* = 5.3 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 7.09 – 7-02 (m, 2H), 6.84 (d, *J* = 1.5 Hz, 1H), 6.79 (t, *J* = 4.9 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.06 (q, *J* = 6.6 Hz, 2H), 2.92 (q, *J* = 6.5 Hz, 2H), 2.39 – 2.24 (m, 6H), 2.14 (s *br*, 3H), 1.59 – 1.47 (m, 4H), 1.36 (s, 9H) ppm (A signal of 2 protons around 3.4 ppm is masked by water). ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 170.4, 161.3, 158.5, 158.4, 156.9, 155.6, 133.8, 128.3, 126.3, 123.0, 122.8, 122.8, 122.2, 122.1, 121.4, 118.7, 118.5, 117.9, 107.6, 104.7, 104.5, 104.2, 77.4, 54.6, 54.6, 41.5, 38.2, 37.5, 36.7, 36.2, 36.1, 36.0, 35.6, 35.5, 28.3, 26.9, 26.6 ppm. MS (ESI): *m*/*z* calcd. for $C_{39}H_{55}N_{12}O_9$ ($[M+H]^+$): 835.9; found 835.7. HRMS (MALDI): *m*/*z* calcd. for $C_{39}H_{55}N_{12}O_9$ ($[M+H]^+$): 835.42095; found 835.42168.

Py-Im-Py-Py-*γ*-Py-Py-Py-Py-*β*-linker-Boc 23

Compound **22** (50.0 mg, 59.5 µmol, 1.0 eq) and Pd/C (5 mg, 10% on active charcoal) were suspended in DMF (2 mL) and stirred for 16 h under hydrogen.

Compound **18** (41.3 mg, 71.9 µmol, 1.2 eq) was dissolved in DMF (1.5 mL) and cooled to 0 °C. Then HBTU (29.0 mg, 77.4 µmol, 1.3 eq) and DIPEA (20.0 µL, 119 µmol, 2.0 eq) were added and stirred for 15 min. Afterwards, the solution was added to the freshly prepared amine and stirred for 4.5 h at rt. Thereafter, the suspension was filtered through celite and DCM (40 mL) was added followed by an aqueous solution of $NaHCO_3$ (50%, 40 mL). The layers were separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed, and the crude product purified twice by column chromatography (1. DCM/MeOH 9:1 w. 1% Et_3N and 2. DCM/MeOH 9:1 w. 1% NH_3). Polyamide **23** was obtained as light brown solid (50.0 mg, 36.6 µmol, 62 %). R_f = 0.28 (DCM/MeOH 5:1 + 1 % NH_3). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.22 (s, 1H), 9.97 (s, 1H), 9.94 (s, 1H), 9.92 – 9-86 (m, 3H), 9.84 (s, 1H), 8.06 (t, *J* = 5.7 Hz, 1H), 7.99 (t, *J* = 5.6 Hz, 1H), 7.86 (t, *J* = 5.5 Hz, 1H), 7.55 (s, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.26 – 7-22 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 (d, *J* = 1.7 Hz, 1H), 7.11 (dd, *J* = 4.0, 1.7 Hz, 1H), 7.08 – 7.03 (m, 2H), 7.00 – 6.97 (m, 1H), 6.91 (d, *J* = 1.7 Hz, 1H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.84 (d, *J* = 1.7 Hz, 1H), 6.76 (t, *J* = 5.4 Hz, 1H), 6.06 (dd, *J* = 3.9, 2.5 Hz, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.22 (q, *J* = 6.5 Hz, 2H), 3.06 (q, *J* = 6.7 Hz, 2H), 2.92 (q, *J* = 6.6 Hz, 2H), 2.35 – 2.20 (m, 8H), 2.09 (s, 3H), 1.84 – 1.76 (m, 2H), 1.55 – 1.45 (m, 4H), 1.36 (s, 9H) ppm (A signal of 2 protons around 3.4 ppm is masked by water). ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 170.4, 169.3, 161.3, 161.2, 158.8, 158.5, 158.5, 158.5, 158.4, 155.8, 155.6, 136.2, 134.1, 128.9, 124.6, 123.1, 123.0, 122.8, 122.8, 122.7, 122.2, 122.2, 122.2, 122.1, 122.0, 121.2, 118.5, 118.4, 118.2, 117.9, 114.6, 113.8, 107.0, 104.7, 104.7, 104.3, 104.2, 104.0, 77.4, 54.8, 54.7, 41.7 38.3, 38.2, 36.8, 36.4, 36.2, 36.1, 36.0, 36.0, 35.6, 35.5, 34.9, 33.3, 28.3, 27.1, 26.8, 25.7 ppm. MS (ESI): *m*/*z* calcd. for $C_{66}H_{86}N_{21}O_{12}$ ($[M+H]^+$): 1364.7; found 1364.7. HRMS (MALDI): *m*/*z* calcd. for $C_{66}H_{86}N_{21}O_{12}$ ($[M+H]^+$): 1364.6759; found 1364.2140.

Py-Im-Py-Py-γ-Py-Py-Py-Py-β-linker-NH_2, polyamide 24

Compound **23** (20 mg, 16 µmol) was dissolved in DCM/TFA (1:1, 1 mL) and stirred for 1.5 h at 0 °C. The solvent was removed under reduced pressure and the brown solid was dried. The crude product, obtained in quantitative yield, was used for the synthesis of adaptor **1** without further purification.

MS (ESI): *m*/*z* calcd. for $C_{61}H_{78}N_{21}O_{10}$ ($[M+H]^+$): 1264.6; found 1264.6.
m/*z* calcd. for $C_{61}H_{79}N_{21}O_{10}$ ($[M+2H]^{2+}$): 632.8; found 633.0.

HRMS (MALDI): *m*/*z* calcd. for $C_{61}H_{78}N_{21}O_{10}$ ($[M+H]^+$): 1264.6235; found 1264.4244.

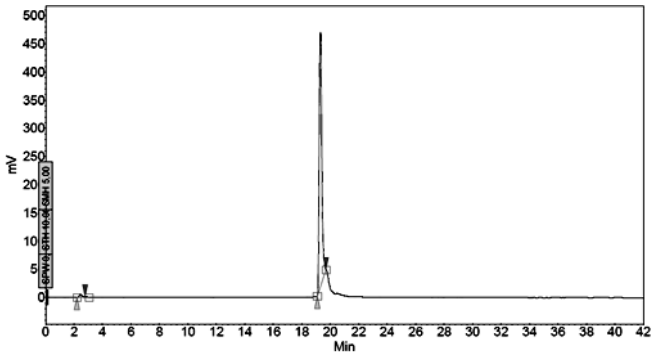
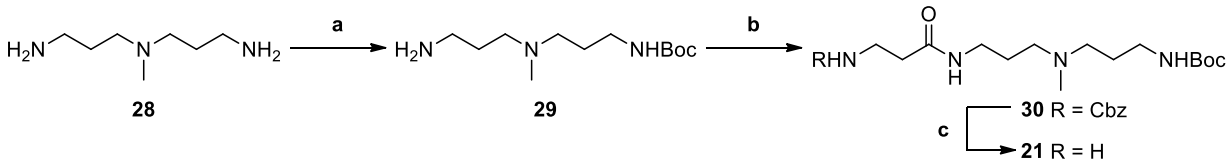


Figure S1. *rp*-HPLC-chromatogram after purification of **24**, using a linear gradient from 10 % B to 70 % B in 30 min. A: 0.1 % TFA in H_2O; B: Acetonitrile.

Synthesis of linker 21



Scheme S2. a) Boc_2O, 1,4-dioxane, rt, 51 %; b) *Cbz*-β-Ala-OH, HOBt, DIC, DIPEA, DMF, 60 °C, 73 %; c) H_2 (1 bar), Pd/C, MeOH, rt, 96 %.

***tert*-Butyl 3-((3-aminopropyl)(methyl)amino)propylcarbamate 29 (RN: 87530-14-1)**

Amine **28** (15.0 mL, 92.8 mmol, 4.1 eq) was dissolved in 1,4-dioxane (25 mL). Subsequently a solution of Boc_2O (5.01 g, 22.9 mmol, 1.0 eq) in 1,4-dioxane (25 mL) was added dropwise. The resulting solution was stirred for 20 h at rt and then evaporated. The residue was redissolved in water (40 mL) and extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified twice by column chromatography (1. DCM/MeOH 5:1 + 5 % Et_3N, 2. DCM/MeOH 2:1 + 5 % NH_3) and **29** was obtained as a colorless oil (2.88 g, 11.7 mmol, 51 %). R_f = 0.31 (DCM/MeOH 2:1 + 5 % NH_3). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 5.37 (s, 1H), 3.16 (q, *J* = 6.0 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 6.9 Hz, 4H), 2.18 (s, 3H), 1.94 (s *br*, 2H), 1.69 – 1.56 (m, 4H), 1.43 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 156.3, 79.0, 56.4, 55.8, 42.2, 40.6, 40.0, 30.8, 28.6, 27.1 ppm. MS (ESI): *m*/*z* calcd. for $C_{12}H_{28}N_3O_2$ ($[M+H]^+$): 246.2; found 246.2. HRMS (MALDI): *m*/*z* calcd. for $C_{12}H_{28}N_3O_2$ ($[M+H]^+$): 246.21760; found 246.21791.

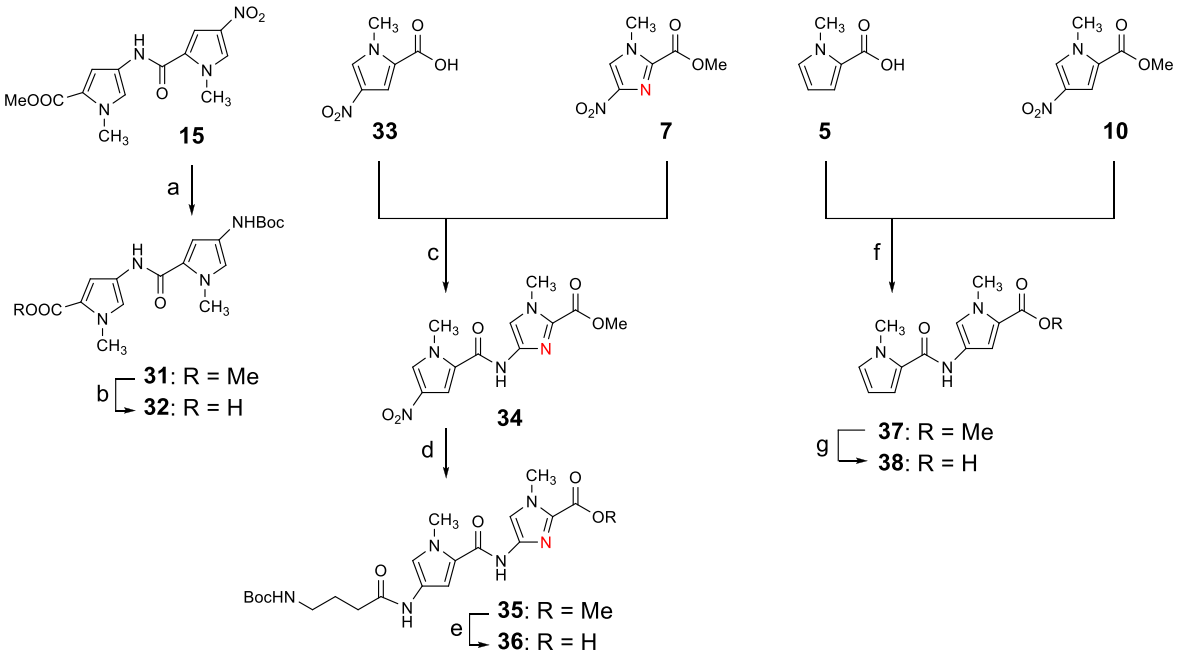
Cbz-*β*-linker-Boc 30 (RN: 2170549-22-9)

Cbz-*β*-alanine (1.84 g, 8.25 mmol, 1.1 eq), HOBt (1.27 g, 8.25 mmol, 1.1 eq) and DIC (2.3 mL, 15 mmol, 2.0 eq) were dissolved in dry DMF (15 mL). The mixture was stirred for 22 h at rt. Subsequently, a mixture of **29** (1.84 g, 7.50 mmol, 1.0 eq) and DIPEA (2.6 mL, 15 mmol, 2 eq) in DMF (3 mL) was added and the resulting solution was stirred for 24 h at rt. The resulting suspension was filtered and an aqueous solution of $NaHCO_3$ (100 mL, 20%) was added. The aqueous layer was extracted with DCM (3x, 40 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography (EtOAc/MeOH 6:1 + 1 % Et_3N) to obtain **30** as a colorless oil (2.70 g, 5.99 mmol, 73 %). R_f = 0.5 (EtOAc/MeOH 2:1 + 1 % Et_3N). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 5H), 7.10 (s *br*, 1H), 5.59 (s *br*, 1H), 5.17 – 4.96 (m, 3H), 3.47 (q, *J* = 6.0 Hz, 2H), 3.37 – 3.27 (m, 2H), 3.17 (q, *J* = 6.2 Hz, 2H), 2.56 – 2.34 (m, 6H), 2.20 (s, 3H), 1.75 – 1.59 (m, 4H), 1.43 (s, 9H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 171.5, 156.6, 156.3, 136.8, 128.6, 128.2, 79.4, 66.7, 56.0, 55.6, 41.7, 39.0, 38.5, 37.5, 36.1, 28.6, 27.6, 25.9 ppm.

Linker 21

Compound **30** (625 mg, 1.39 mmol, 1.0 eq) was dissolved in MeOH (10 mL). Pd/C (70 mg, 10 % on active charcoal) was added and the suspension was stirred for 18 h at rt under hydrogen. Thereafter, the suspension was filtrated over celite and the solvent was evaporated. Compound **21** was obtained as a colorless oil (420 mg, 1.33 mmol, 96 %). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.86 (t, *J* = 5.2 Hz, 1H), 6.77 (t, *J* = 5.2 Hz, 1H), 3.04 (q, *J* = 6.8 Hz, 2H), 2.91 (q, *J* = 6.7 Hz, 2H), 2.72 (t, *J* = 6.6 Hz, 2H), 2.26 – 2.20 (m, 4H), 2.14 (t, *J* = 6.6 Hz, 2H), 2.08 (s, 3H), 1.53 – 1.45 (m, 4H), 1.36 (s, 9H) ppm (the NH_2 signal could not be observed due to a fast exchange with water). ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 171.2, 155.6, 77.3, 54.8, 54.8, 41.7, 39.0, 38.3, 36.7, 28.3, 27.2, 26.9 ppm (an alkyl signal was covered by the solvent peak). MS (ESI): *m*/*z* calcd. for $C_{15}H_{33}N_4O_3$ $([M+H])^+$ = 317.3; found 317.3.

Solid phase synthesis of polyamide 39



Scheme S3. a) H_2, Pd/C, Boc_2O, MeOH, 82 %; b) NaOH, MeOH/H_2O, 81 %; c) **7**, H_2, Pd/C, EtOAc, then **33**, HOBt, DIC, DIPEA, DMF, 77 %; d) **34**, H_2, Pd/C, EtOAc, then Boc-GABA-OH, HOBt, DIC, DIPEA, DMF, 53 %; e) KOH, MeOH/H_2O, 76 %; f) H_2, Pd/C, EtOAc, then **5**, HOBt, DIC, DIPEA, DMF, 89 %; g) NaOH, MeOH/H_2O, 91 %.

Boc-Py-Py-OMe 31 (RN: 126092-97-5)

Compound **15** (1.74 g, 5.68 mmol, 1.0 eq), Boc_2O (2.48 g, 11.4 mmol, 2.0 eq) and Pd/C (180 mg, 10 % on activated charcoal) were suspended in MeOH (10 mL). The mixture was stirred for 18 h at 45 °C and 40 bar H_2-pressure. The catalyst was removed by filtration through celite. The solvent was evaporated to obtain **31** as a colorless foam (1,75 g, 4.65 mmol, 82 %). ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 9.85 (s, 1H), 9.10 (s, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.83 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 160.8, 158.4, 152.9, 123.0, 122.6, 122.4, 120.7, 118.5, 117.2, 108.4, 103.8, 78.3, 51.0, 36.2, 36.0, 28.2 ppm. MS (ESI): *m*/*z* calcd. for $C_{18}H_{23}N_4O_5$ ($[M-H]^-$): 375.2; found 375.2.

Boc-Py-Py-OH 32 (RN: 126092-98-6)

Compound **31** (500 mg, 1.33 mmol, 1.0 eq) was dissolved in MeOH (3 mL) and 2 M NaOH (10 mL, 20 mmol, 15.0 eq) was added. The mixture was stirred for 4 h at rt and subsequently acidified with 1 M HCl. Afterwards the mixture was extracted with EtOAc. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated to obtain **32** as a brown solid (389 mg, 1.07 mmol, 81 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 12.13 (s *br*, 1H), 9.81 (s, 1H), 9.09 (s, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 6.88 (s, 1H), 6.85 – 6.78 (m, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 1.45 (s, 9H) ppm (the sample contained some EtOAc and the yield was corrected accordingly). ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 162.0, 158.4, 152.9, 122.7, 122.7, 122.4, 120.3, 119.5, 117.1, 108.4, 103.8, 78.3, 36.1, 36.1, 28.2 ppm. MS (ESI): *m*/*z* calcd. for $C_{17}H_{23}N_4O_5$ ($[M+H]^+$): 363.2; found 363.2. HRMS (MALDI): *m*/*z* calcd. for $C_{17}H_{22}N_4NaO_5$ ($[M+Na]^+$): 385.14824; found 385.14664.

1-Methyl-4-nitro-1*H*-pyrrole-2-carboxylic acid (O_2N-Py-OH) 33 (RN: 13138-78-8)

Compound **8** (2.52 g, 9.3 mmol, 1.0 eq) was dissolved in aqueous KOH (23 mL, 46 mmol, 5.0 eq) and stirred for 2 h at rt. Subsequently, the mixture was acidified with 1 M HCl. The precipitate was filtered, washed with EtOAc and dried in vacuum. **33** was obtained as a colorless solid (740 mg, 2.41 mmol, 77 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 8.05 (d, J = 2.0 Hz, 1H), 7.07 (d, J = 2.1 Hz, 1H), 3.92 (s, 3H) ppm (the COOH-signal was not observable due to a fast exchange). ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 161.9, 133.7, 127.5, 109.4, 39.5, 37.3 ppm. MS (ESI): m/z calcd. for $C_6H_5N_2O_4$ ($[M-H]^-$): 169.0; found 168.9.

O_2N-Py-Im-OMe 34 (RN: 169770-26-7)

Compound **33** (590 mg, 3.47 mol, 1.1 eq), HOBt (530 mg, 3.47 mmol, 1.1 eq, 12 % H_2O) and DIC (1.1 mL, 6.9 mmol, 2.2 eq) were dissolved in dry DMF (5 mL) and stirred for 29 h at rt.

Compound **7** (580 mg, 3.20 mmol, 1 eq) was dissolved in EtOAc (10 mL) and Pd/C (70 mg, 10 % on activated charcoal) was added. The suspension was stirred for 23 h at rt under hydrogen. Subsequently the catalyst was removed by filtration through celite and the solvent was evaporated. The residue was redissoved in dry DMF (4 mL) and the above mentioned mixture as well as DIPEA (1.1 mL, 6.3 mmol, 2 eq) was added. The resulting solution was heated to 60 °C and stirred for 3 h, 16 h at rt and further 3 h at 60 °C. Afterwards the solution was poured on ice water (50 mL) and the precipitate was collected. The crude product was purified by column chromatography and **34** was obtained as a colorless solid (740 mg, 2.41 mmol, 77 %). R_f = 0.45 (cyclohexane/EtOAc 1:3). ^{1}H-NMR (250 MHz, DMSO-d_6) δ = 11.13 (s, 1H), 8.19 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 2.0 Hz, 1H), 7.68 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.82 (s, 3H) ppm.

Boc-γ-Py-Im-OMe 35

Boc-GABA-OH (538 mg, 2.65 mmol, 1.1 eq), HOBt (407 mg, 2.65 mmol, 1.1 eq, 12 % H_2O) and DIC (820 µL, 5.30 mmol, 2.2 eq) were dissolved in dry DMF (10 mL) and stirred for 26 h at rt.

Compound **34** (740 mg, 2.40 mmol, 1.0 eq) and Pd/C (70 mg, 10 % on activated charcoal) were suspended in EtOAc (10 mL) and the mixture was stirred in a steel autoclave for 17 h at 40 °C and 40 bar H_2-pressure. Subsequently, the catalyst was removed by filtration through celite and the solvent was evaporated. After that, the above-mentioned solution as well as DIPEA (820 mL, 4.80 mmol, 2.0 eq) were added and the mixture was stirred for 48 h at rt. The resulting suspension was filtered and washed with EtOAc. The filtrate was added to an aqueous solution of $NaHCO_3$ (100 mL, 20 %) and then extracted with EtOAc (3x, 40 mL) and DCM (3x, 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (DCM/MeOH 99:1 to 9:1) to obtain **35** as a colorless solid (586 mg, 1.26 mmol, 53 %). R_f = 0.79 (DCM/MeOH 9:1). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.65 (s, 1H), 9.80 (s, 1H), 7.66 (s, 1H), 7.28 (d, J = 1.8 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.82 (t, J = 5.5 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 2.93 (q, J = 6.7 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.37 (s, 9H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 169.3, 159.0, 158.7, 155.7, 137.9, 130.7, 122.1, 121.6, 119.4, 115.5, 104.8, 77.5, 51.8, 36.4, 35.5, 33.1, 28.3, 25.9 ppm (a signal around 39 ppm is masked by the solvent signal). MS (ESI): m/z calcd. for $C_{21}H_{31}N_6O_6$ ($[M+H]^+$): 463.2; found 463.1. HRMS (MALDI): m/z calcd. for $C_{21}H_{30}N_6NaO_6$ ($[M+Na]^+$): 485.21190; found 485.21173.

Boc-γ-Py-Im-OH 36

Compound **35** (200 mg, 432 µmol, 1 eq) was suspended in a mixture of MeOH/H_2O (1:1, 8 mL) and a 10 M solution of KOH in H_2O (0.2 mL, 2.0 mmol, 4.6 eq) was added. Subsequently, the suspension was stirred for 21.5 h at rt. Afterwards, MeOH was evaporated and the residue was acidified with 1 M HCl.

The resulting precipitate was collected and dried in vacuum. **36** was obtained as a colorless solid (147 mg, 327 µmol, 76 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 10.60 (s, 1H), 9.81 (s, 1H), 7.60 (s, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.83 (t, *J* = 5.4 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 2.93 (q, *J* = 6.7 Hz, 2H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.37 (s, 9H) ppm (COOH signal not observable). ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 169.3, 160.1, 158.7, 155.7, 137.4, 131.7, 122.1, 121.7, 119.3, 115.2, 104.7, 77.5, 36.4, 35.6, 33.1, 28.3, 25.9 ppm (a signal around 39 ppm is masked by the solvent). MS (ESI): *m*/*z* calcd. for $C_{20}H_{29}N_6O_6$ ([M+H]$^+$): 449.2; found 449.3. HRMS (MALDI): *m*/*z* calcd. for $C_{20}H_{28}N_6NaO_6$ ([M+Na]$^+$): 471.19625; found 471.19662.

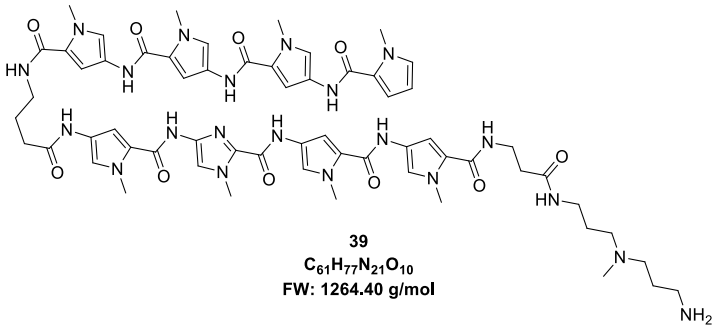
Py-Py-OMe 37 (RN: 295805-46-8)

Compound **10** (500 mg, 2.70 mmol, 1.0 eq) and Pd/C (50 mg, 10 % on activated charcoal) were suspended in EtOAc (10 mL) and stirred in a H_2-atmosphere for overnight. The suspension was filtered through celite to remove the catalyst, the solvent was evaporated, and the residue dried in vacuum.
Compound **5** (400 mg, 3.00 mmol, 1.1 eq), HOBt (460 mg, 3.00 mmol, 1.1 eq, 88 %) were dissolved in dry DMF (5 mL) and DIC (930 µL, 6.00 mmol, 2.2 eq) was added. The resulting mixture was stirred overnight and afterwards added to the freshly prepared amine. DIPEA (460 µL, 5.4 mmol, 2 eq) was added and the solution was heated to 60 °C for 5 h. Afterwards the solution was stirred at rt overnight. The reaction mixture was poured in H_2O (20 mL) and was extracted with EtOAc. The combined organic layers were washed with a conc. $NaHCO_3$ solution, H_2O and brine and dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography (cyclohexane/EtOAc 3:1 to 1:1). Yield: 630 mg, 2.40 mmol, 89 %. R_f = 0.58 (cyclohexane/EtOAc 3:1). ^{1}H-NMR (250 MHz, DMSO-d_6) δ = 9.81 (s, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.90 – 6.86 (m, 2H), 6.06 (dd, *J* = 3.9, 2.5 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H) ppm.

Py-Py-OH 38 (RN: 268727-24-8)

Compound **37** (630 mg, 2.4 mmol, 1.0 eq) was suspended in MeOH (8 mL) and a 1 M solution of NaOH in H_2O (15 mL, 15 mmol, 6.3 eq) was added. The mixture was heated to reflux for 2 h and was stirred for further 18 h at rt. Afterwards the solution was extracted with EtOAc and the aqueous layer was acidified with 2 M HCl. The resulting solution was extracted with EtOAc; the organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated to obtain **38** as a yellow solid (580 mg, 2.34 mmol, 91 %). ^{1}H-NMR (500 MHz, DMSO-d_6) δ = 12.15 (s *br*, 1H), 9.78 (s, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.89 (dd, *J* = 3.9, 1.6 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 6.05 (dd, *J* = 3.7, 2.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H) ppm. ^{13}C-NMR (126 MHz, DMSO-d_6) δ = 162.0, 158.6, 128.2, 125.3, 122.6, 120.3, 119.5, 112.6, 108.3, 106.7, 36.2, 36.2 ppm. MS (ESI): *m*/*z* calcd. for $C_{12}H_{14}N_3O_3$ ([M+H]$^+$): 248.1; found 248.2.

Py-Py-Py-Py-γ-Py-Im-Py-Py-β-linker-NH_2 39



39
$C_{61}H_{77}N_{21}O_{10}$
FW: 1264.40 g/mol

Compound **39** was synthesized on solid support in a 5 mL springe.[2] Boc-*β*-Ala-Pam-resin (101 mg, 0.5 mmol/g) was used. The resin was equilibrated in DMF for 30 min. Afterwards the Boc group was removed with a mixture of TFA/H_2O/phenol (92.5/2.5/5; two times, 1 mL, 5 min). After washing with DMF (4x 2 mL), the resin was equilibrated in THF (1 mL, 2 min). Meanwhile, the Boc-protected amino acids (**32**, **36** and **38**, 200 µmol, 4 eq) and triphosgene (66 µmol, 1.3 eq) were dissolved in THF (1 mL). Collidine (606 µmol, 12 eq) was added and the mixture was activated for 1 min. Then, DIPEA (404 µmol, 8 eq) was added and the mixture was transferred to the deprotected resin. The solution was shaken for 1.5 h and after that, the reaction mixture was removed. After washing with DMF (4x 2 mL), unreacted material was capped (Ac_2O (100 µl) and DIPEA (175µl) in 1 mL DMF, 5 min) and the resin was washed with DMF (4x 2 mL). This procedure was repeated until the full peptide chain was assembled on the PAM-resin. Afterwards the resin was dried in vacuum. To liberate the peptide, the resin was incubated with a large excess of amine **28** (1 mL) for 20 h at 55 °C. The mixture was diluted with MeOH (200 µL) and the polyamide was precipitated by adding Et_2O (1.8 mL) and cooling to -20 °C. The crude polyamide was purified by semi preparative HPLC and freeze dried to yield **39** (6 mg, ~10 %). The structure was confirmed by MALDI-MS: calcd. for $C_{61}H_{77}N_{21}O_{10}$ ($[M^{\bullet}]^+$): 1263.6157; found 1263.2139.

Synthesis of adaptors 1 and 2 [3]

The DNA part including the 5' amino linker was assembled from fast deprotection amidites on a standard support. 10 mg of the support (~250 nmol) were suspended in DCM (1 mL) for 30 min. The MMT group was then removed by incubation with 3 % trichloroacetic acid in dry DCM (0.5 mL) for 5 min. The support was washed with DCM (0.5 mL) and the acid treatment was repeated. Afterwards, the support was washed five times with acetonitrile (0.5 mL). Then a solution of DIPEA (1.7 µL, 10 µmol) and 1,6-diisocyanatohexane (8.42 µL, 48 µmol) in 1 mL of dry acetonitrile was added. After incubation for 18 h at room temperature, the support was washed five times with acetonitrile. Subsequently, a solution of the polyamide (e.g. **24**; 2.5 µmol, 10 eq.) in dry MeOH (150 µL) and DIPEA (10 – 25 µL) in dry acetonitrile (750 µL) were added. The mixture was mildly shaken for 24 h at room temperature and afterwards washed five times with acetonitrile (0.5 mL). To detach the product, the solid support was incubated with aqueous ammonia (32 %, 0.5 mL) for 30 min at room temperature. This procedure was repeated three times and the combined ammonia solutions were heated to 55 °C for 5 h. After removal of the solvent in a vacuum centrifuge, the dry residue was dissolved in a small volume of saturated aqueous urea solution, mixed with some 2x loading buffer (8 M urea, 20 mM EDTA, 0.2 % orange G), heated to 90 °C for 5 – 10 min and then purified by electrophoresis in a 16 % denaturing polyacrylamide gel (7 M urea, 1x TBE buffer, acrylamide : bisacrylamide 19 : 1). The electrophoresis was run at 230 – 250 V in 0.5x TBE buffer until the dye had moved to the mid of the gel. Bands containing the pure adaptors **1** or **2** were visualized by UV shadowing, excised, and extracted from the gel matrix over night with elution buffer (500 mM NaOAc pH 7.0, 2 mM EDTA, 0.1 % SDS). Afterwards, the solution was passed through a centrifugal filter (VWR, 516-0235, 13000x g), mixed with a threefold volume of EtOH and kept overnight at -20 °C. The precipitated product was isolated by centrifugation, dissolved in water, and desalted by gel filtration (NAP-10). Finally, the product was identified by mass spectrometry and the concentration was determined via UV absorption (Nanodrop 200c).

Adaptor 1:

Py-Im-Py-Py-γ-Py-Py-Py-Py-β-DMDPA-C_6-C_6-$^{5'}$TTTTTGGCGAGGAGGGGCGTGGCCGGC

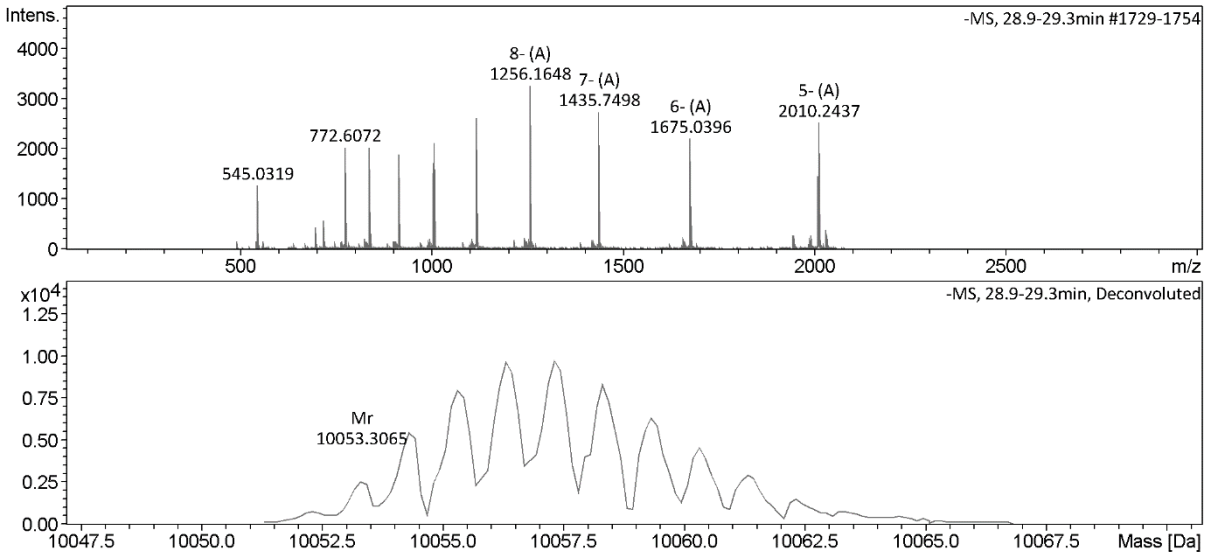


Figure S2. Mass spectrum of adaptor **1** (ESI – TOF; Bruker micrOTOF-Q II with Agilent 1200 Series HPLC and MultoKrom 5-C18 column; a gradient from 95% A (400mM HFIP and 16.3mM TEA in H_2O) and 5% B (MeOH) to 100% B was used.). Top: Original data. Bottom: Deconvolution. *m*/*z* calcd. for $C_{340}H_{434}N_{131}O_{179}P_{27}$ ($[M]^-$):10051.2; found 10053.3.

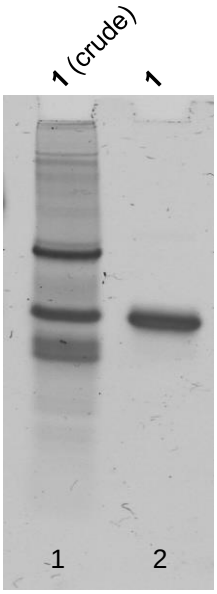


Figure S3. Purity check of adaptor **1**. Lane 1: crude product; lane 2: adaptor **1** after preparative gel electrophoresis (conditions see page S16).

Adaptor 2:

Py-Py-Py-Py-γ-Py-Im-Py-Py-β-DMDPA-C_6-C_6-$^{5'}$TTTTTGGCGAGGAGGGGCGTGGCCGGC

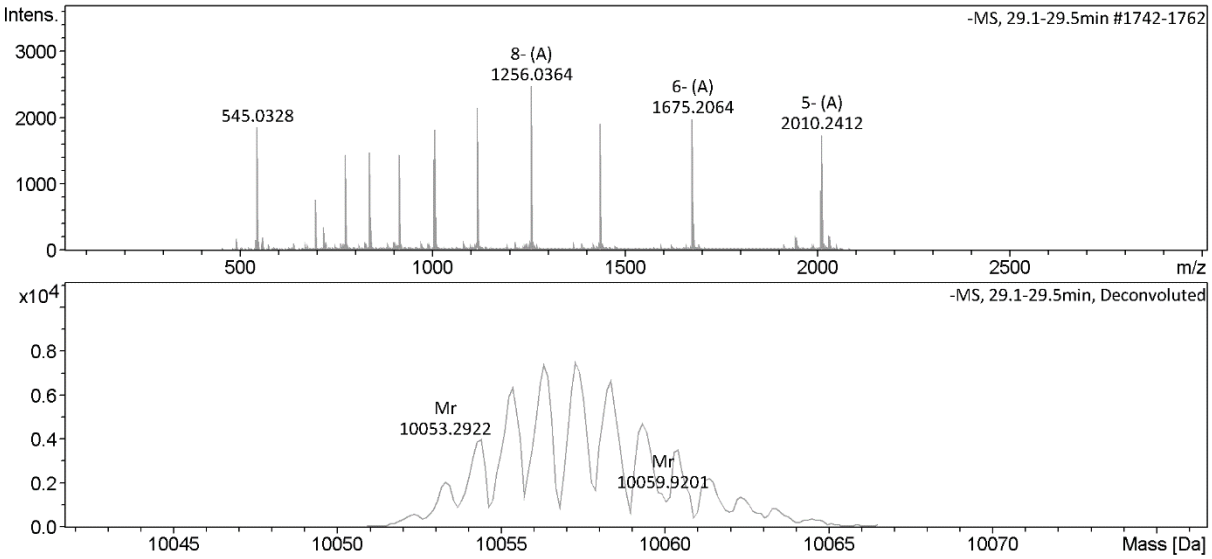


Figure S4. Mass spectrum of adaptor **2** (ESI – TOF; Bruker micrOTOF-Q II with Agilent 1200 Series HPLC and MultoKrom 5-C18 column; a gradient from 95% A (400mM HFIP and 16.3mM TEA in H_2O) and 5% B (MeOH) to 100% B was used.). Top: Original data. Bottom: Deconvolution. *m*/*z* calcd. for $C_{340}H_{434}N_{131}O_{179}P_{27}$ ($[M]^-$):10051.2; found 10053.3.

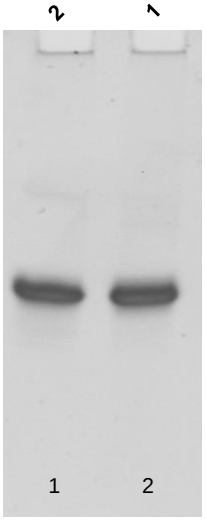


Figure S5. Purity check of adaptors after gel electrophoresis (conditions see page S16):
Lane 1: adaptor **2**; Lane 2: adaptor **1**.

Analytical dPAGE used for the purity check of adaptors 1 and 2

The oligonucleotides (1 µM) were dissolved in a loading buffer (4 M urea, 10 mM EDTA, 0.1 % orange G) and heated to 90 °C for 5 to 10 min. Analytical dPAGE (16 % (7 M urea, 1x TBE-buffer; acrylamide:bisacrylamide 19:1) was performed at 200 – 220 V using an 0.5 x Tris-borate-EDTA (TBE)-running buffer. Subsequently the gel was stained with SYBR Gold (Thermo Fisher Scientific; 1:10000 in 10 mM Tris-HCl pH 7.5, 1 mM EDTA).

Isolation of a byproduct

From the crude reaction mixtures containing adaptors **1** or **2**, a byproduct with a molecular mass of 17414 could be isolated. It is formed when the bifunctional 1,6-diisocyanatohexane connects the amino linkers of two DNA strands:

$^{3'}$CGGCCGGTGCGGGGAGGAGCGGTTTTT$^{5'}$-C_6-C_6-C_6-$^{5'}$TTTTTGGCGAGGAGGGGCGTGGCCGGC$^{3'}$

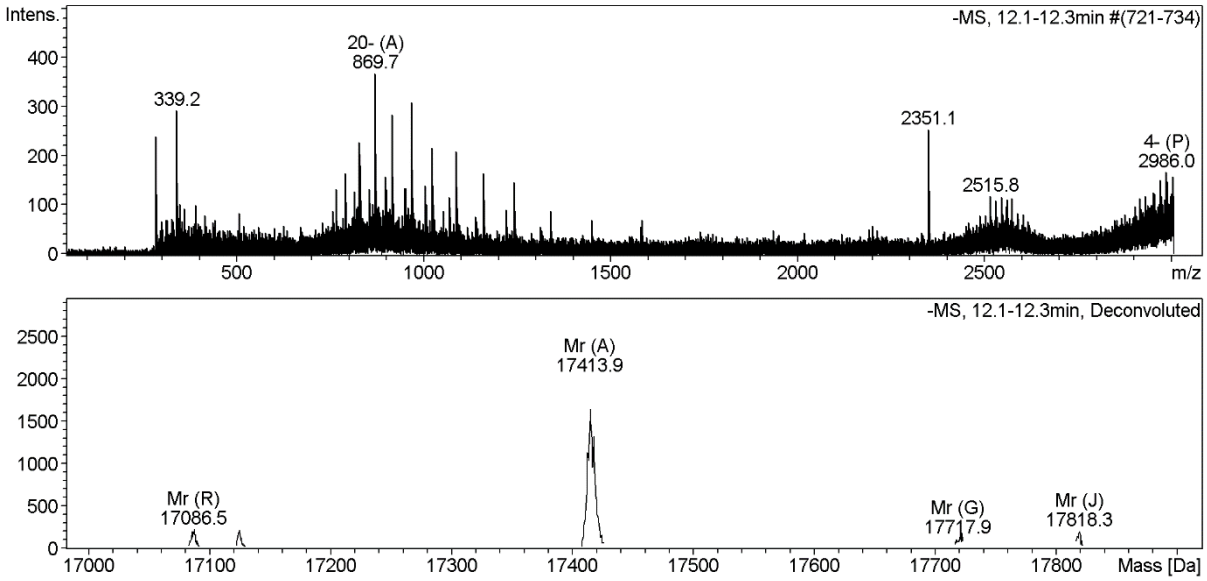


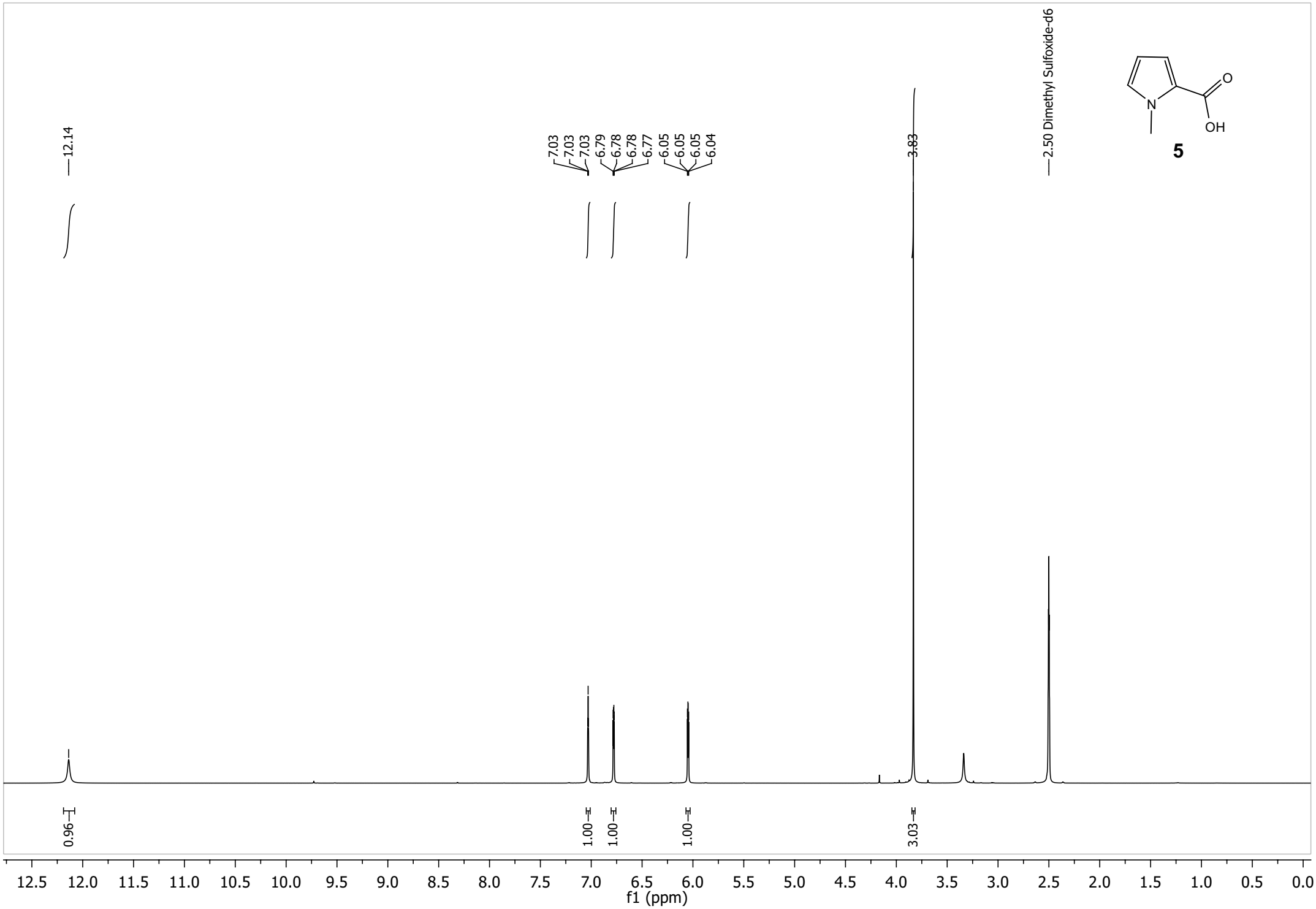
Figure S6. Mass spectrum of a byproduct containing two DNA strands (ESI – TOF; Bruker micrOTOF-Q II with Agilent 1200 Series HPLC and MultoKrom 5-C18 column; a gradient from A (5 mM TEA in H_2O) to 100% B (MeOH) was used). Top: Original data. Bottom: Deconvolution. *m/z* calcd. for $C_{550}H_{702}N_{218}O_{336}P_{54}$ ($[M]^-$):17407.0; found 17413.9

References

[1] M. Bialer, B. Yagen, R. Mechoulam, *Tetrahedron* **1978**, *34*, 2389–2391.

[2] I. Singh, C. Wendeln, A. W. Clark, J. M. Cooper, B. J. Ravoo, G. A. Burley, *J. Am. Chem. Soc.* **2013**, *135*, 3449–3457.

[3] T. Kubo, M. Morikawa, H. Ohba, M. Fujii, *Org. Lett.* **2003**, *5*, 2623–2626.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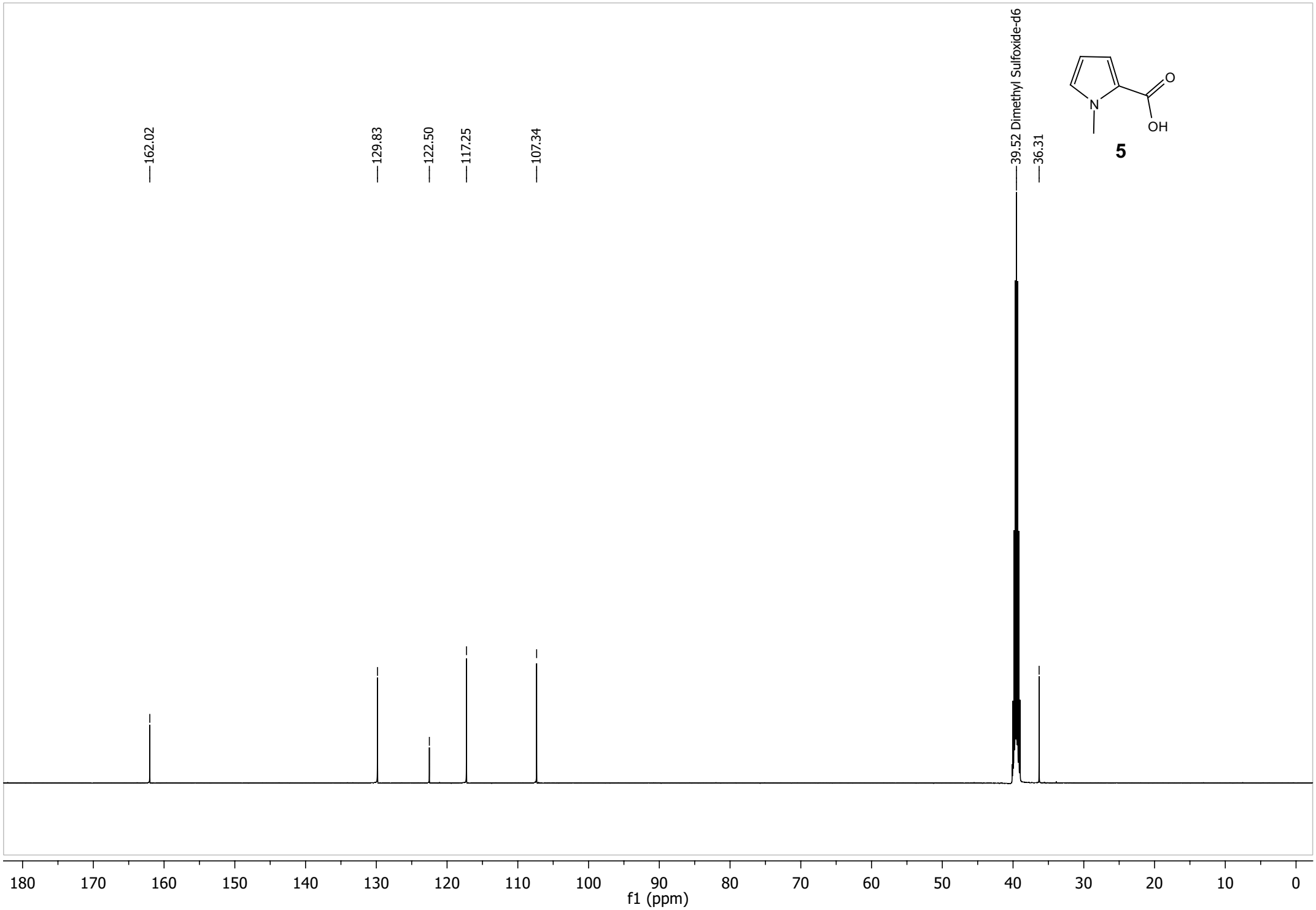
7.03
7.03
6.79
6.78
6.78
6.77
6.05
6.05
6.05
6.04
3.83
2.50 Dimethyl Sulfoxide-d6
O
N
OH
5
0.96
1.00
1.00
1.00
3.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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117.25
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O
N
OH
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30
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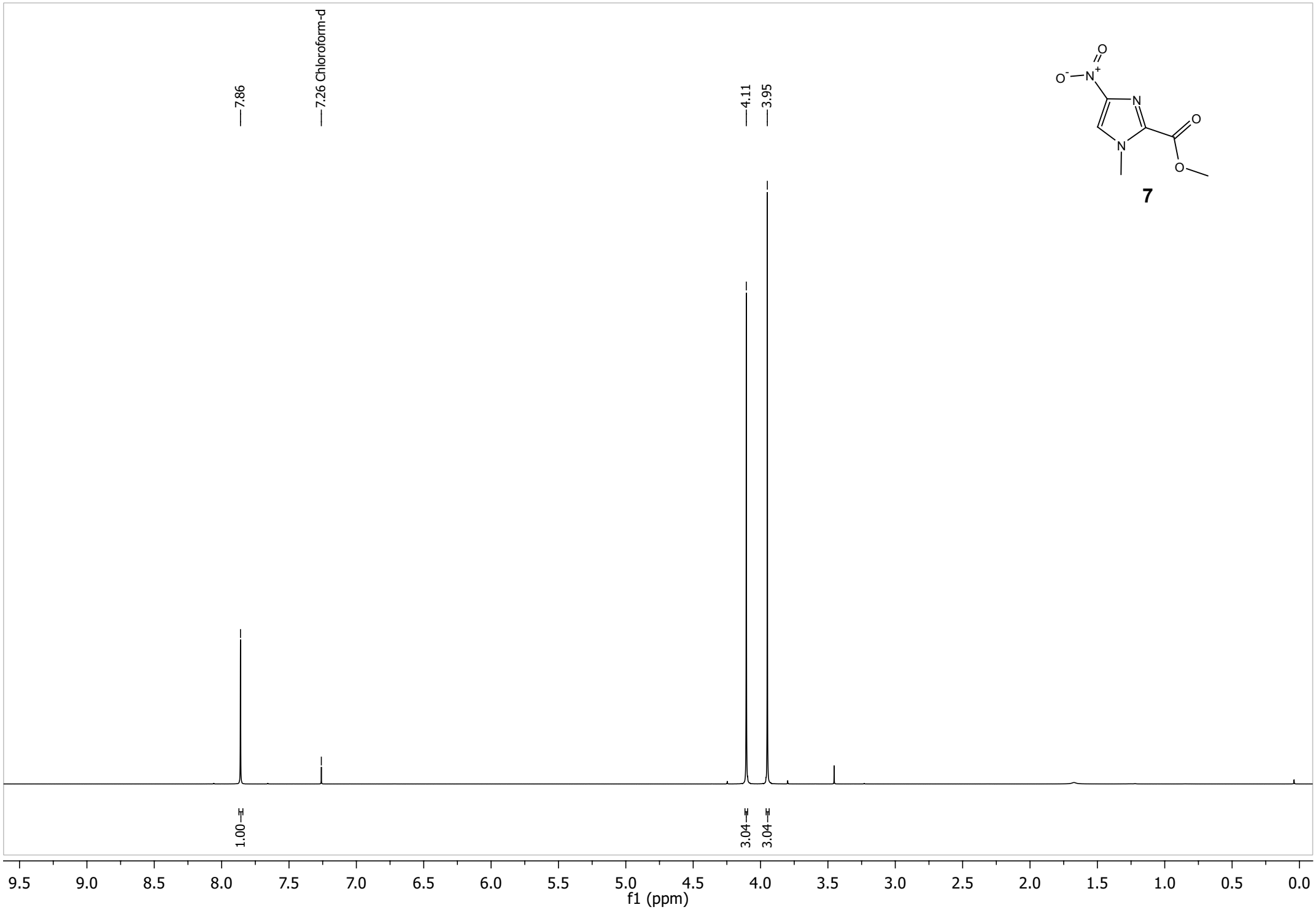
10
0
f1 (ppm)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9.0
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7.0
6.5
6.0
5.5
5.0
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1.0
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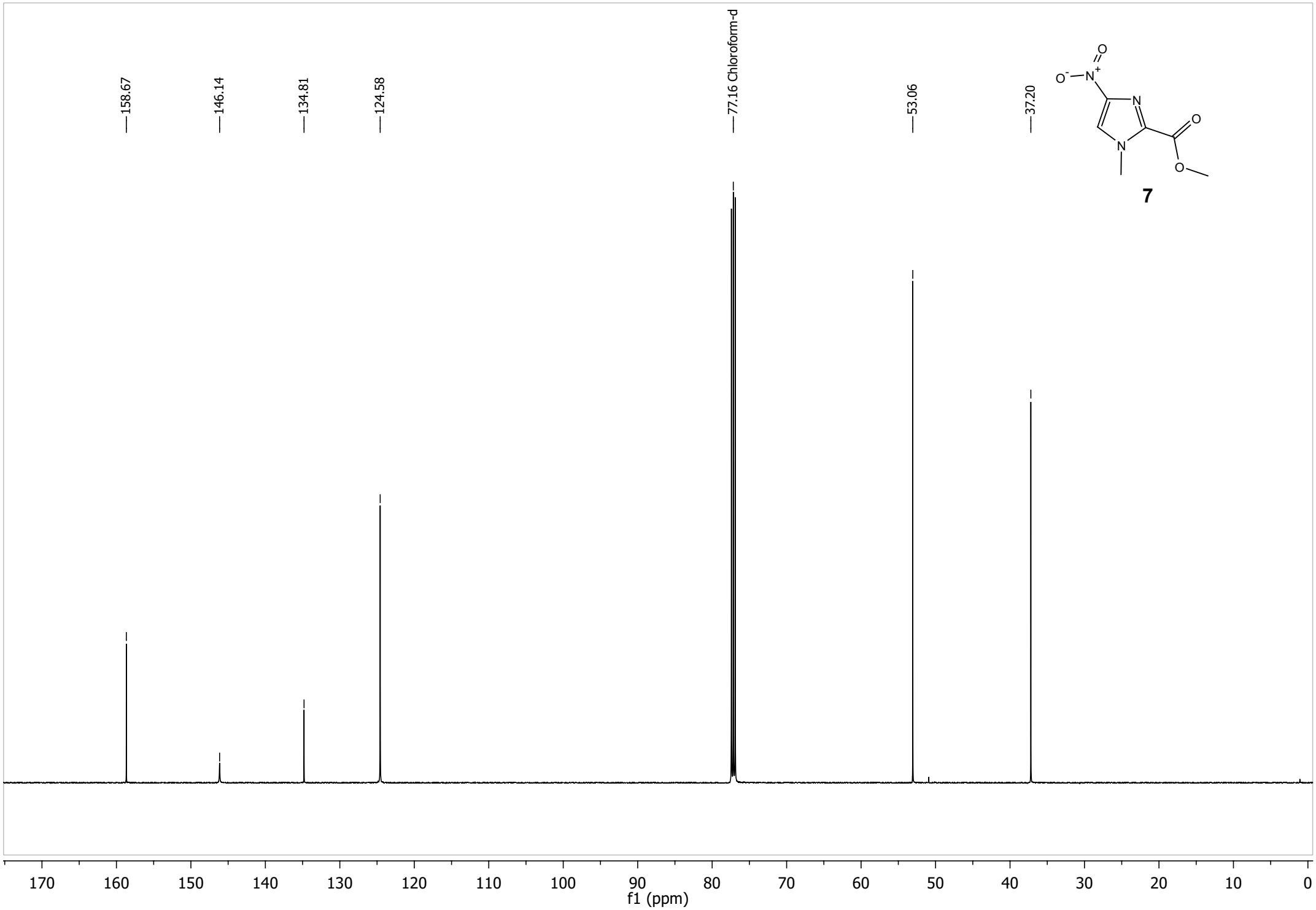
0.0
f1 (ppm)
7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77.16 Chloroform-d
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37.20
7
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10
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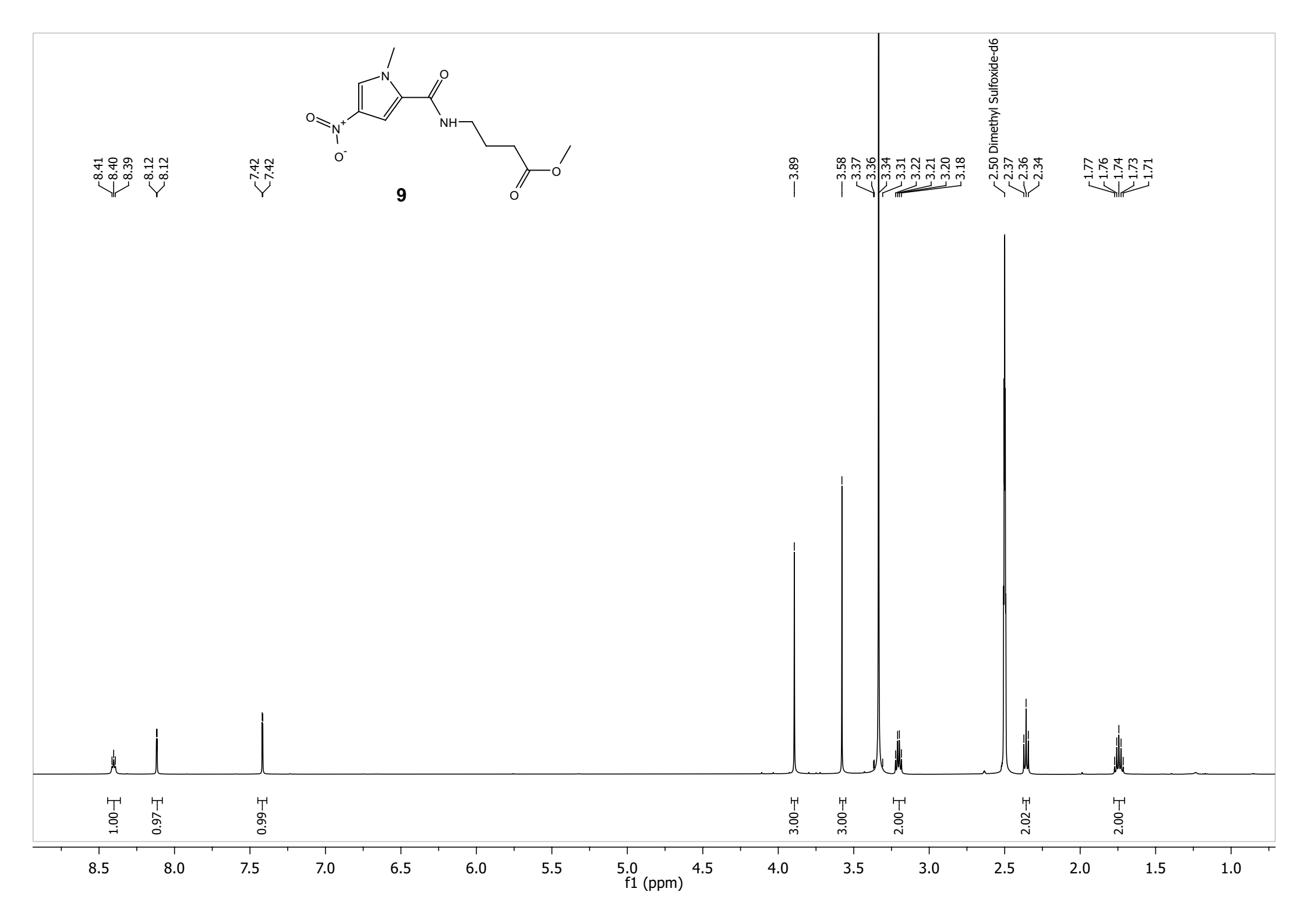
f1 (ppm)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3.37
3.36
3.34
3.31
3.22
3.21
3.20
3.18
2.50 Dimethyl Sulfoxide-d6
2.37
2.36
2.34
1.77
1.76
1.74
1.73
1.71
1.00
0.97
0.99
3.00
3.00
2.00
2.02
2.00
8.5
8.0
7.5
7.0
6.5
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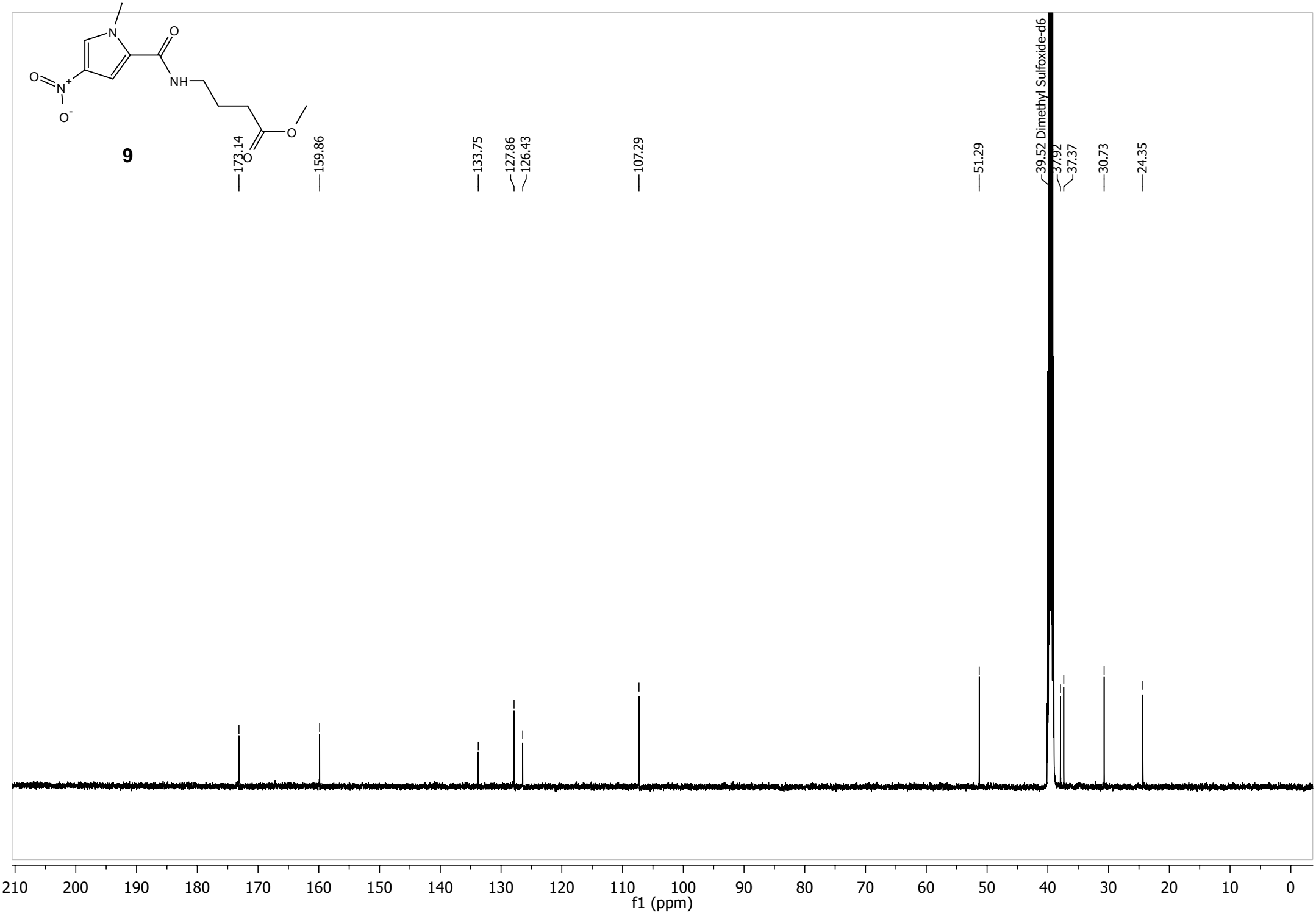
1.0
f1 (ppm)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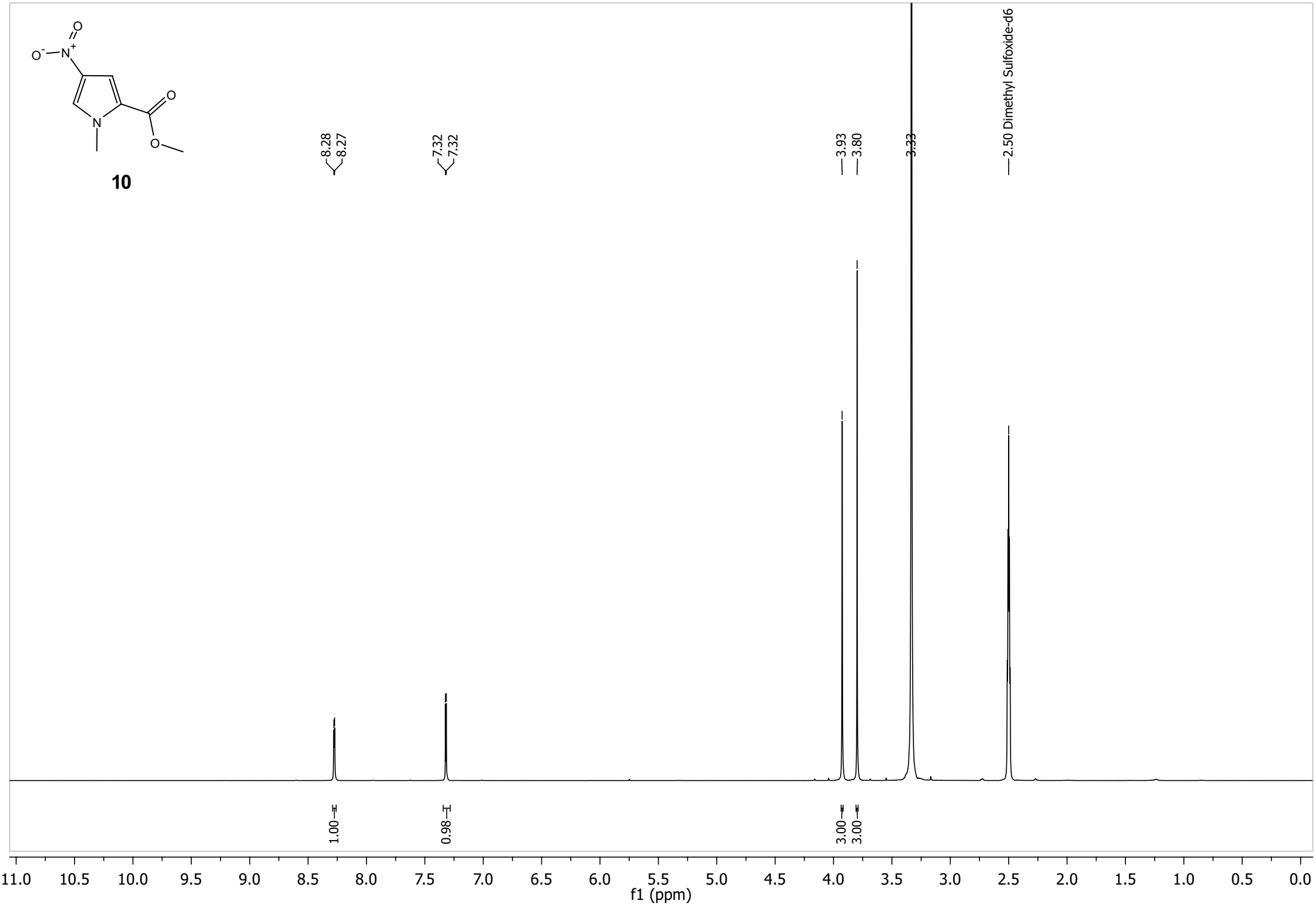
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3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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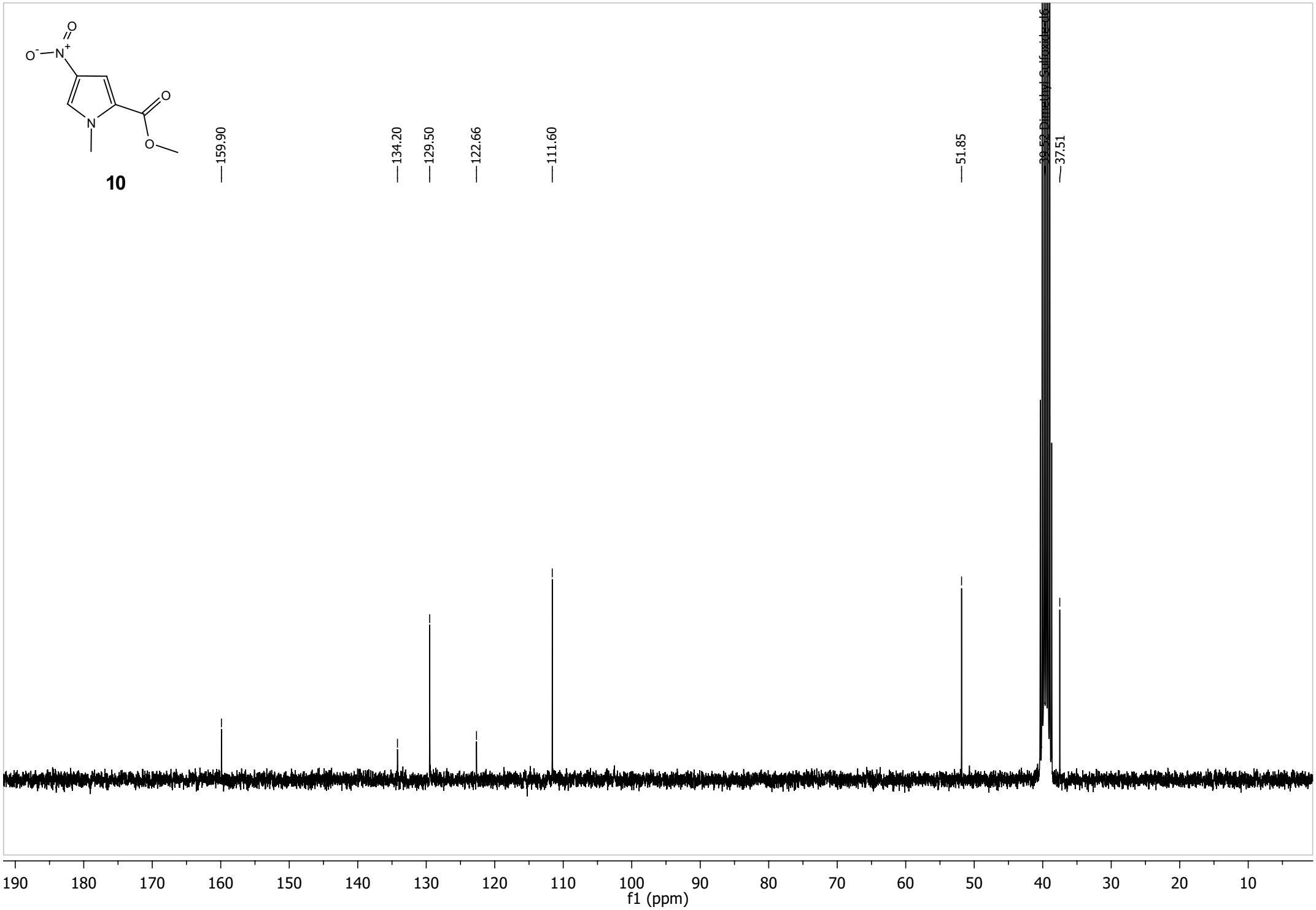
f1 (ppm)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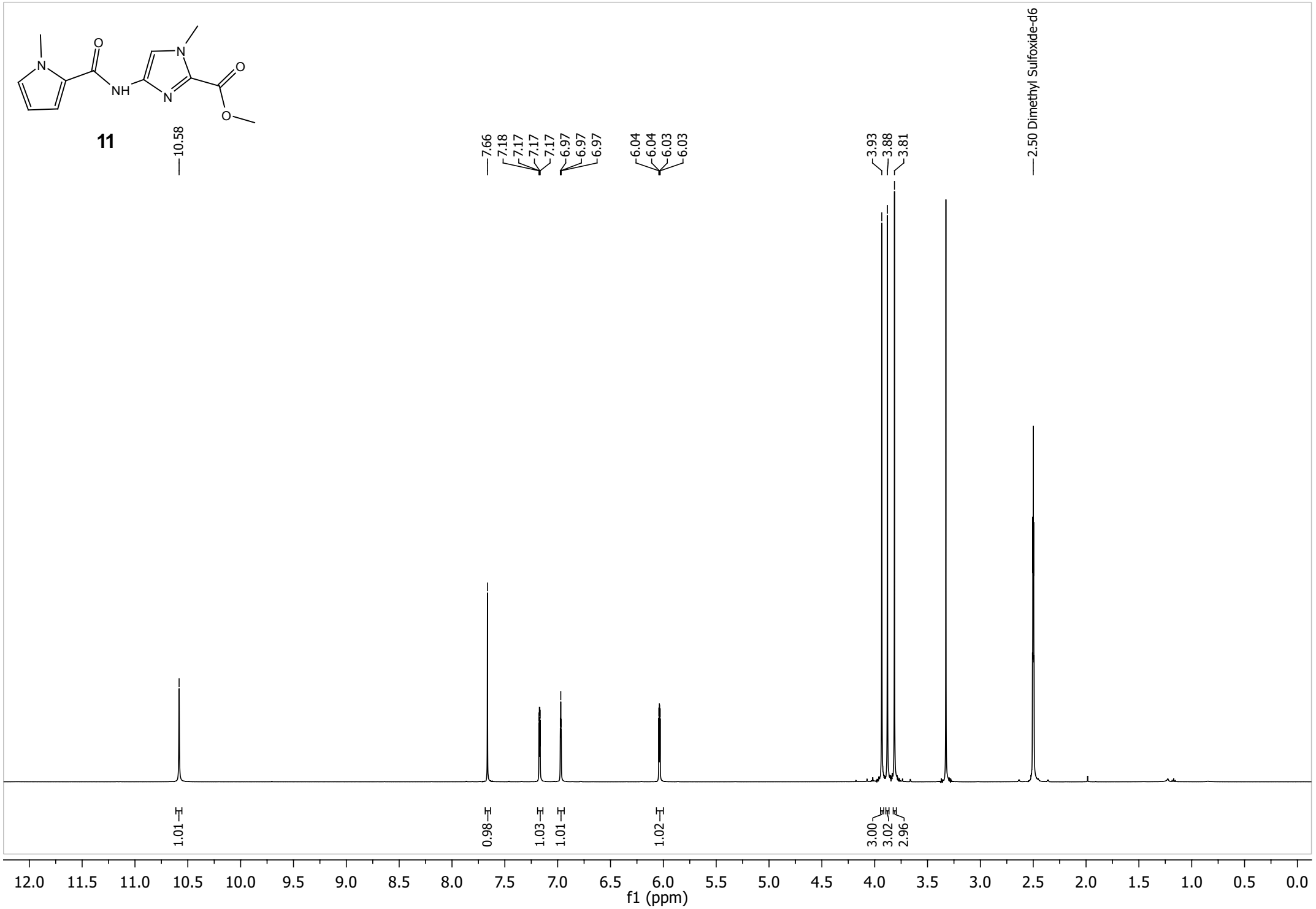
30
20
10
f1 (ppm)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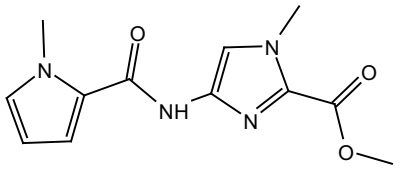
7.17
7.17
6.97
6.97
6.97
6.04
6.04
6.03
6.03
3.93
3.88
3.81
2.50 Dimethyl Sulfoxide-d6
1.01
0.98
1.03
1.01
1.02
3.00
3.02
2.96
f1 (ppm)

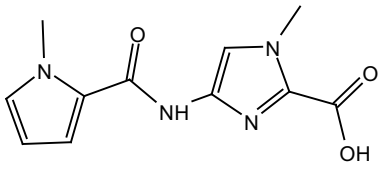


11

158.93
158.70
137.90
130.68
128.94
124.39
115.25
114.01
106.98
51.73
39.52 Dimethyl Sulfoxide-d6
36.48
35.41

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)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N
NH
N
N
O
OH

12

10.55
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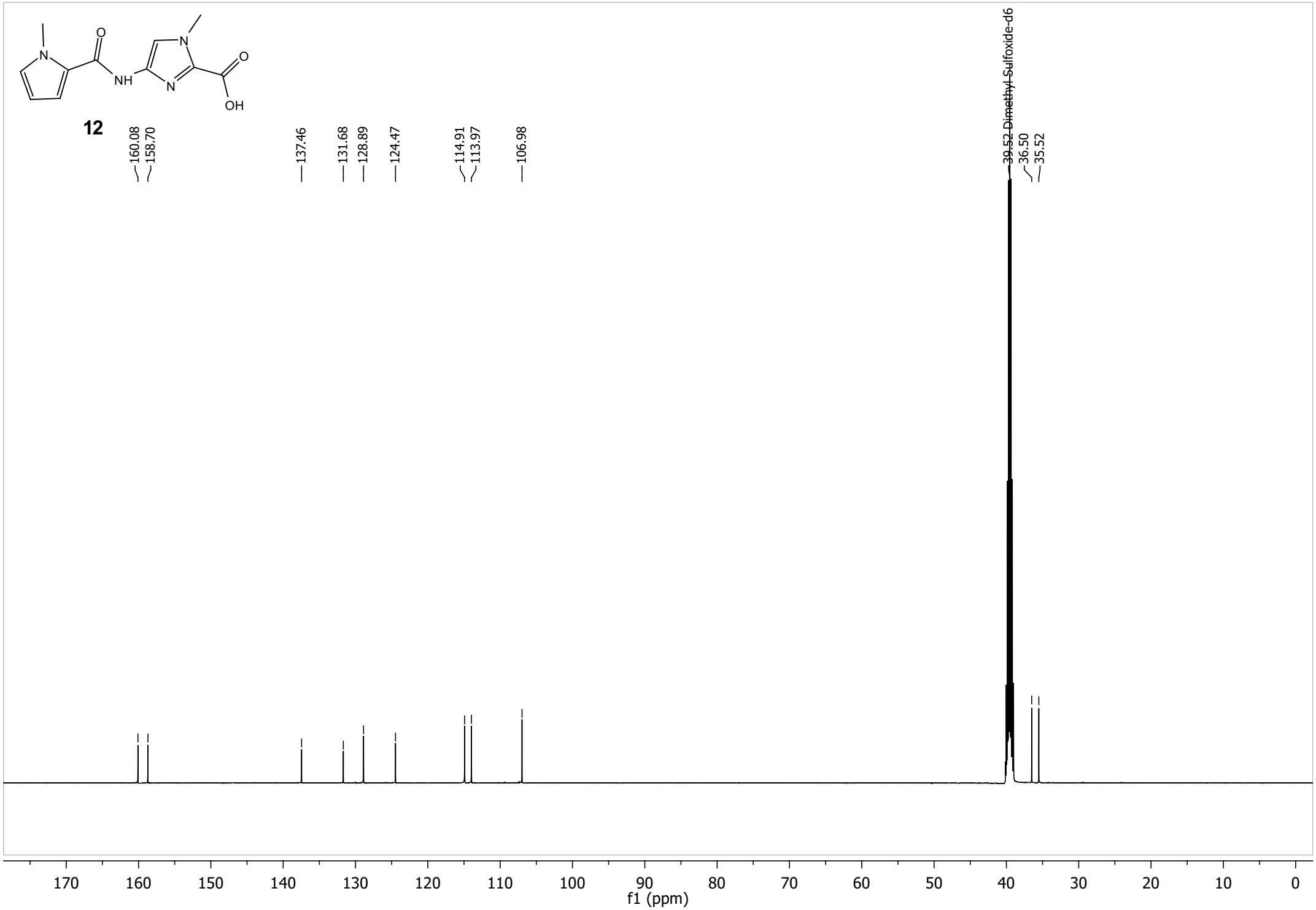
7.16
7.16
6.97
6.97
6.96
6.04
6.04
6.03
6.03
3.92
3.88
2.50 Dimethyl Sulfoxide-d6
1.00
1.00
1.00
1.00
1.00
3.01
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


12
160.08
158.70
137.46
131.68
128.89
124.47
114.91
113.97
106.98
39.52 Dimethyl Sulfoxide-d6
36.50
35.52
170
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140
130
120
110
100
90
80
70
60
50
40
30
20
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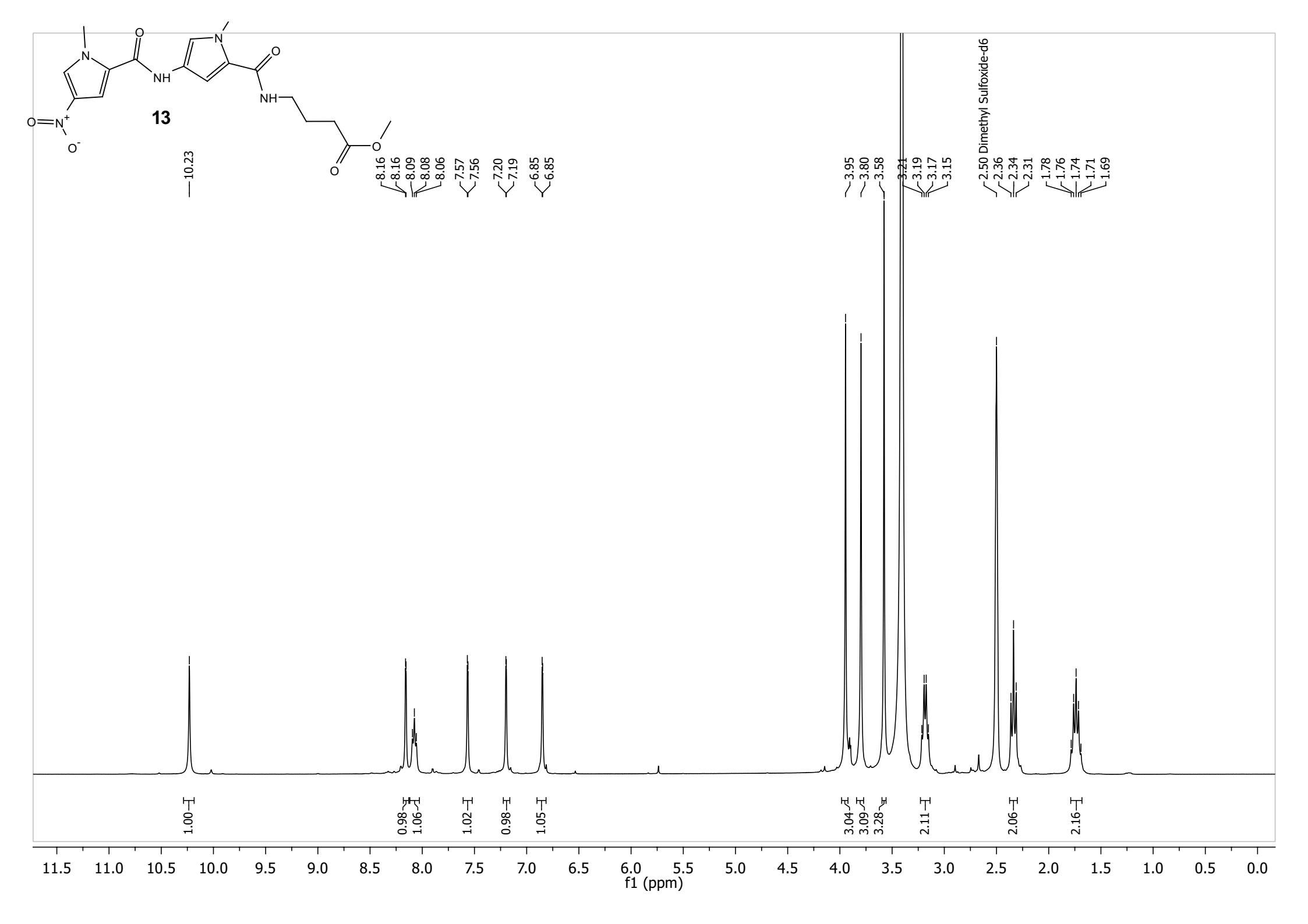
0
f1 (ppm)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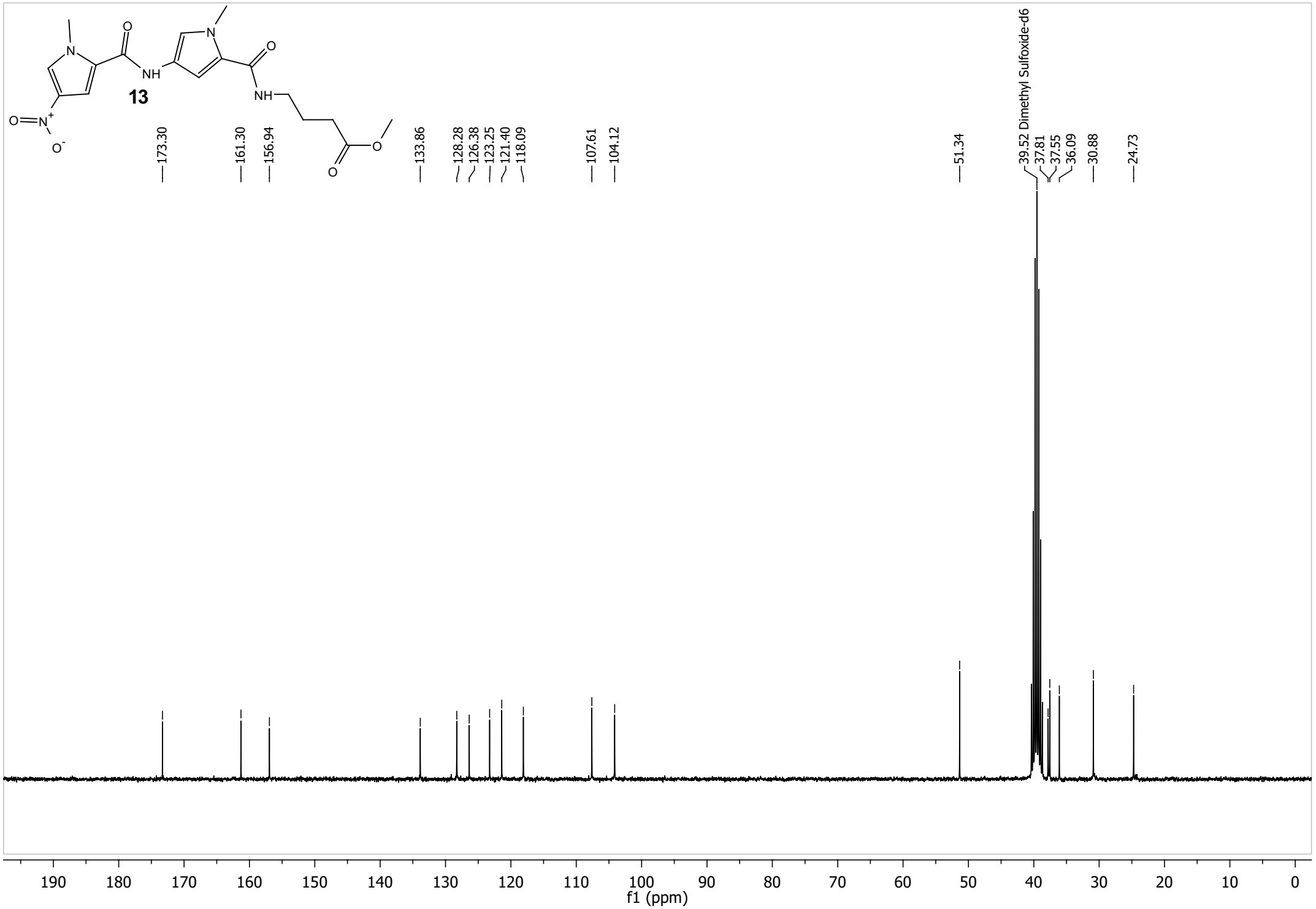
8.16
8.09
8.08
8.06
7.57
7.56
7.20
7.19
6.85
6.85
3.95
3.80
3.58
3.21
3.19
3.17
3.15
2.50 Dimethyl Sulfoxide-d6
2.36
2.34
2.31
1.78
1.76
1.74
1.71
1.69
1.00
0.98
1.06
1.02
0.98
1.05
3.04
3.09
3.28
2.11
2.06
2.16
f1 (ppm)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156.94
133.86
128.28
126.38
123.25
121.40
118.09
107.61
104.12
51.34
39.52 Dimethyl Sulfoxide-d6
37.81
37.55
36.09
30.88
24.73
190
180
170
160
150
140
130
120
110
100
90
80
70
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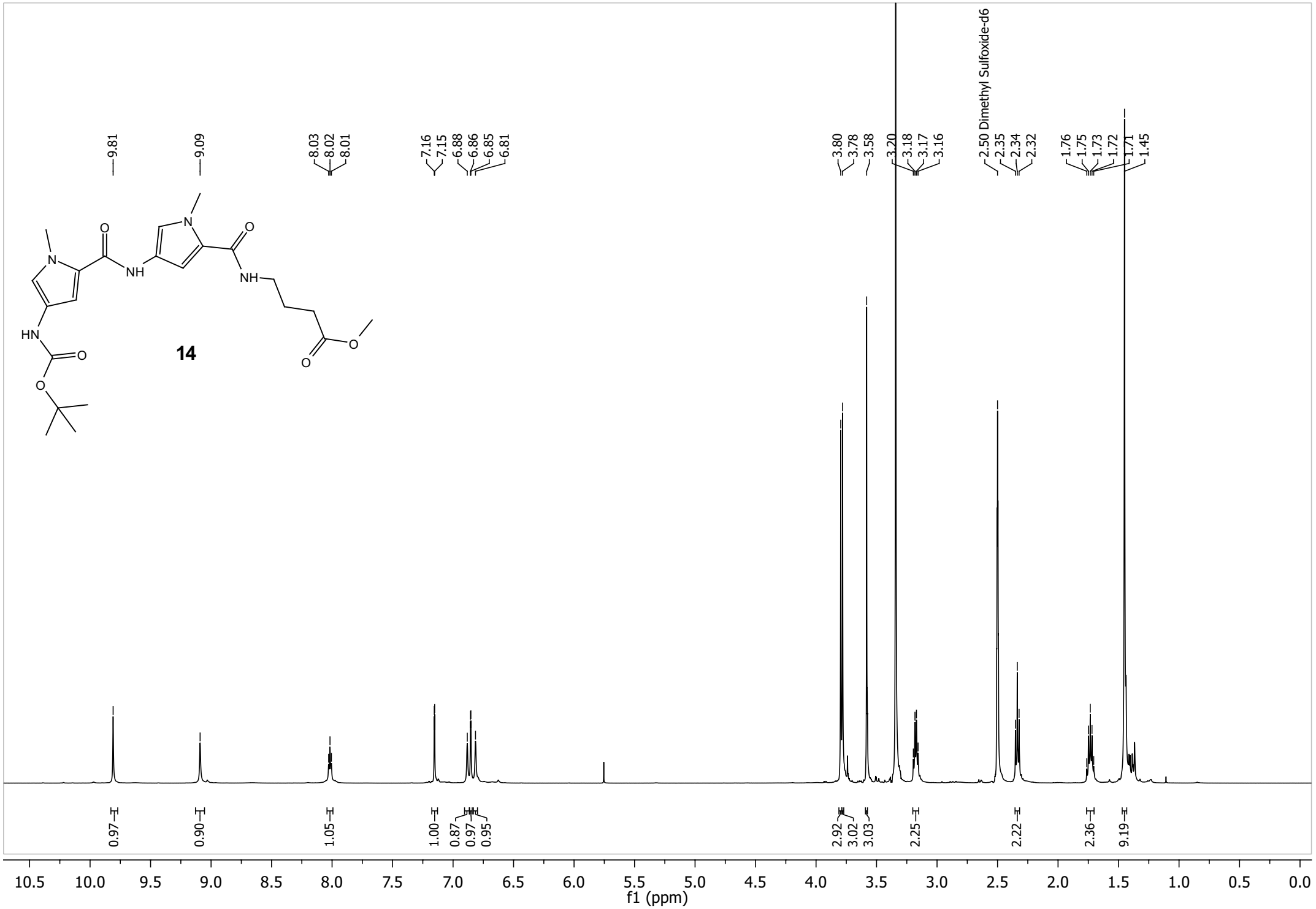
50
40
30
20
10
0
f1 (ppm)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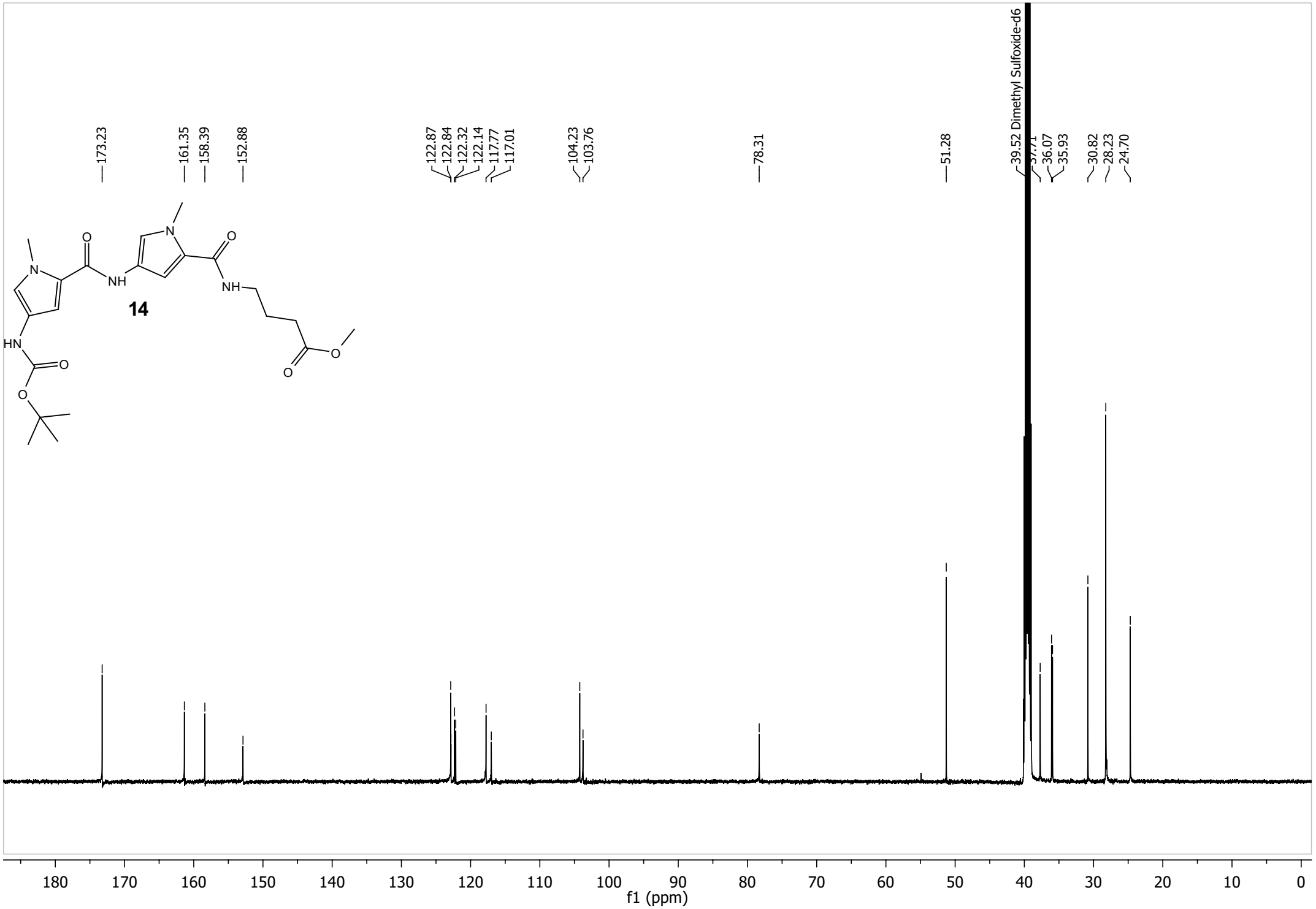
9.09
8.03
8.02
8.01
7.16
7.15
6.88
6.86
6.85
6.81
3.80
3.78
3.58
3.20
3.18
3.17
3.16
2.50 Dimethyl Sulfoxide-d6
2.35
2.34
2.32
1.76
1.75
1.73
1.72
1.71
1.45
14
0.97
0.90
1.05
1.00
0.87
0.97
0.95
2.92
3.02
3.03
2.25
2.22
2.36
9.19
f1 (ppm)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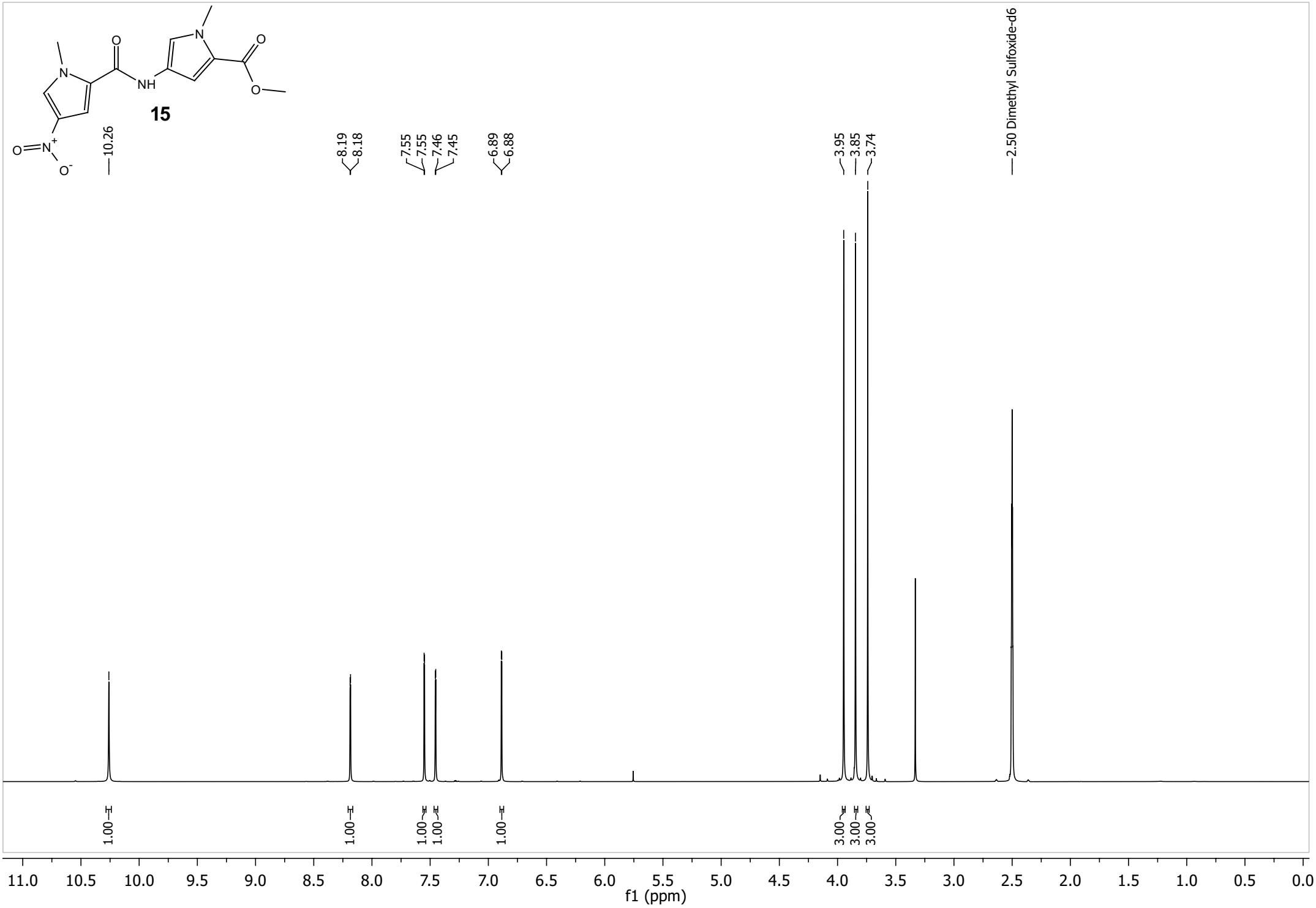
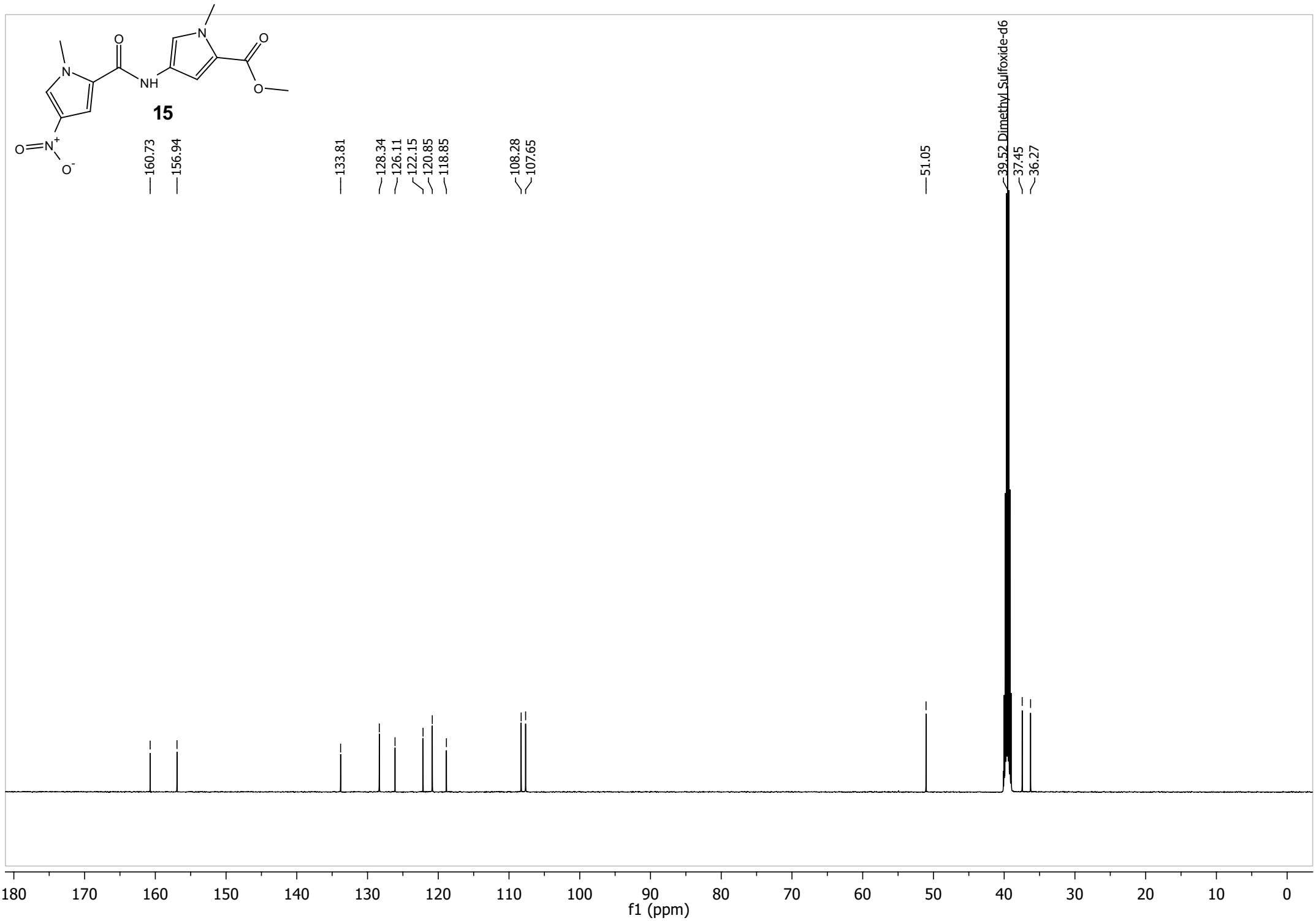
161.35
158.39
152.88
122.87
122.84
122.32
122.14
117.77
117.01
104.23
103.76
78.31
51.28
39.52 Dimethyl Sulfoxide-d6
36.07
35.93
30.82
28.23
24.70
14
f1 (ppm)


15
10.26
8.19
8.18
7.55
7.55
7.46
7.45
6.89
6.88
3.95
3.85
3.74
2.50 Dimethyl Sulfoxide-d6
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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160.73
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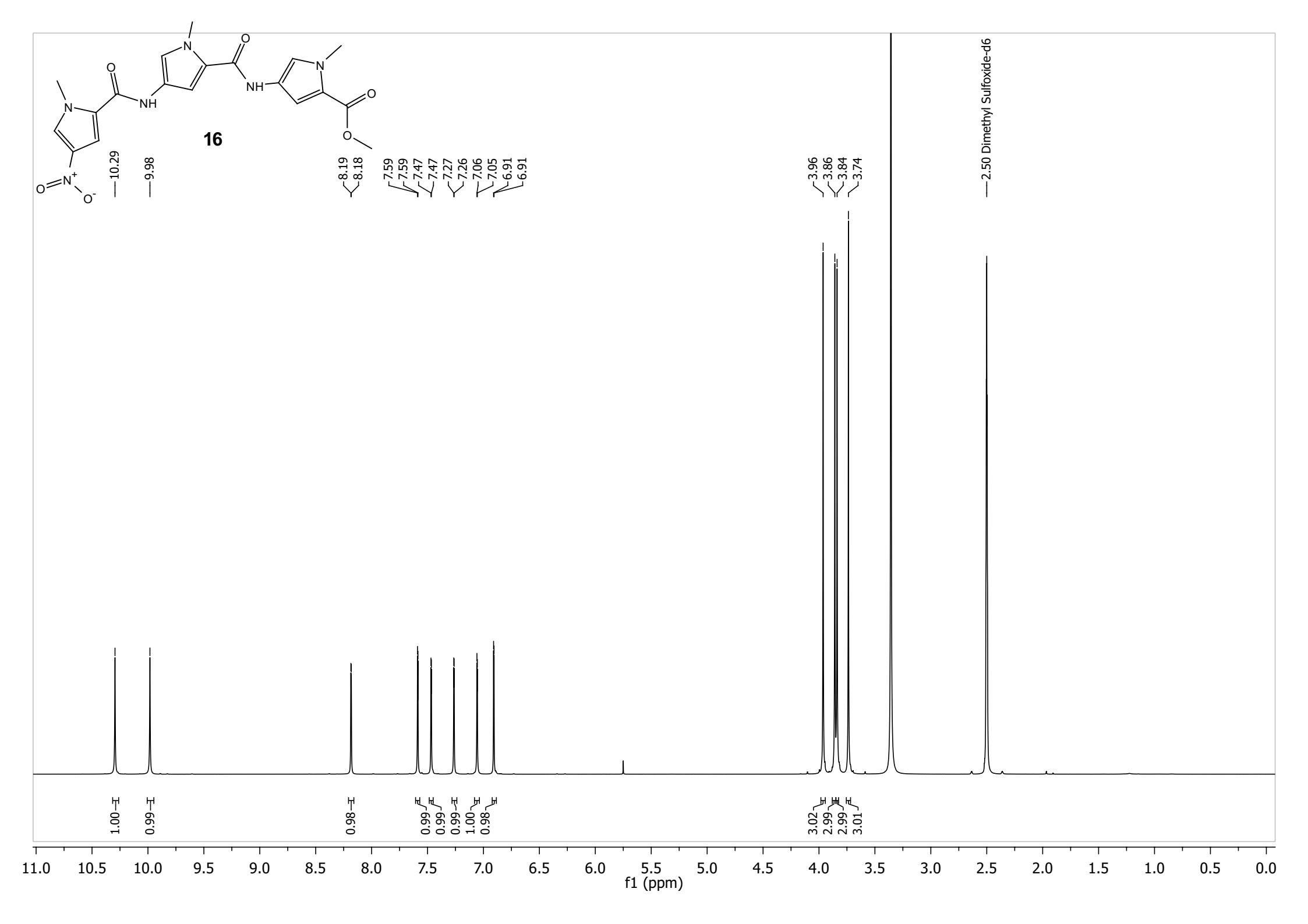
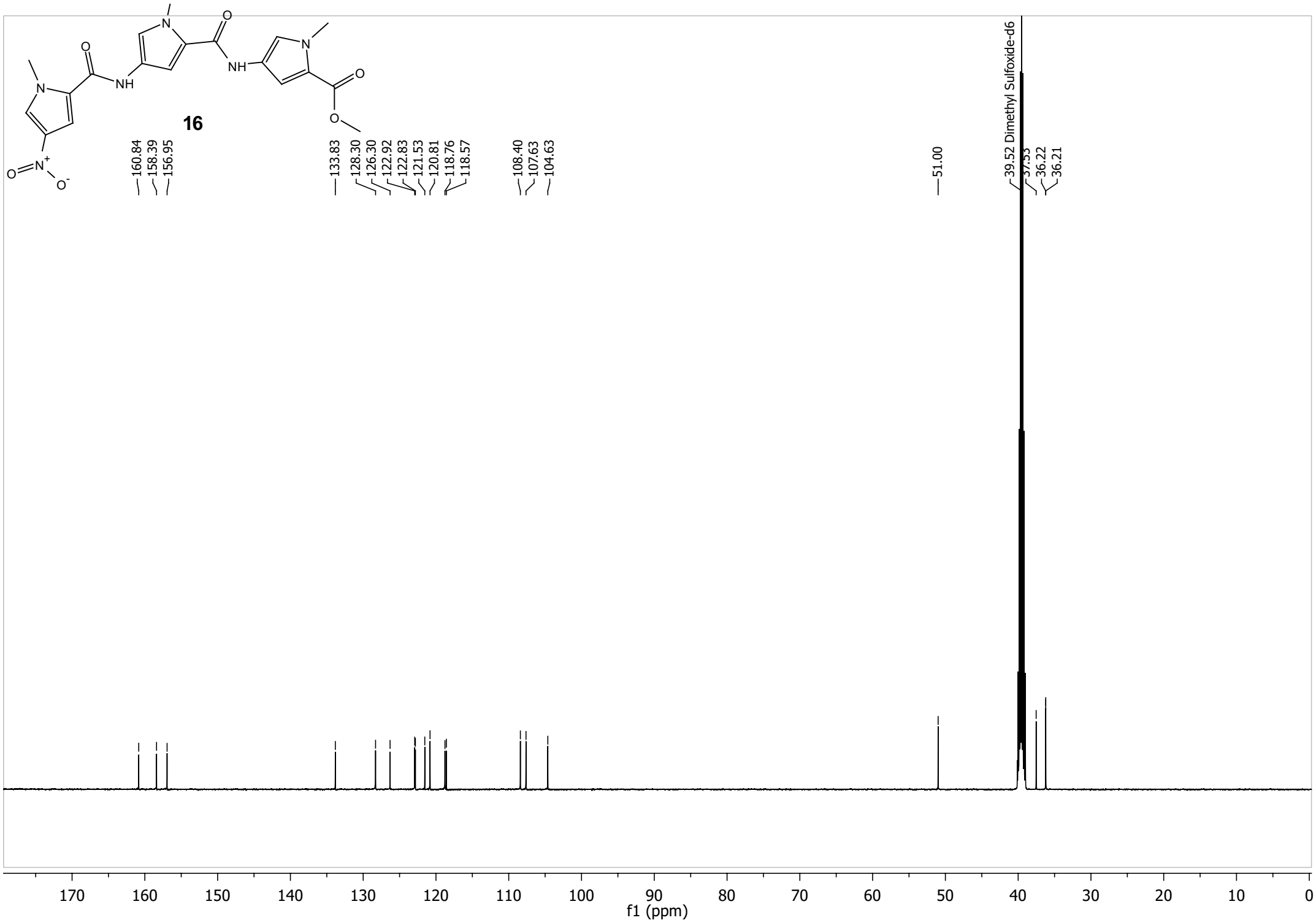
133.81
128.34
126.11
122.15
120.85
118.85
108.28
107.65
51.05
39.52 Dimethyl Sulfoxide-d6
37.45
36.27
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


16
10.29
9.98
8.19
8.18
7.59
7.59
7.47
7.47
7.27
7.26
7.06
7.05
6.91
6.91
3.96
3.86
3.84
3.74
2.50 Dimethyl Sulfoxide-d6
1.00
0.99
0.98
0.99
0.99
0.99
1.00
0.98
3.02
2.99
2.99
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


16
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158.39
156.95
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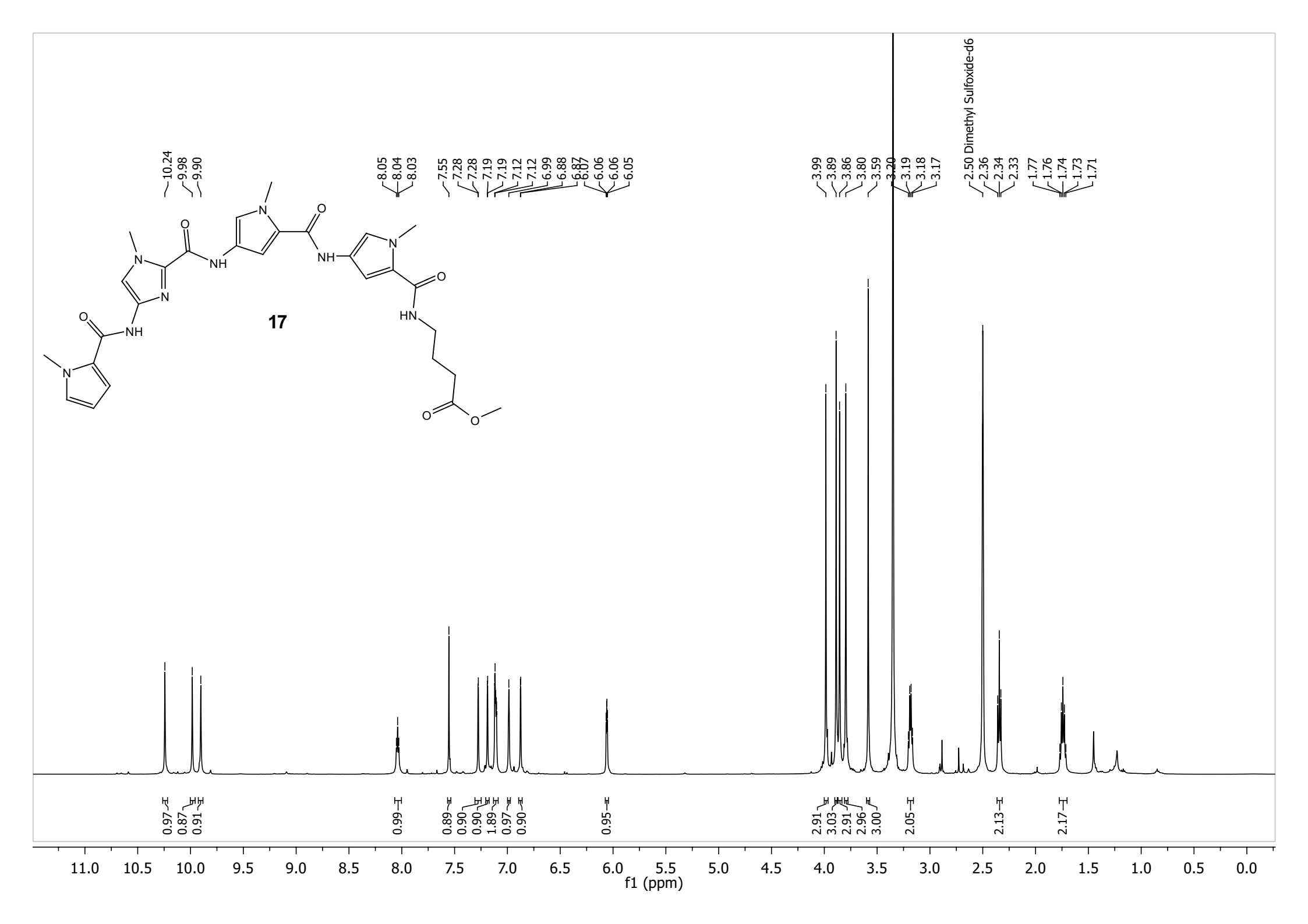
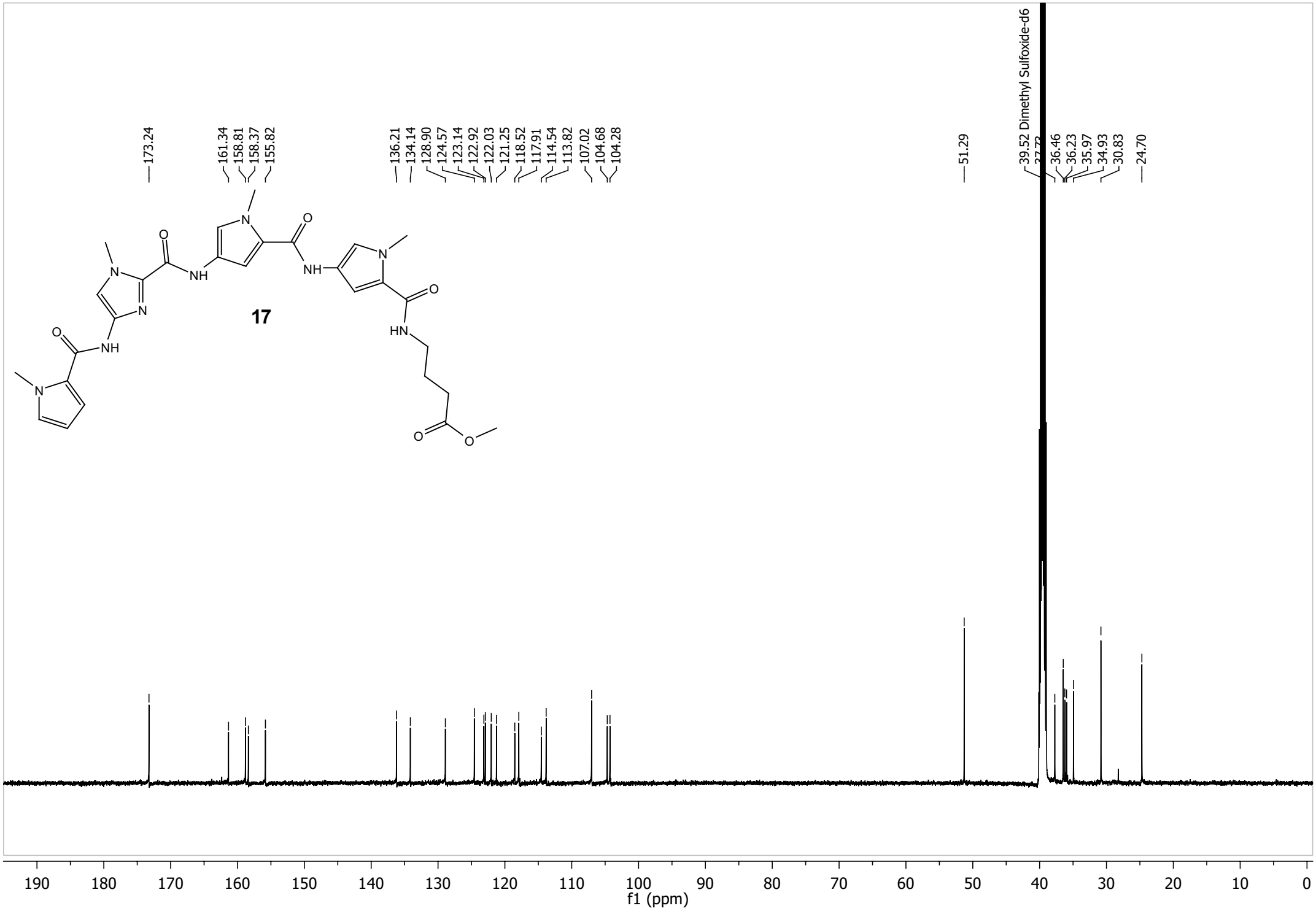
128.30
126.30
122.92
122.83
121.53
120.81
118.76
118.57
108.40
107.63
104.63
51.00
39.52 Dimethyl Sulfoxide-d6
37.33
36.22
36.21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.24
9.98
9.90
8.05
8.04
8.03
7.55
7.28
7.28
7.19
7.19
7.12
7.12
6.99
6.88
6.87
6.07
6.06
6.06
6.05
3.99
3.89
3.86
3.80
3.59
3.20
3.19
3.18
3.17
2.50 Dimethyl Sulfoxide-d6
2.36
2.34
2.33
1.77
1.76
1.74
1.73
1.71
17
0.97
0.87
0.91
0.99
0.89
0.90
0.90
1.89
0.97
0.90
0.95
2.91
3.03
2.91
2.96
3.00
2.05
2.13
2.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.21
134.14
128.90
124.57
123.14
122.92
122.03
121.25
118.52
117.91
114.54
113.82
107.02
104.68
104.28
51.29
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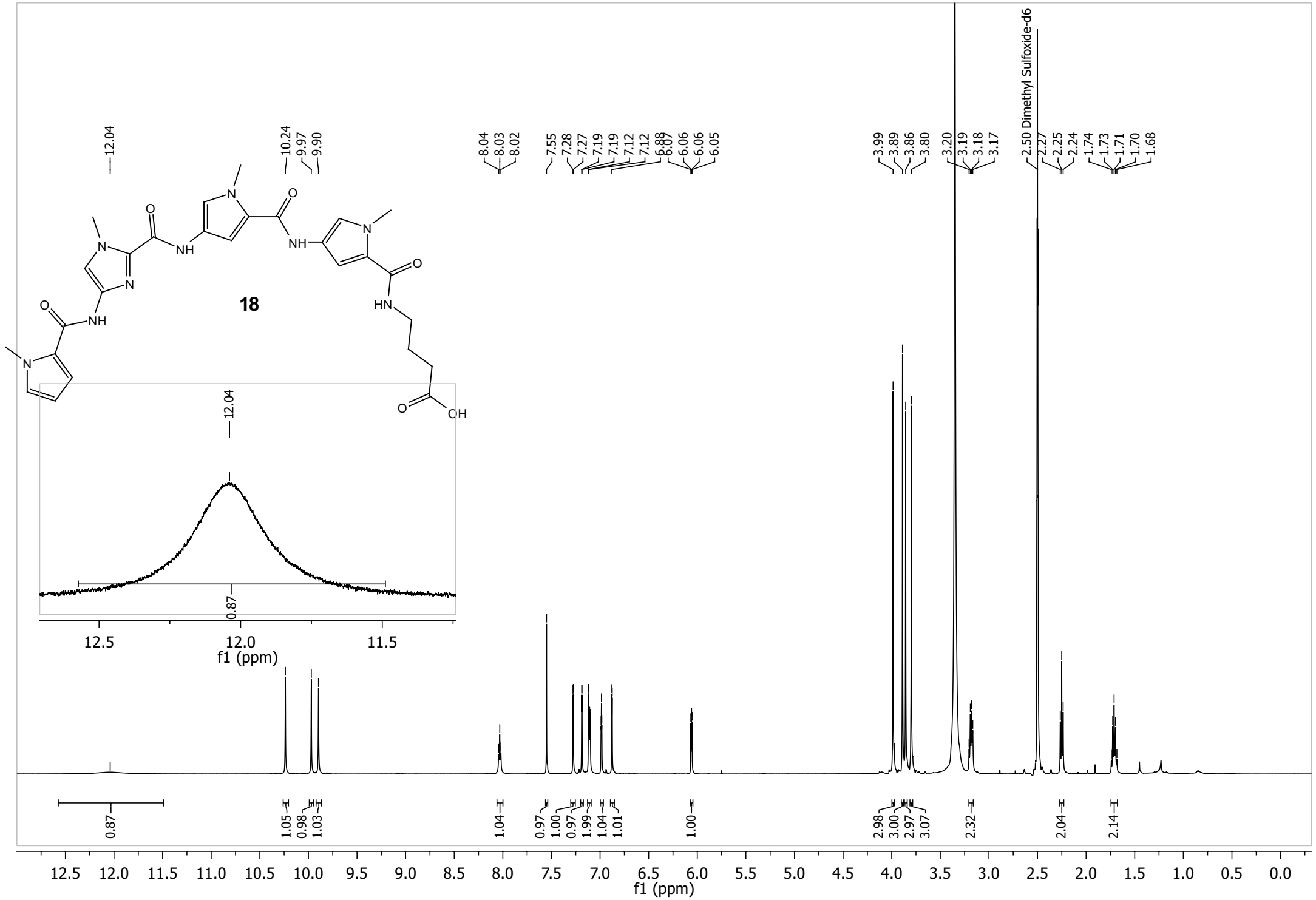
36.46
36.23
35.97
34.93
30.83
24.70
17
f1 (ppm)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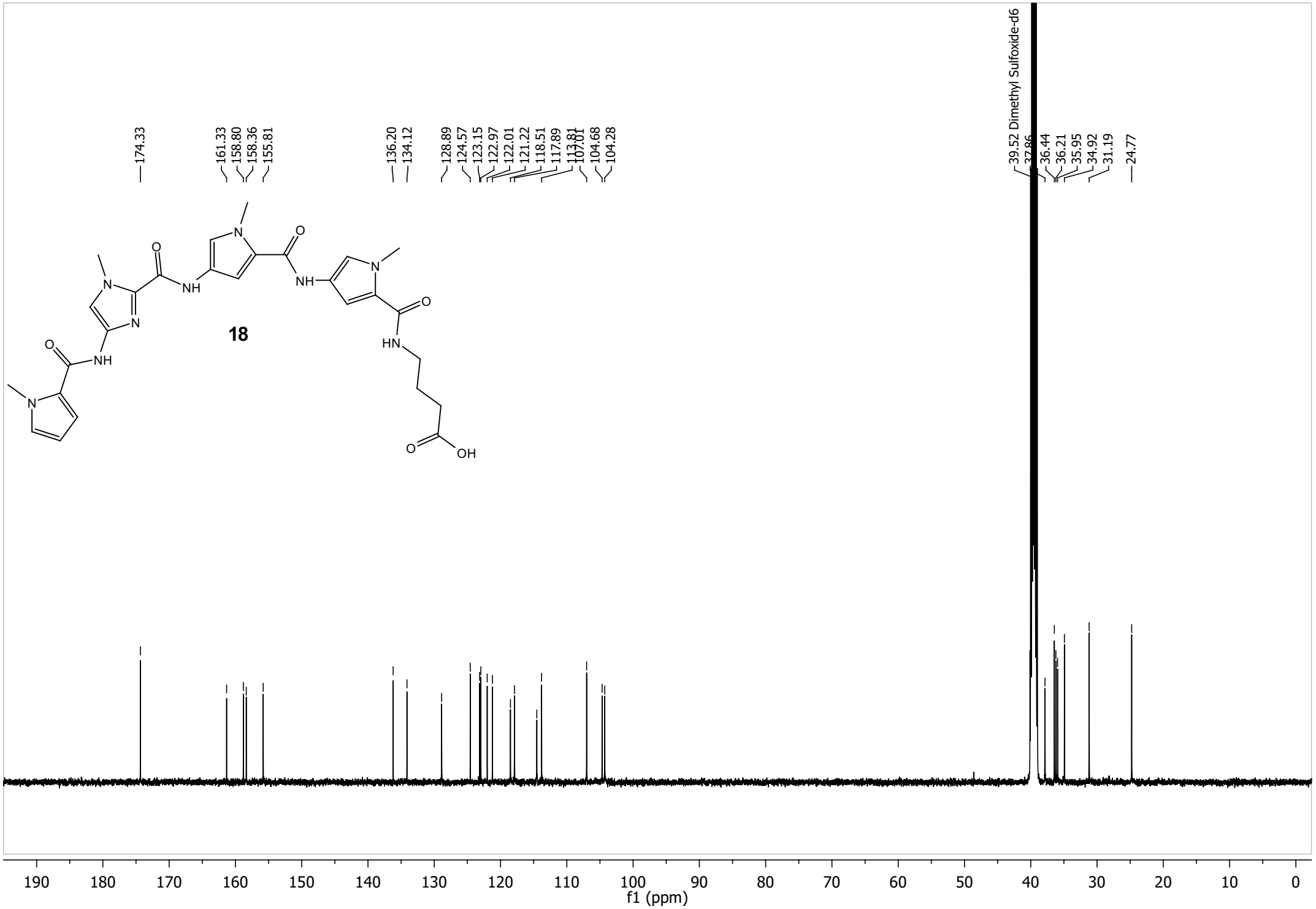
9.90
8.04
8.03
8.02
7.55
7.28
7.27
7.19
7.19
7.12
7.12
6.88
6.87
6.06
6.06
6.05
3.99
3.89
3.86
3.80
3.20
3.19
3.18
3.17
2.50 Dimethyl Sulfoxide-d6
2.27
2.25
2.24
1.74
1.73
1.71
1.70
1.68
18
NH
NH
NH
HN
O
OH
12.04
0.87
12.5
12.0
11.5
f1 (ppm)
0.87
1.05
0.98
1.03
1.04
0.97
1.00
0.97
1.99
1.04
1.01
1.00
2.98
3.00
2.97
3.07
2.32
2.04
2.14
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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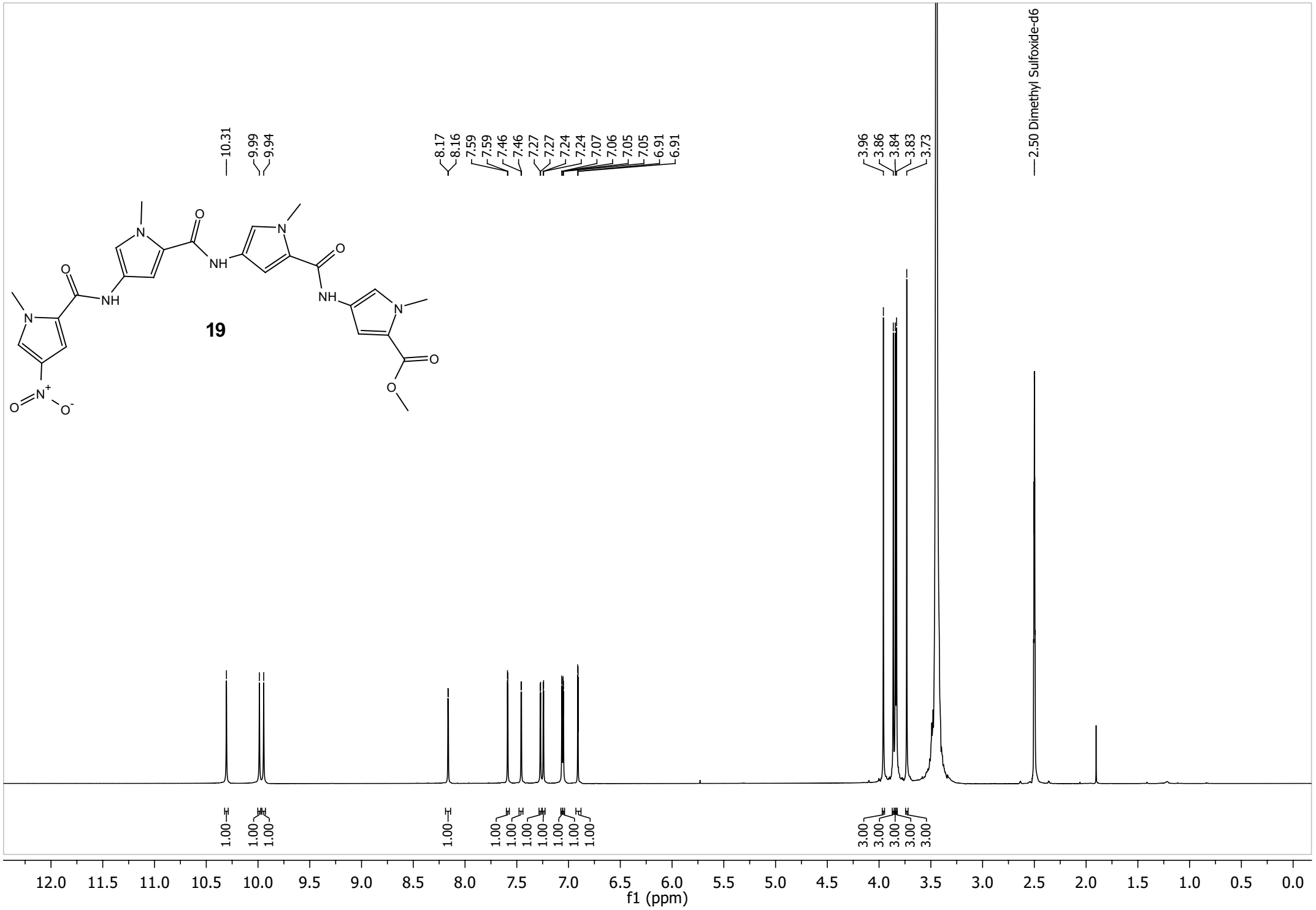
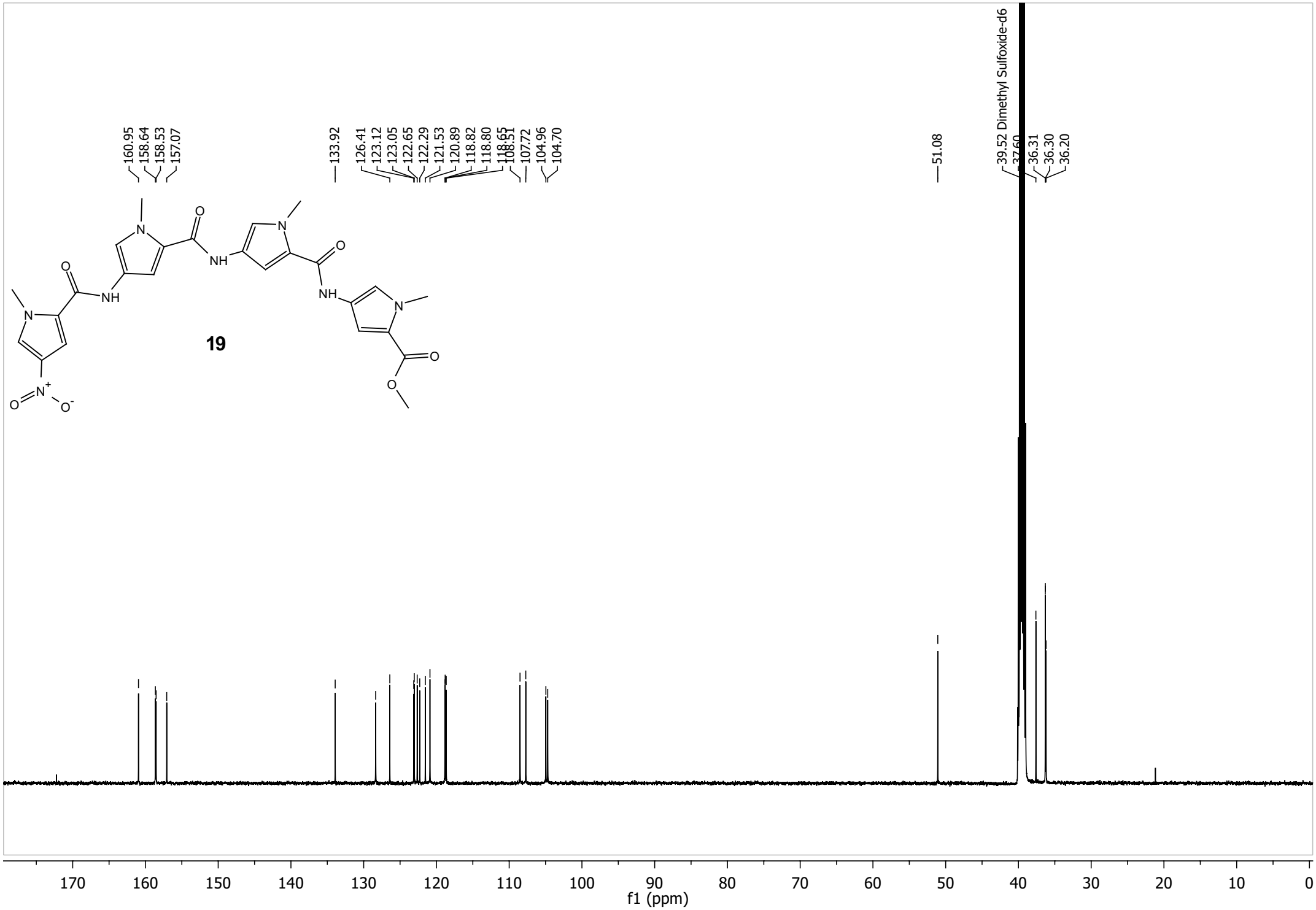
161.33
158.80
158.36
155.81
136.20
134.12
128.89
124.57
123.15
122.97
122.01
121.22
118.51
117.89
113.81
107.01
104.68
104.28
39.52 Dimethyl Sulfoxide-d6
37.86
36.44
36.21
35.95
34.92
31.19
24.77
18
f1 (ppm)


10.31
9.99
9.94
8.17
8.16
7.59
7.59
7.46
7.46
7.27
7.27
7.24
7.24
7.07
7.06
7.05
7.05
6.91
6.91
3.96
3.86
3.84
3.83
3.73
2.50 Dimethyl Sulfoxide-d6
19
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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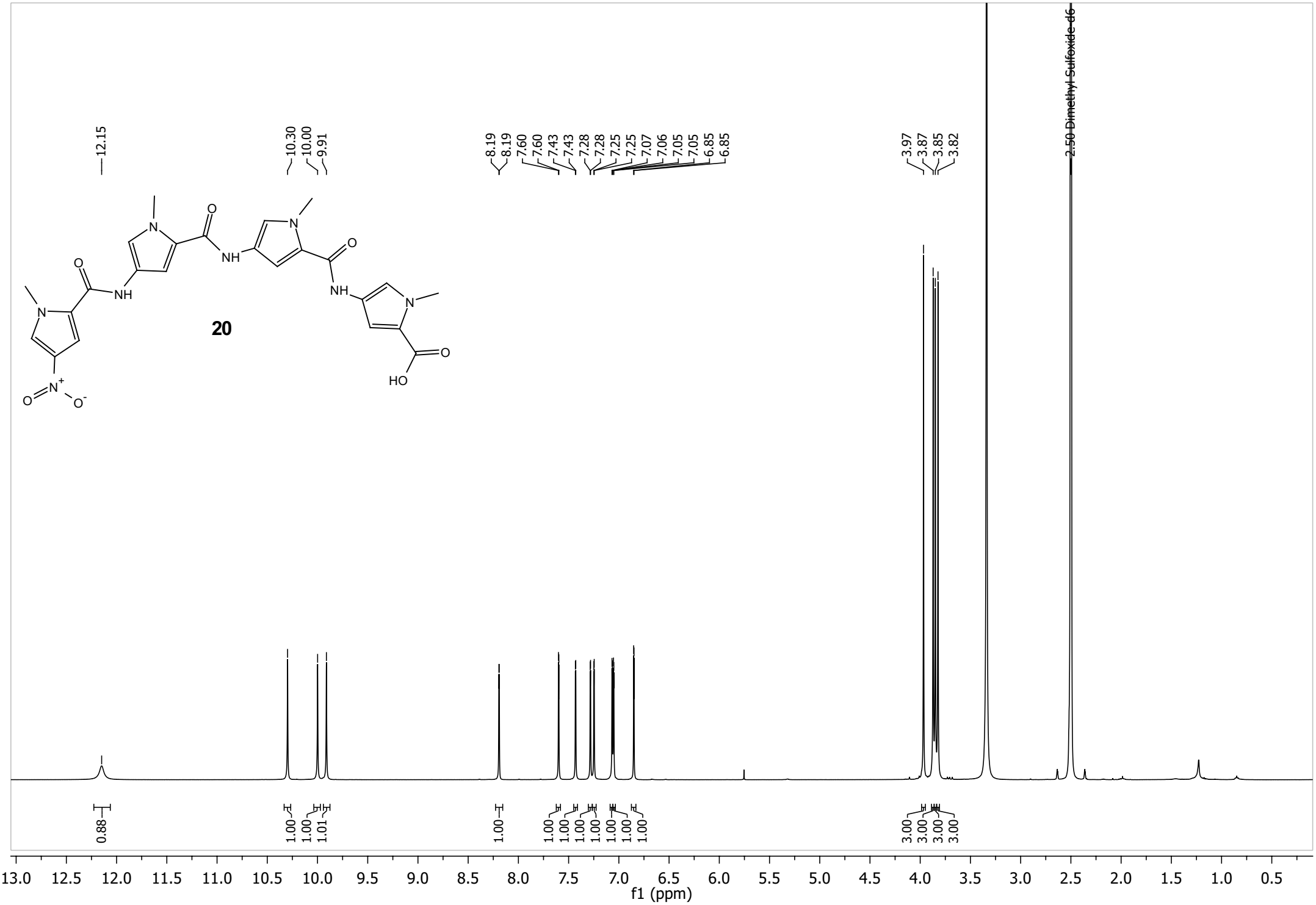
126.41
123.12
123.05
122.65
122.29
121.53
120.89
118.82
118.80
118.65
108.51
107.72
104.96
104.70
51.08
39.52 Dimethyl Sulfoxide-d6
37.60
36.31
36.30
36.20
19
f1 (ppm)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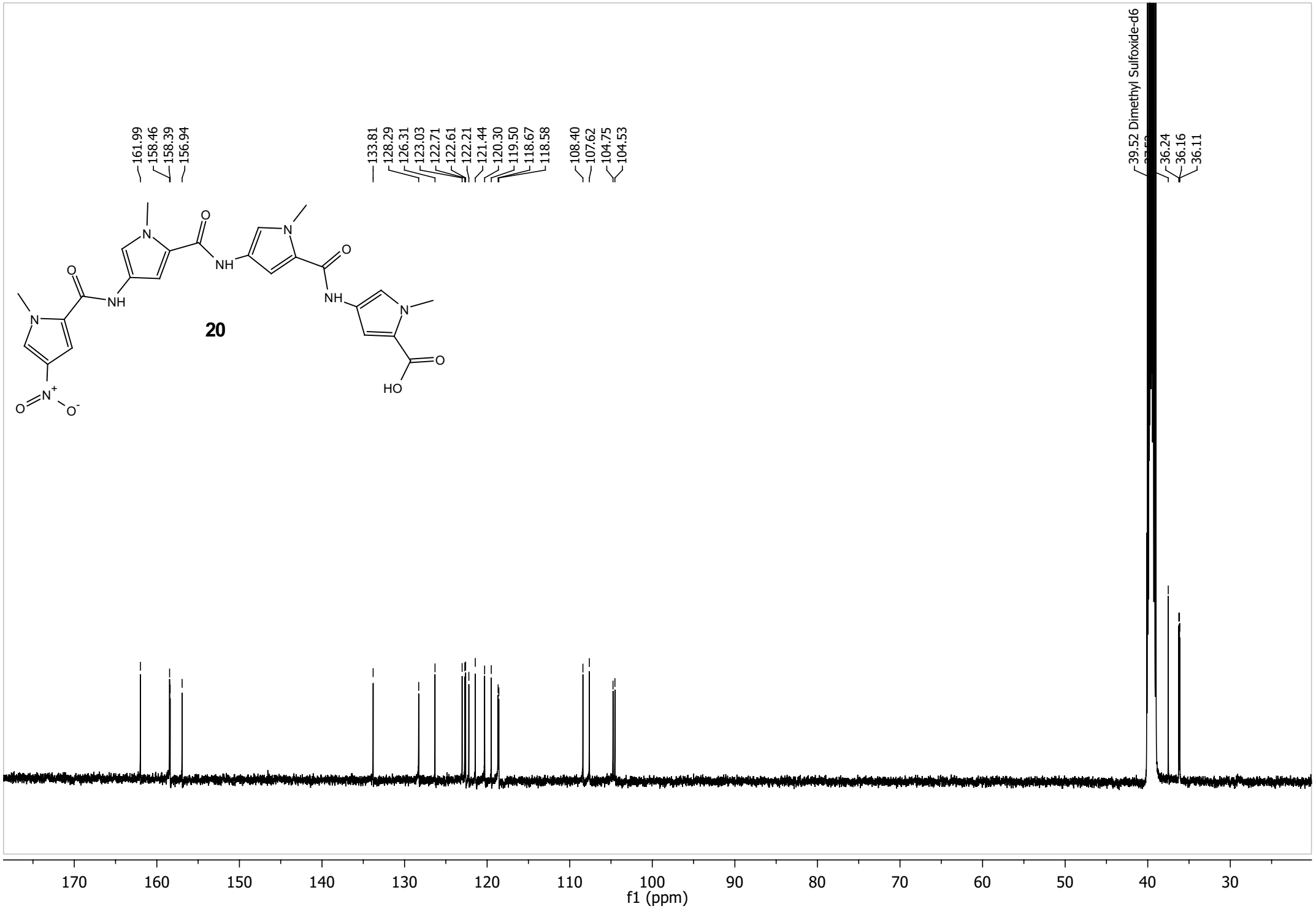
8.19
7.60
7.60
7.43
7.43
7.28
7.28
7.25
7.25
7.07
7.06
7.05
7.05
6.85
6.85
3.97
3.87
3.85
3.82
2.50 Dimethyl Sulfoxide d6
20
0.88
1.00
1.00
1.01
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)


161.99
158.46
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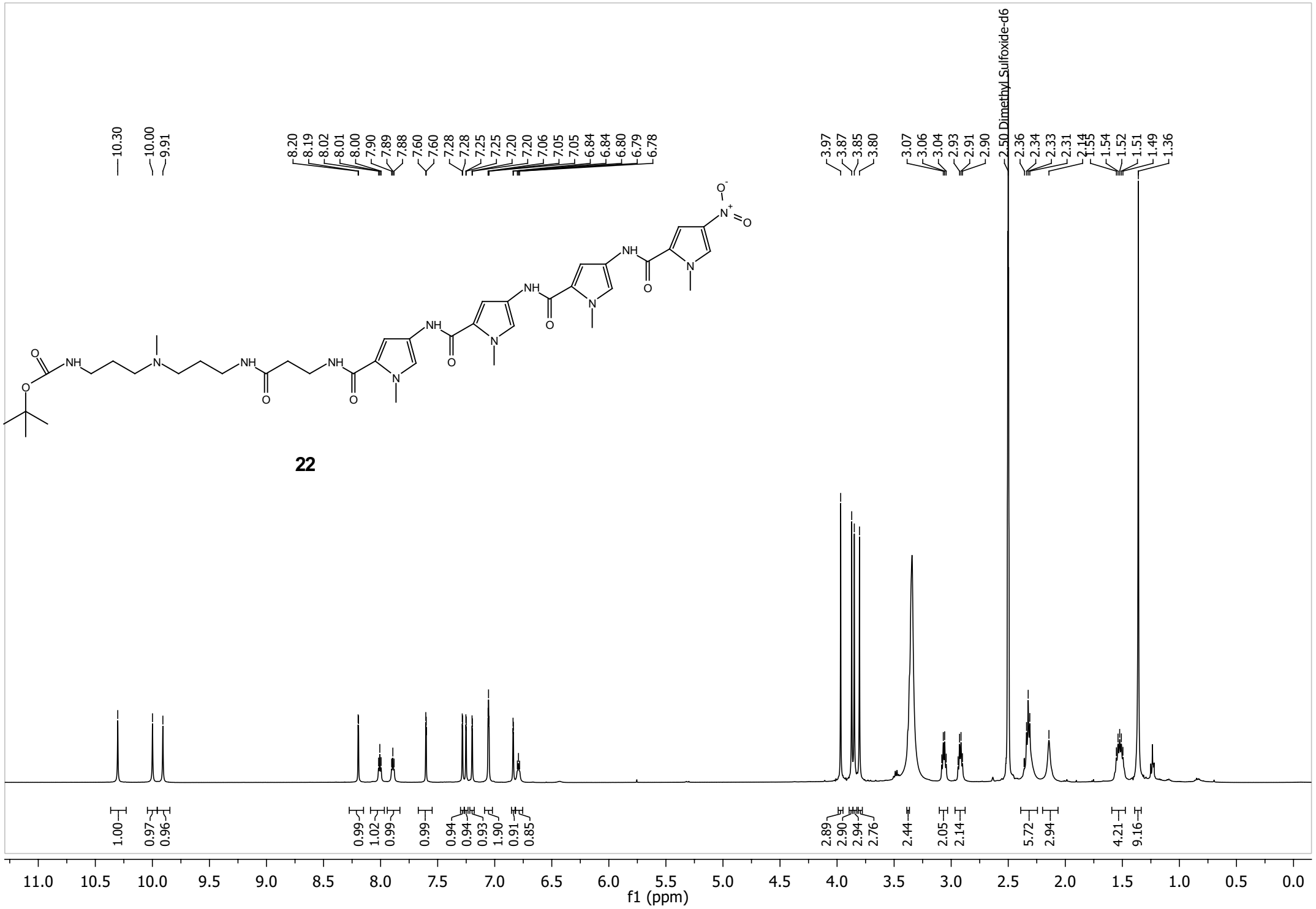
156.94
133.81
128.29
126.31
123.03
122.71
122.61
122.21
121.44
120.30
119.50
118.67
118.58
108.40
107.62
104.75
104.53
39.52 Dimethyl Sulfoxide-d6
36.24
36.16
36.11
20
f1 (ppm)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10.00
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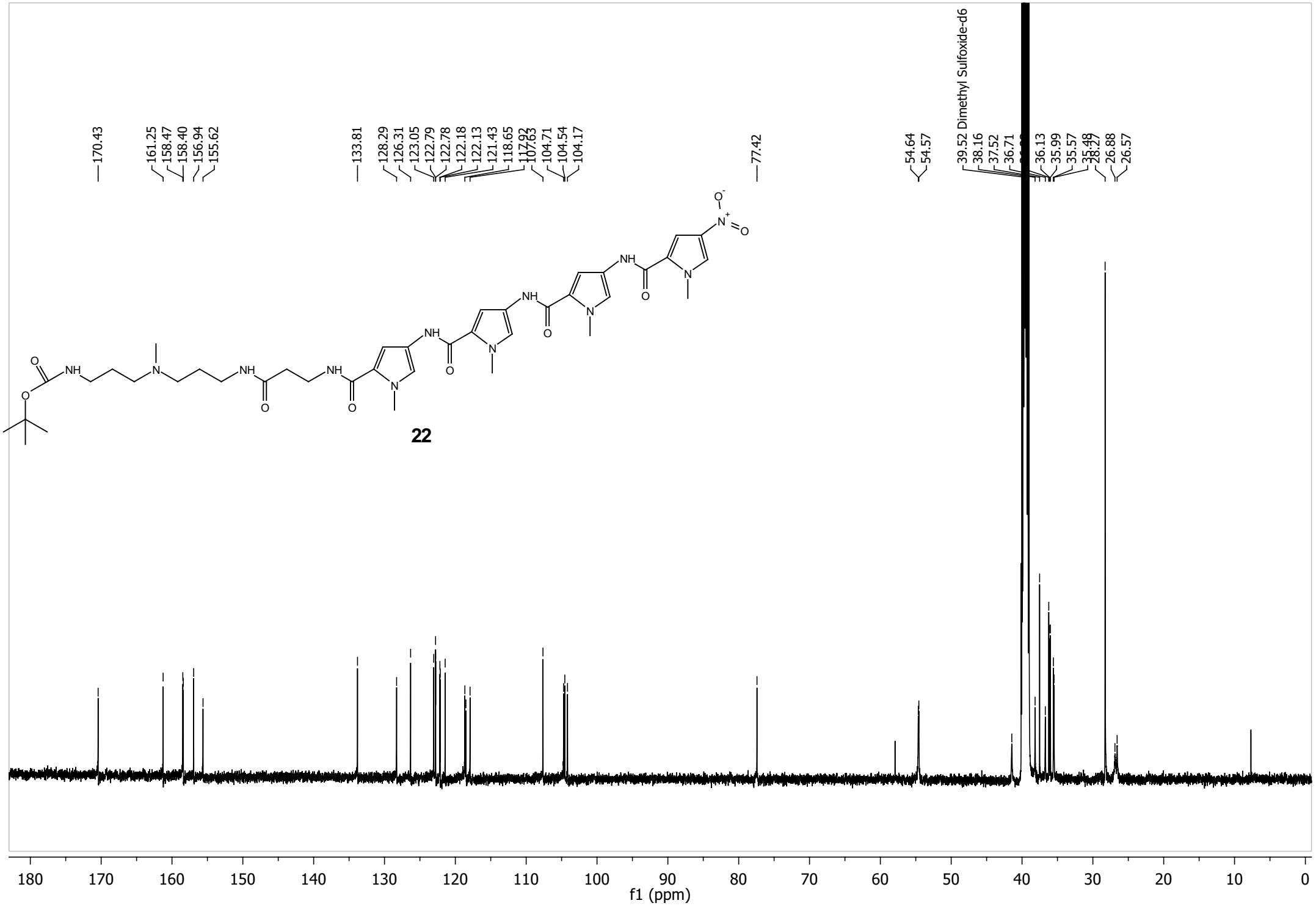
8.19
8.02
8.01
8.00
7.90
7.89
7.88
7.60
7.60
7.28
7.28
7.25
7.25
7.20
7.20
7.06
7.05
7.05
6.84
6.84
6.80
6.79
6.78
3.97
3.87
3.85
3.80
3.07
3.06
3.04
2.93
2.91
2.90
2.50 Dimethyl Sulfoxide-d6
2.36
2.34
2.33
2.31
2.14
1.55
1.54
1.52
1.51
1.49
1.36
1.00
0.97
0.96
0.99
1.02
0.99
0.99
0.94
0.94
0.93
1.90
0.91
0.85
2.89
2.90
2.94
2.76
2.44
2.05
2.14
5.72
2.94
4.21
9.16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

22


170.43
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158.40
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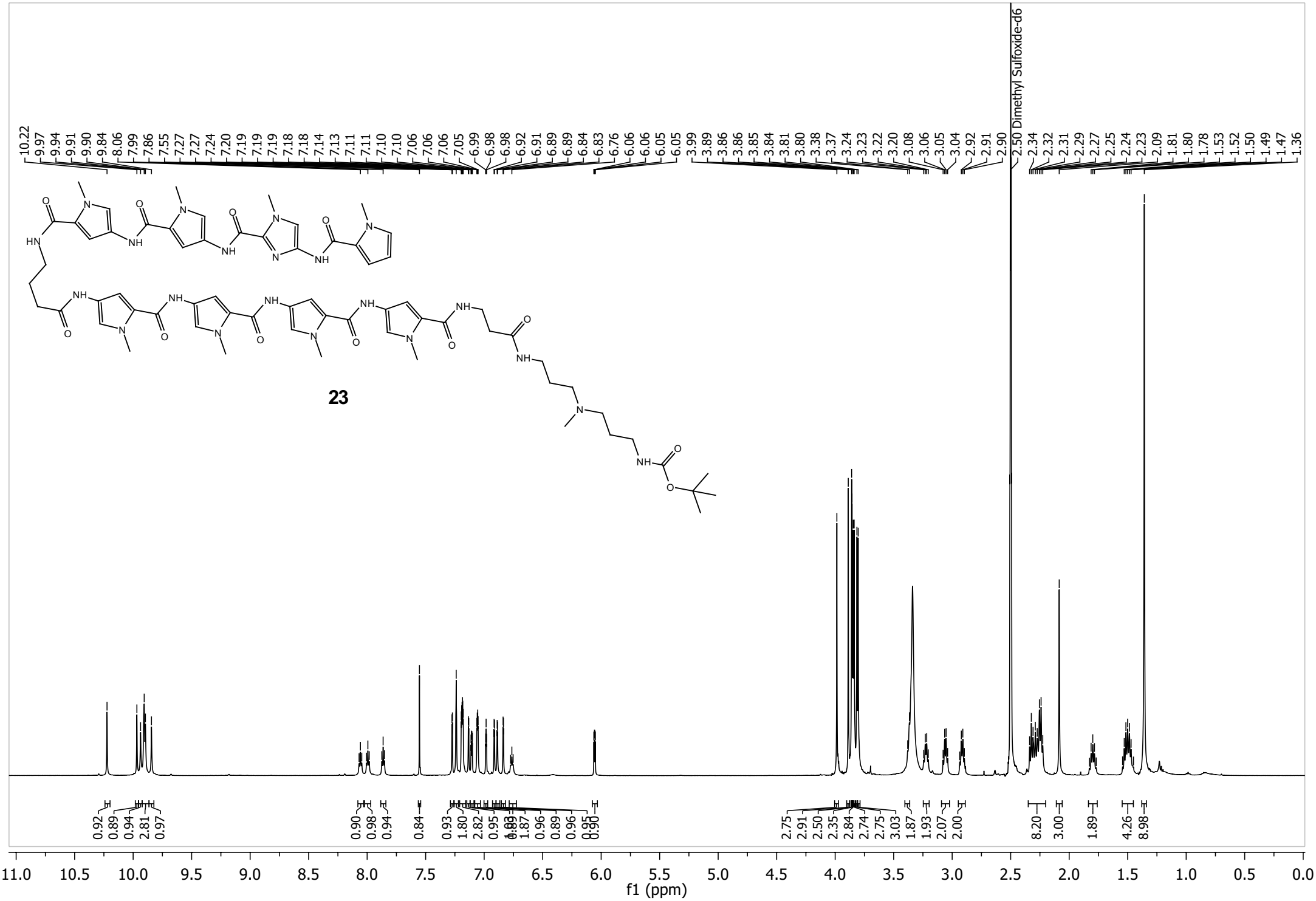
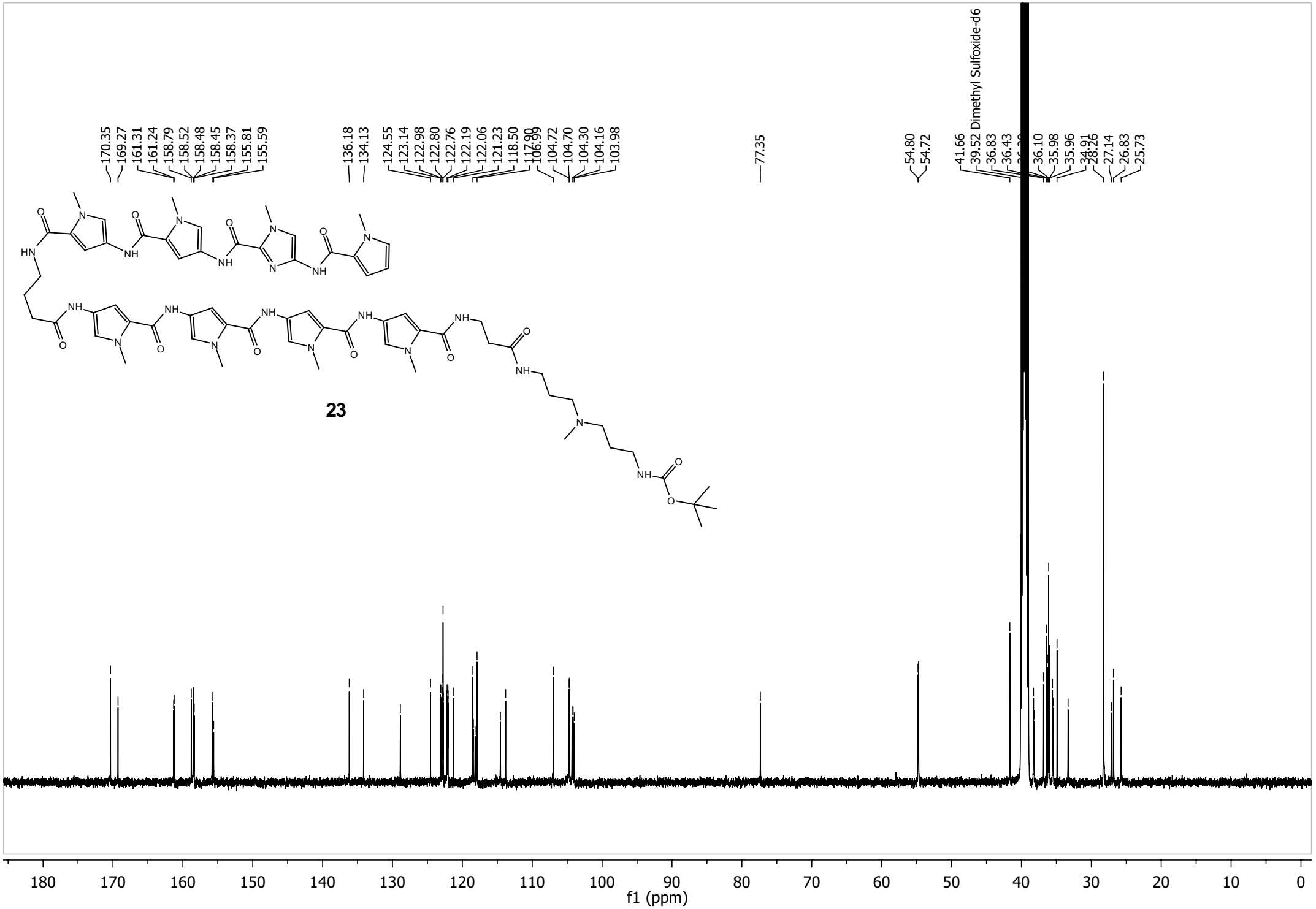
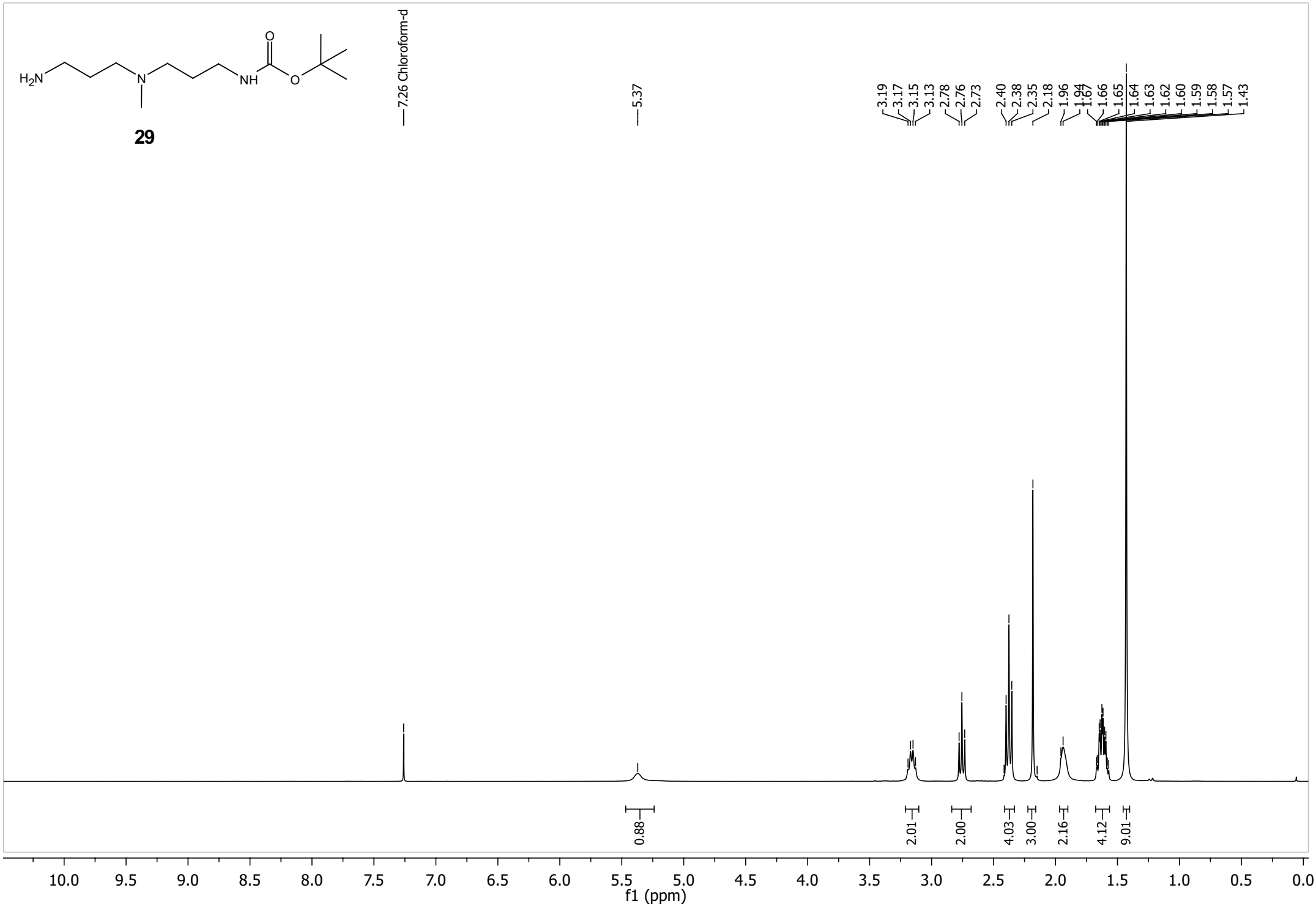
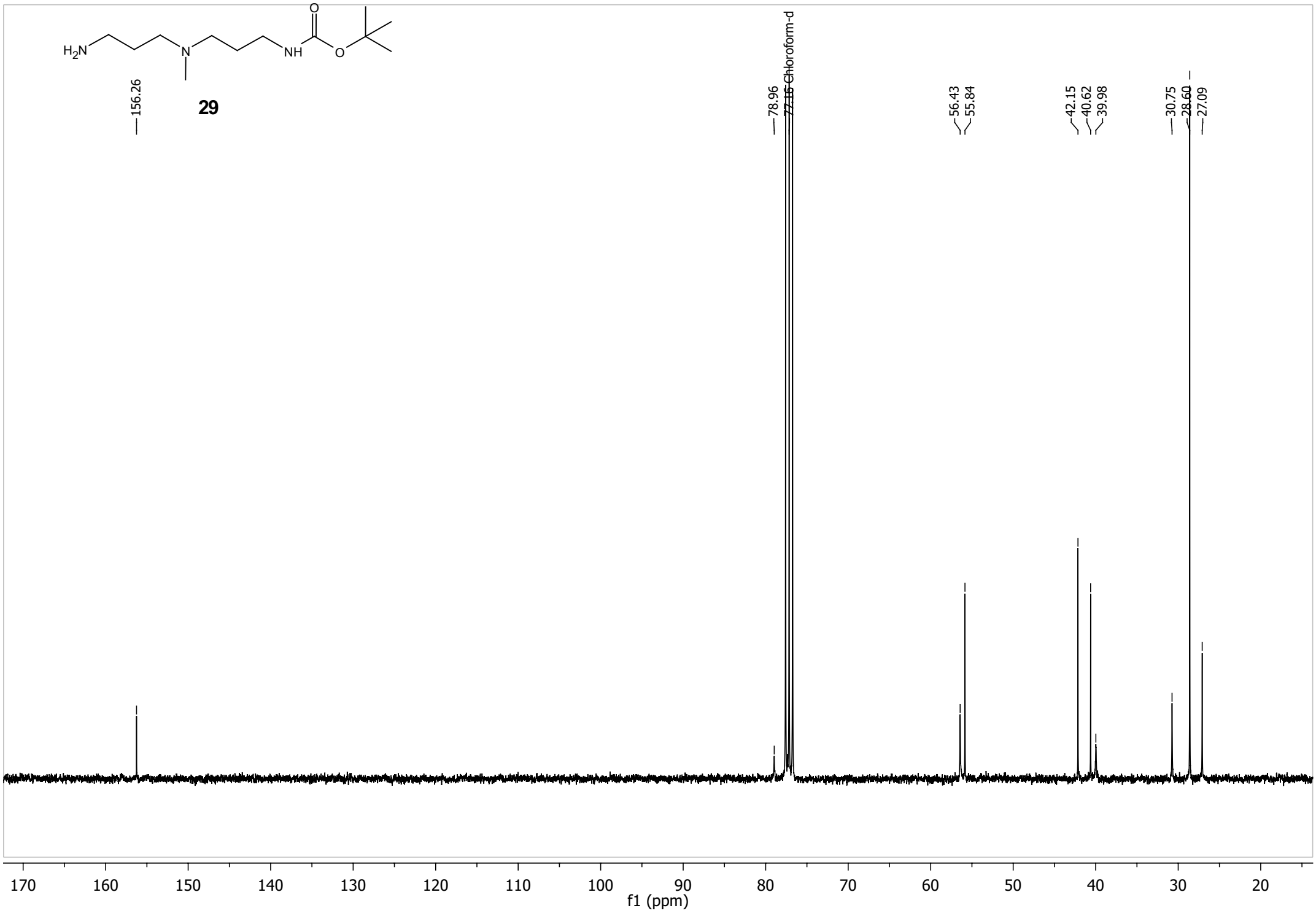
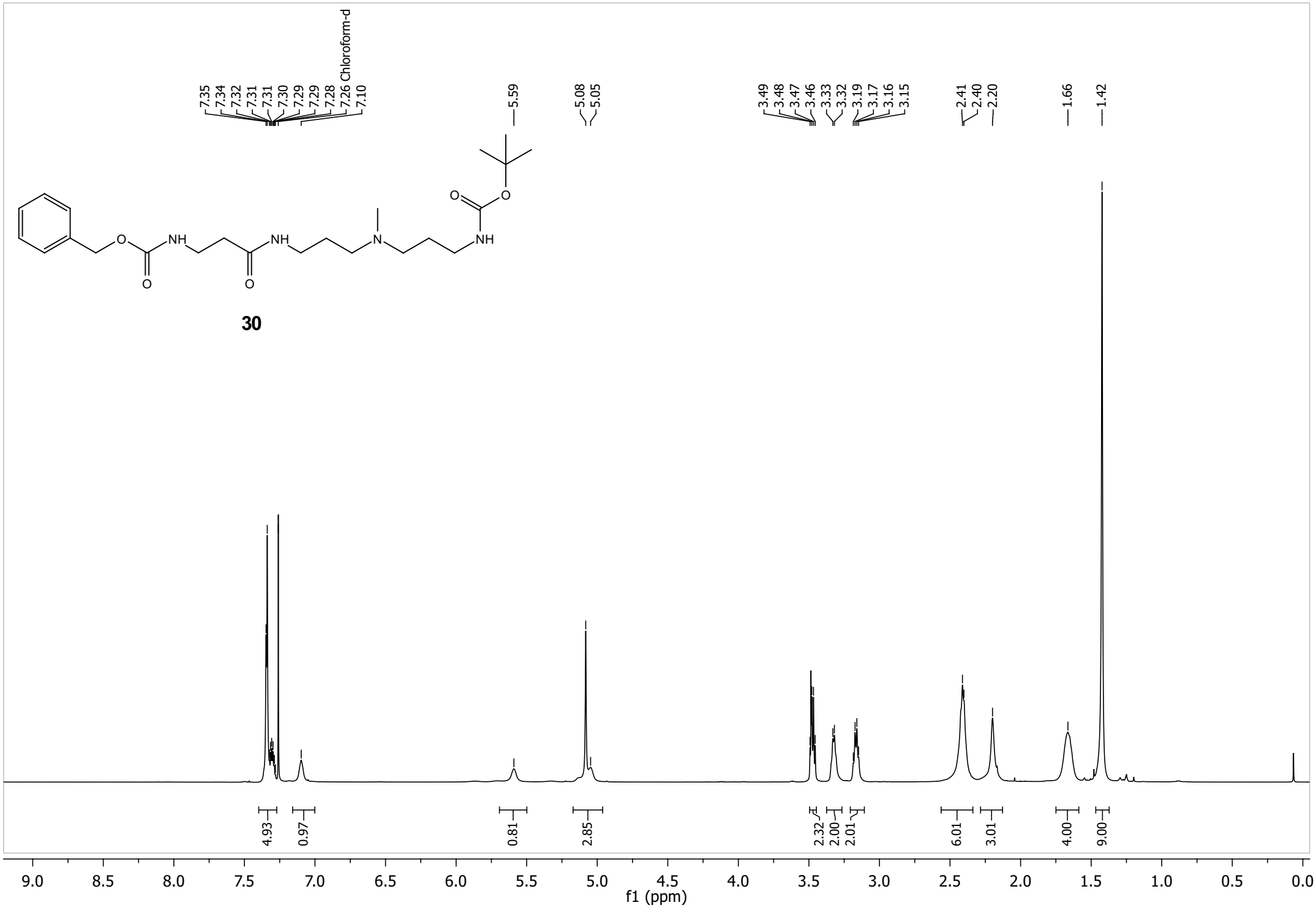
155.62
133.81
128.29
126.31
123.05
122.79
122.78
122.18
122.13
121.43
118.65
117.92
107.63
104.71
104.54
104.17
77.42
54.64
54.57
39.52 Dimethyl Sulfoxide-d6
38.16
37.52
36.71
36.13
35.99
35.57
35.48
28.27
26.88
26.57
22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Dimethyl Sulfoxide-d6
23
f1 (ppm)

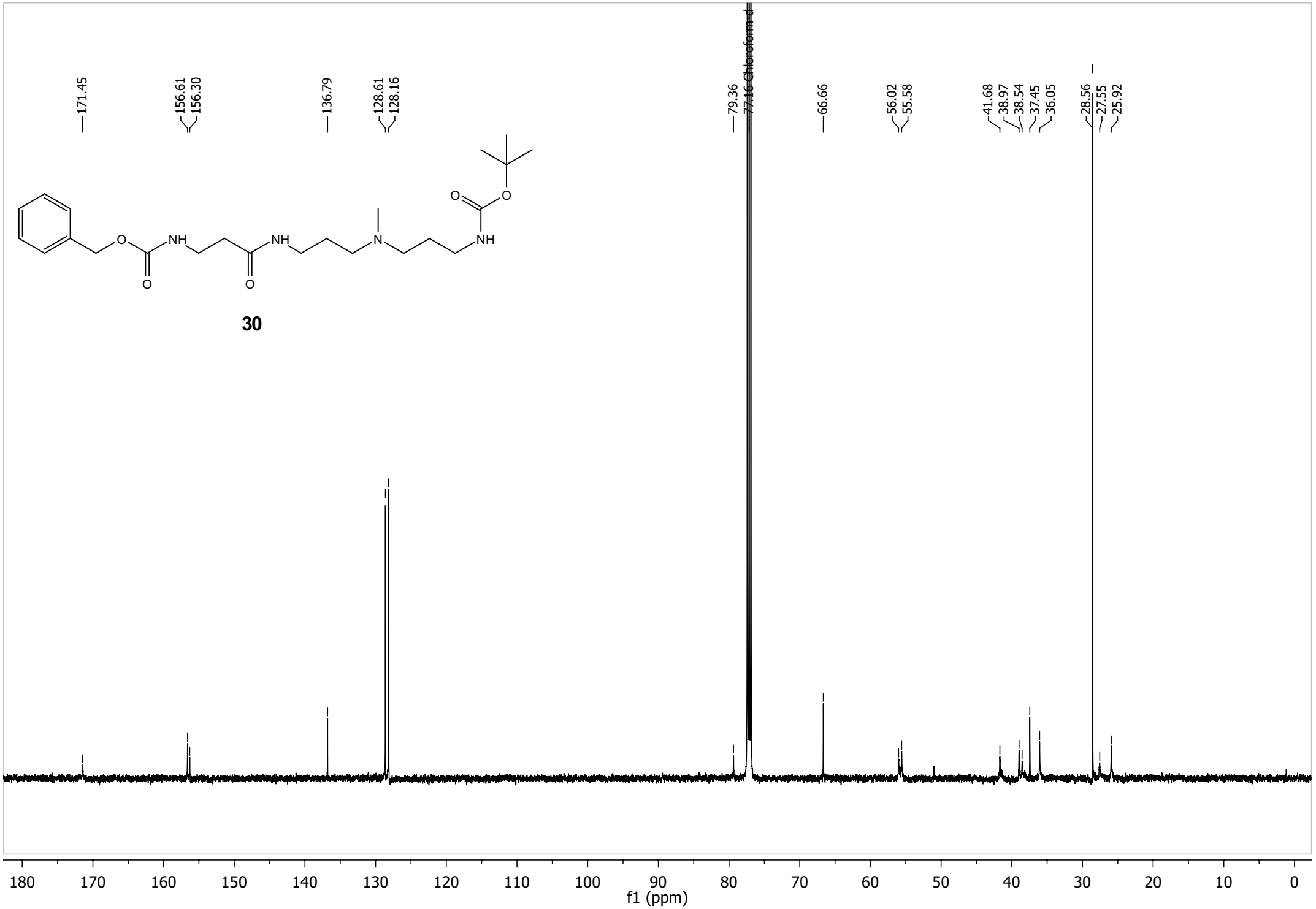

170.35
169.27
161.31
161.24
158.79
158.52
158.48
158.45
158.37
155.81
155.59
136.18
134.13
124.55
123.14
122.98
122.80
122.76
122.19
122.06
121.23
118.50
117.90
106.99
104.72
104.70
104.30
104.16
103.98
77.35
54.80
54.72
41.66
39.52 Dimethyl Sulfoxide-d6
36.83
36.43
36.10
35.98
35.96
34.91
28.26
27.14
26.83
25.73
23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


29
7.26 Chloroform-d
5.37
3.19
3.17
3.15
3.13
2.78
2.76
2.73
2.40
2.38
2.35
2.18
1.96
1.94
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.58
1.57
1.43
0.88
2.01
2.00
4.03
3.00
2.16
4.12
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

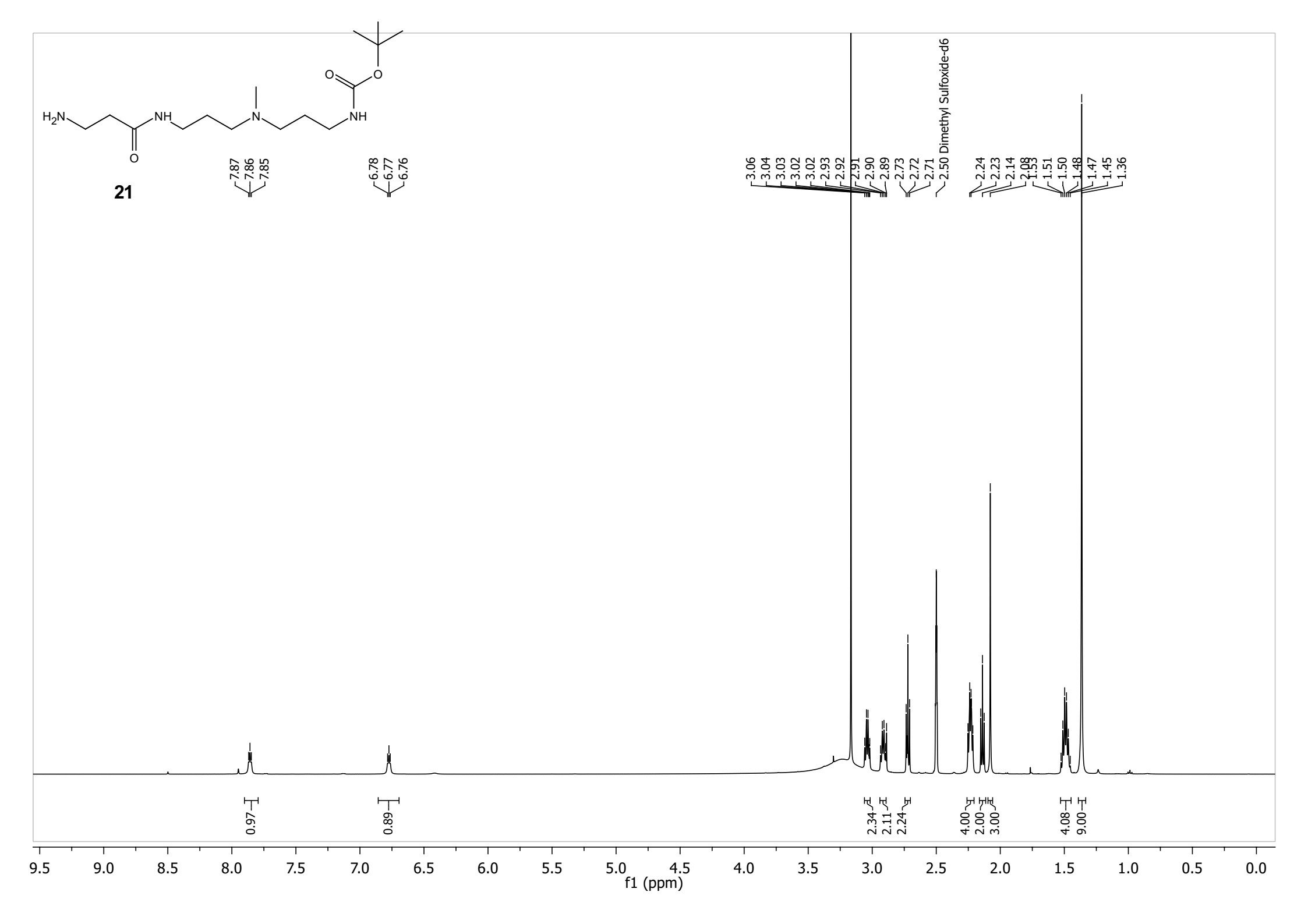

H2N
N
NH
O
O
29
156.26
78.96
77.16 Chloroform-d
56.43
55.84
42.15
40.62
39.98
30.75
28.60
27.09
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

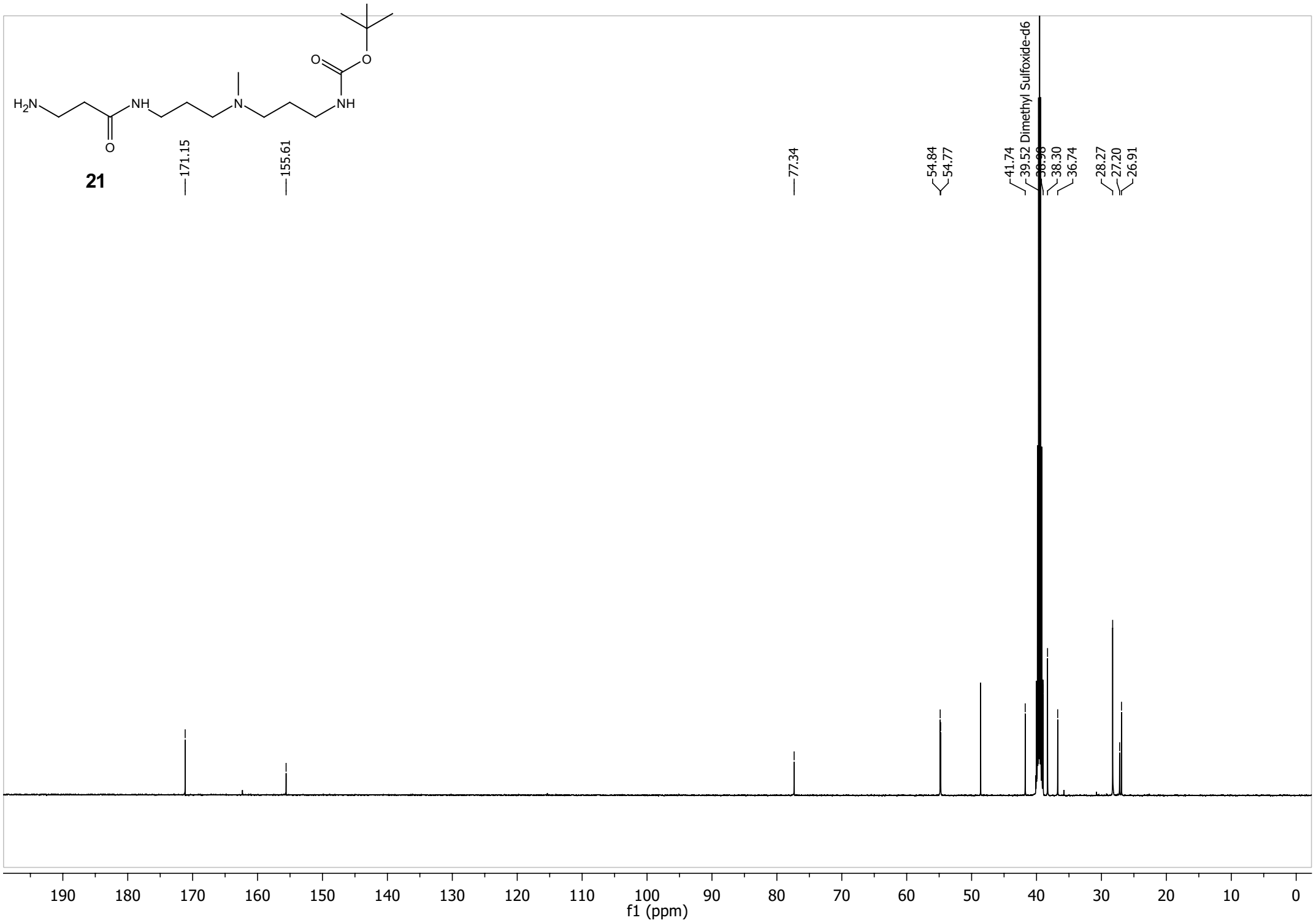

7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26 Chloroform-d
7.10
5.59
5.08
5.05
3.49
3.48
3.47
3.46
3.33
3.32
3.19
3.17
3.16
3.15
2.41
2.40
2.20
1.66
1.42
O
NH
O
NH
N
O
O
NH
O
O
4.93
0.97
0.81
2.85
2.32
2.00
2.01
6.01
3.01
4.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

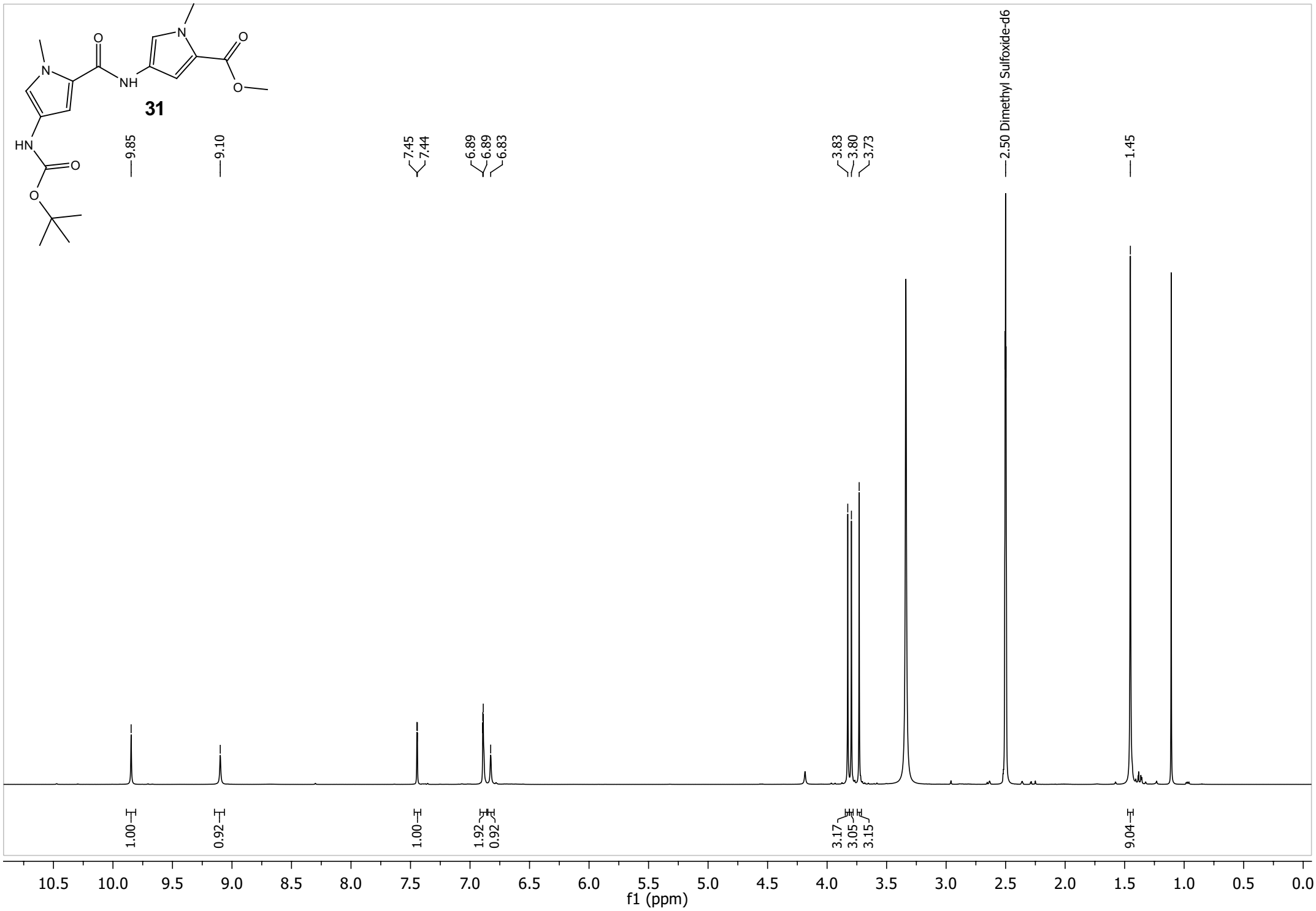
30

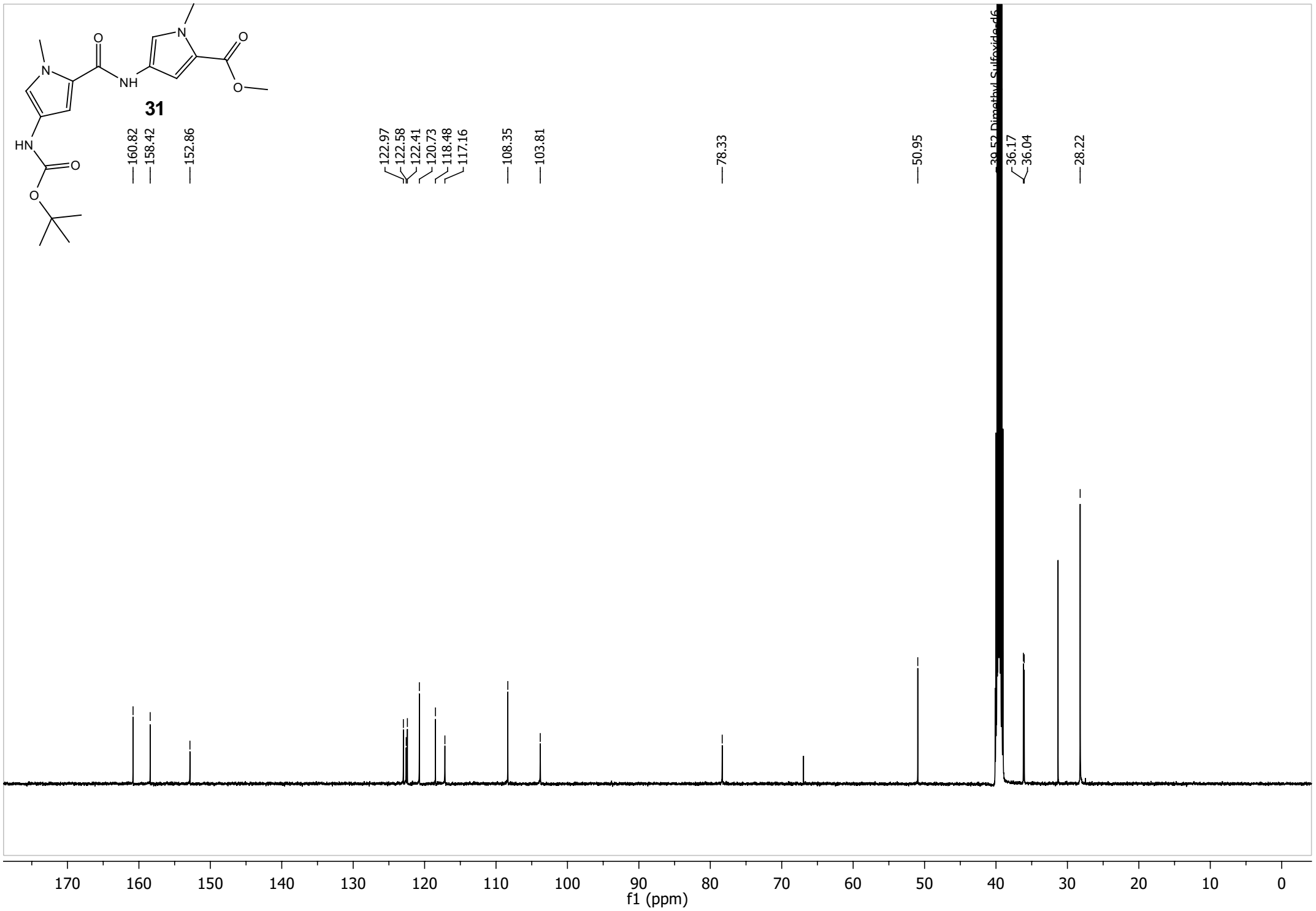

171.45
156.61
156.30
136.79
128.61
128.16
79.36
77.16 Chloroform-d
66.66
56.02
55.58
41.68
38.97
38.54
37.45
36.05
28.56
27.55
25.92
O
NH
N
O
O
O
O
O
NH
NH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

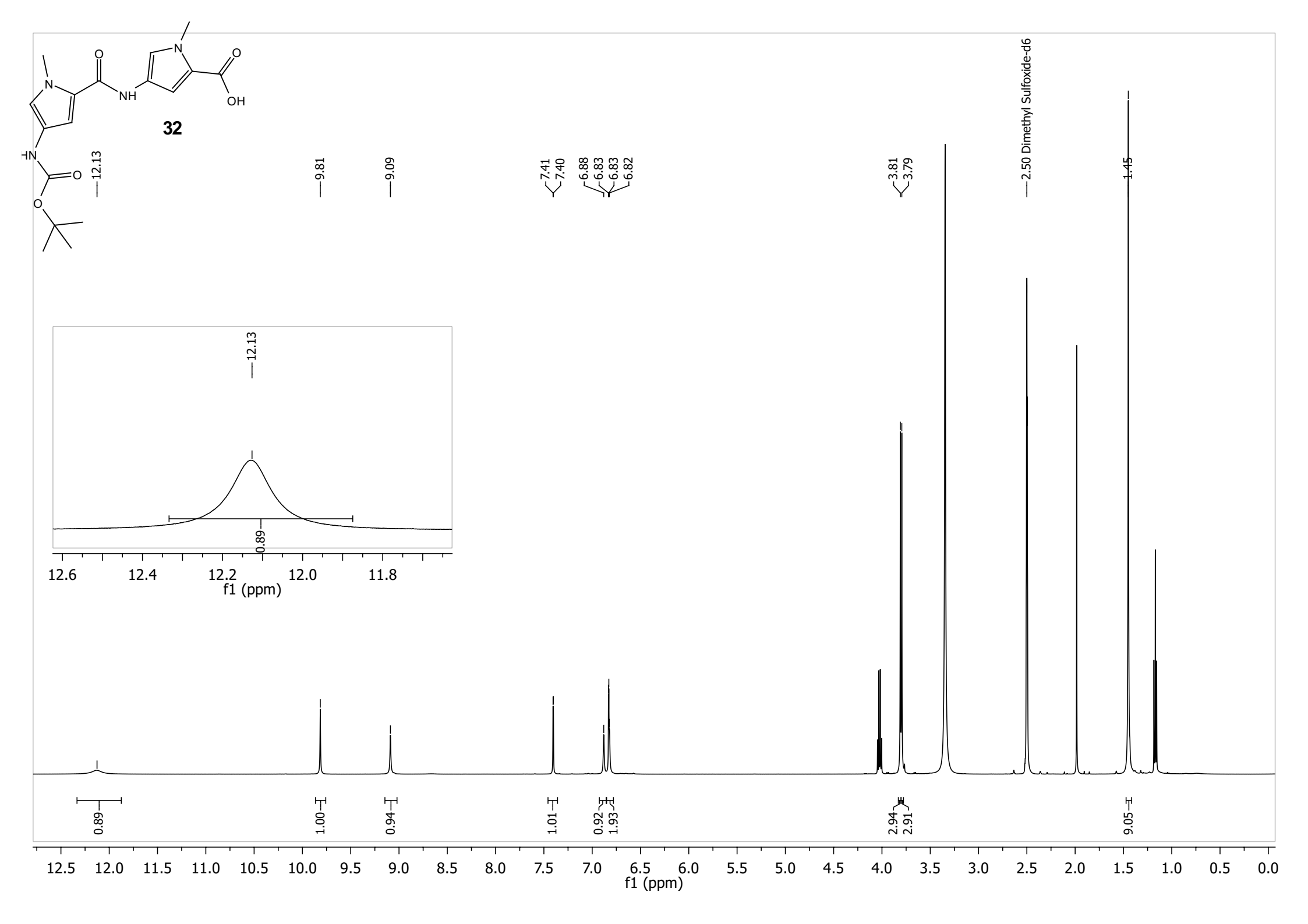
30

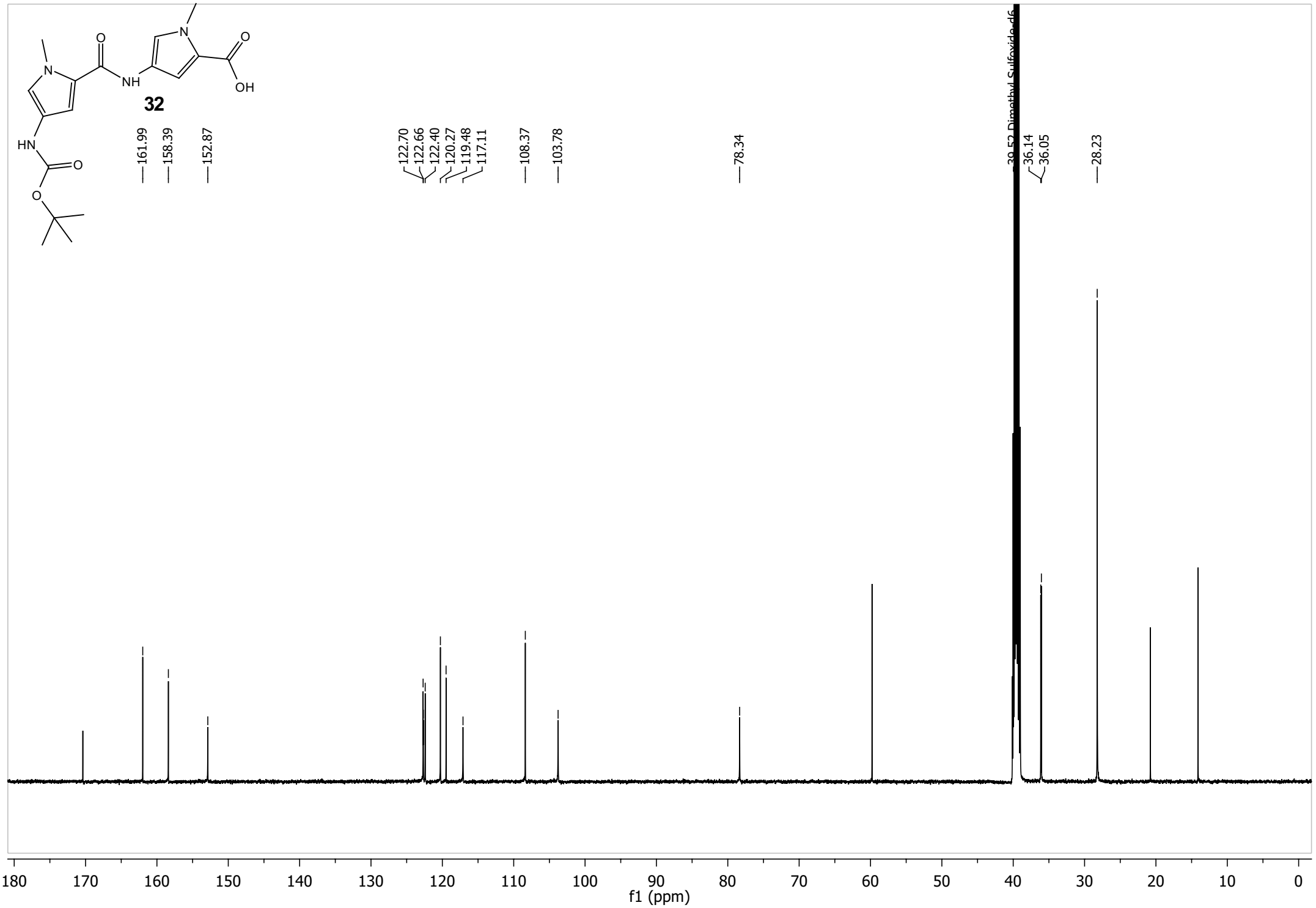

21
Dimethyl Sulfoxide-d6
f1 (ppm)

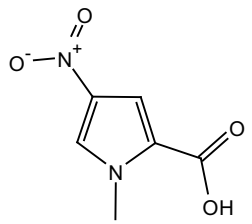

21
171.15
155.61
77.34
54.84
54.77
41.74
39.52 Dimethyl Sulfoxide-d6
38.30
36.74
28.27
27.20
26.91
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


31
9.85
9.10
7.45
7.44
6.89
6.89
6.83
3.83
3.80
3.73
2.50 Dimethyl Sulfoxide-d6
1.45
1.00
0.92
1.00
1.92
0.92
3.17
3.05
3.15
9.04
f1 (ppm)


31
160.82
158.42
152.86
122.97
122.58
122.41
120.73
118.48
117.16
108.35
103.81
78.33
50.95
39.52 Dimethyl Sulfoxide-d6
36.17
36.04
28.22
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

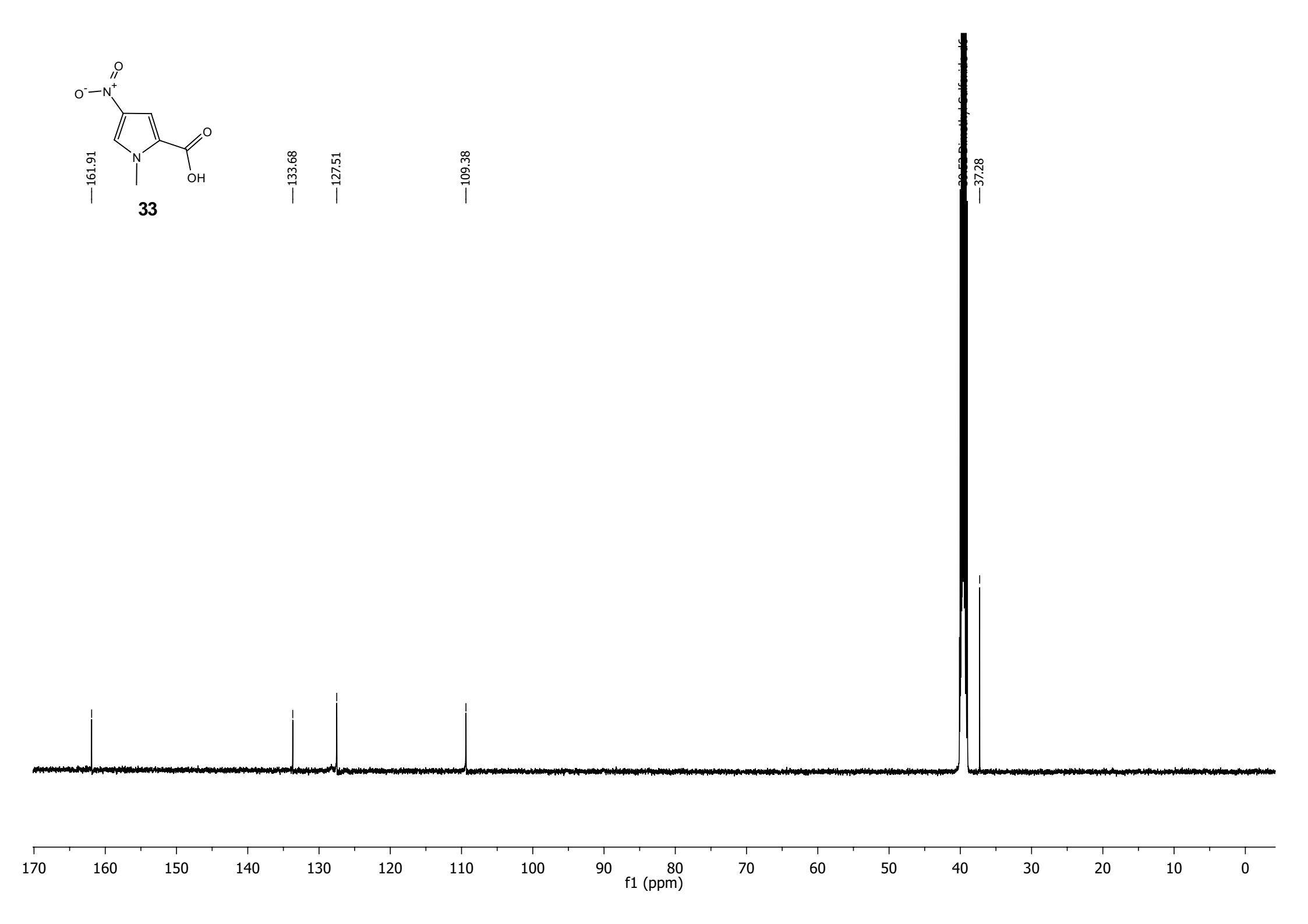

32
12.13
9.81
9.09
7.41
7.40
6.88
6.83
6.83
6.82
3.81
3.79
2.50 Dimethyl Sulfoxide-d6
1.45
0.89
1.00
0.94
1.01
0.92
1.93
2.94
2.91
9.05
f1 (ppm)

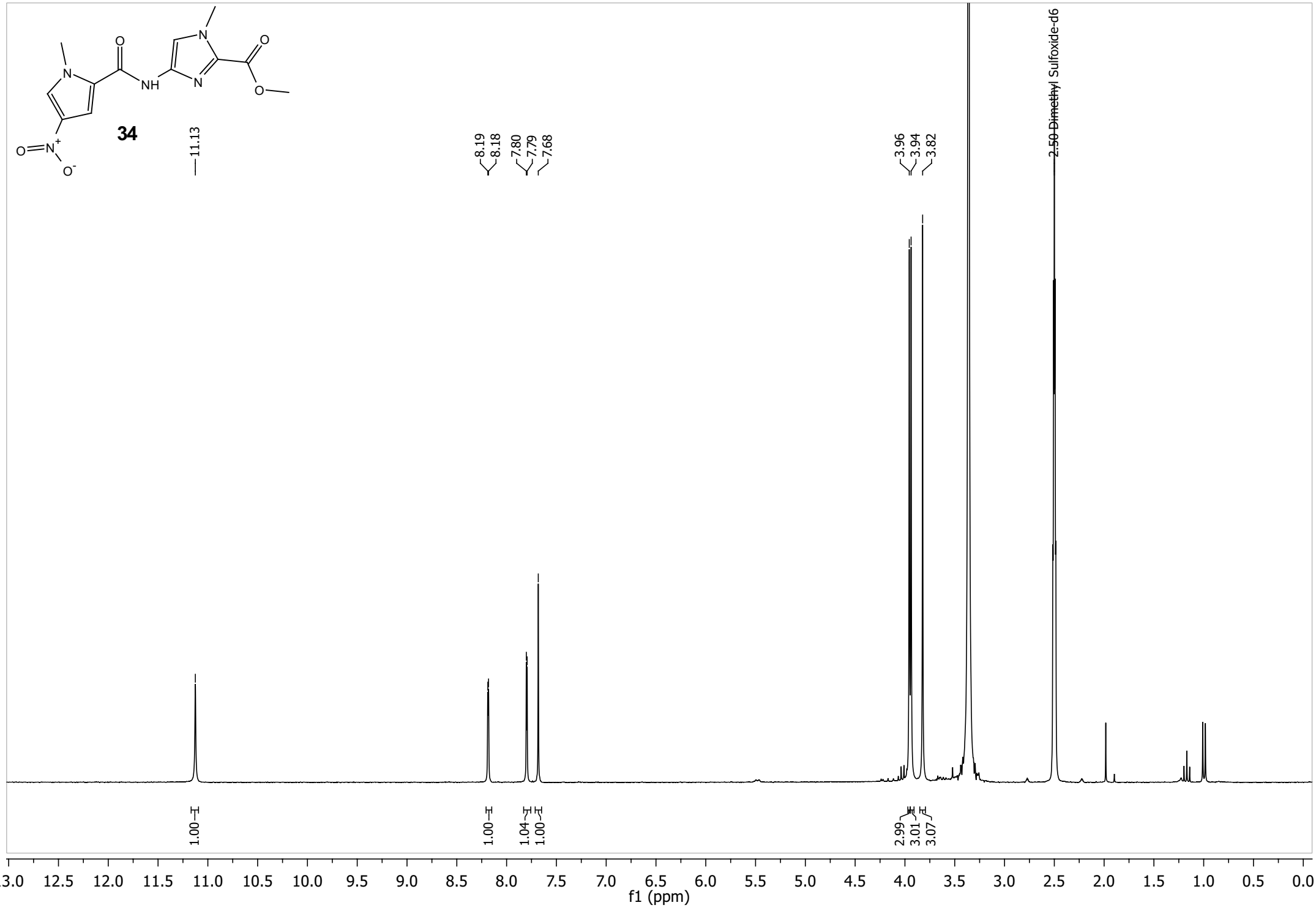

32
161.99
158.39
152.87
122.70
122.66
122.40
120.27
119.48
117.11
108.37
103.78
78.34
39.52 Dimethyl Sulfoxide-d6
36.14
36.05
28.23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

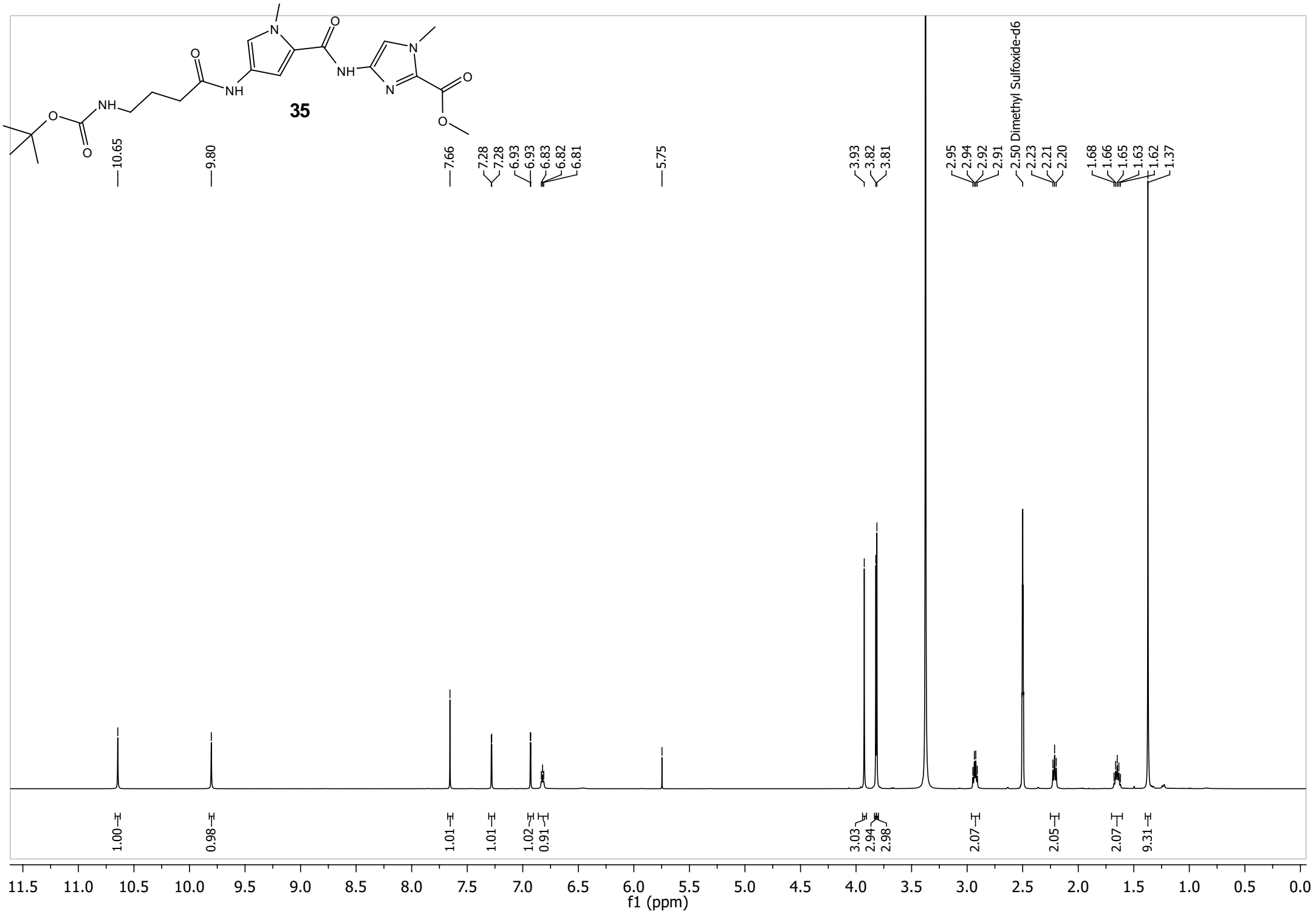


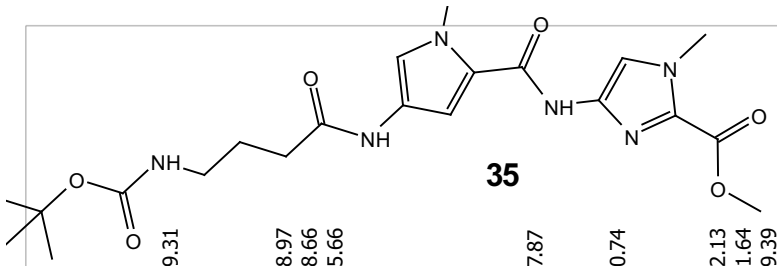
33

8.05
8.05
7.07
7.06
3.92
2.50 Dimethyl Sulfoxide-d6
1.00
1.00
3.32
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O⁻—N⁺
O
N
OH
33
161.91
133.68
127.51
109.38
37.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

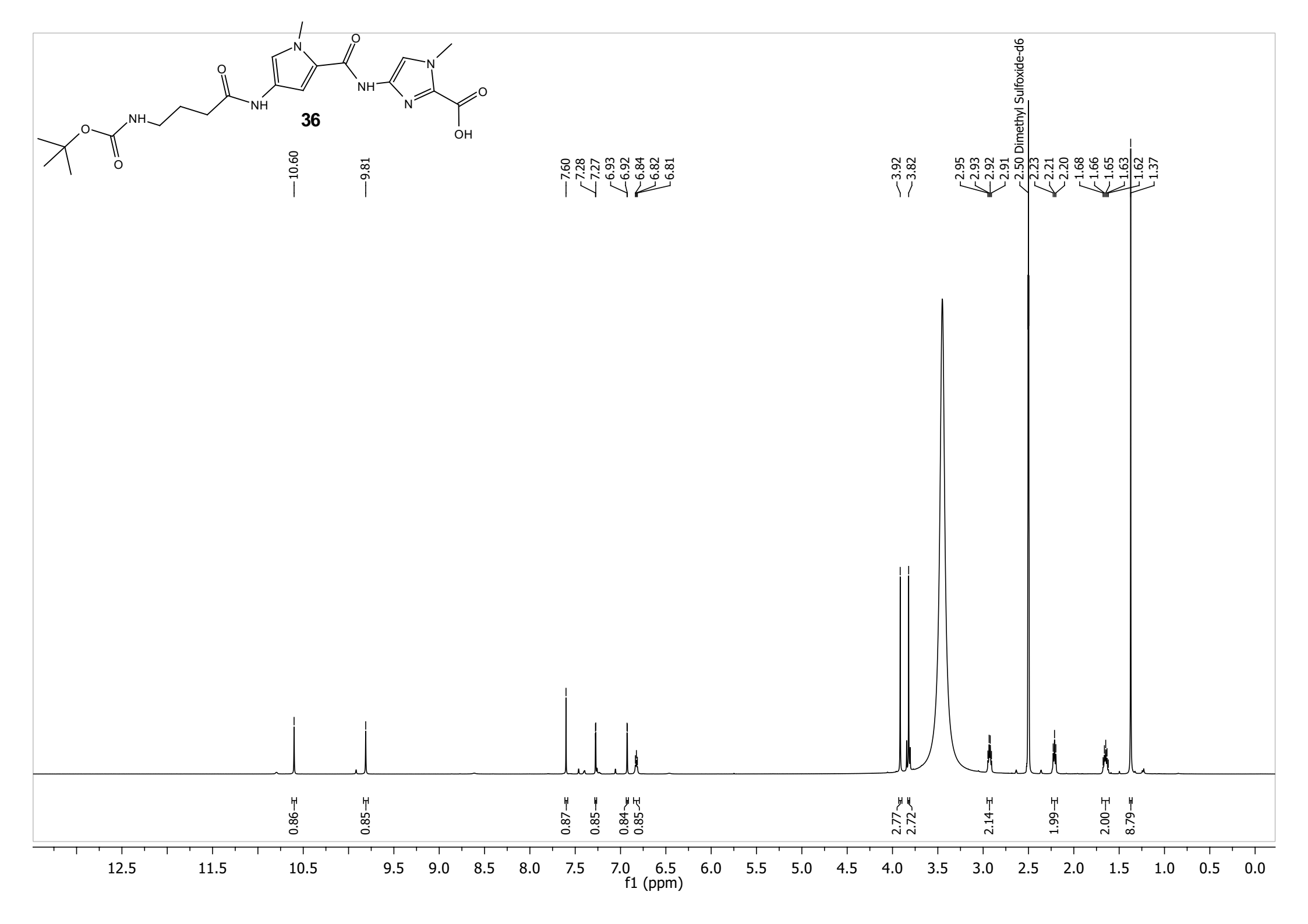

34
11.13
8.19
8.18
7.80
7.79
7.68
3.96
3.94
3.82
2.50 Dimethyl Sulfoxide-d6
1.00
1.00
1.04
1.00
2.99
3.01
3.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

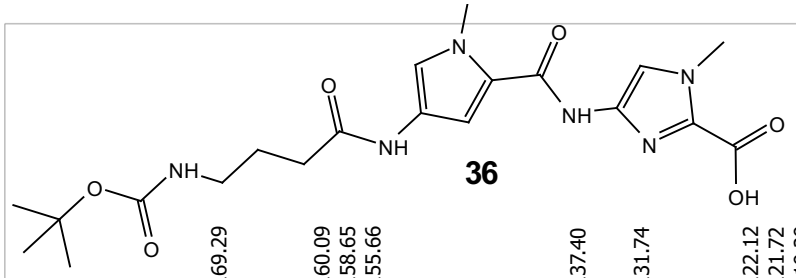

35
10.65
9.80
7.66
7.28
7.28
6.93
6.93
6.83
6.82
6.81
5.75
3.93
3.82
3.81
2.95
2.94
2.92
2.91
2.50 Dimethyl Sulfoxide-d6
2.23
2.21
2.20
1.68
1.66
1.65
1.63
1.62
1.37
1.00
0.98
1.01
1.01
1.02
0.91
3.03
2.94
2.98
2.07
2.05
2.07
9.31
f1 (ppm)



169.31
158.97
158.66
155.66
137.87
130.74
122.13
121.64
119.39
115.51
104.78
77.53
51.80
36.37
35.48
33.05
28.32
25.90

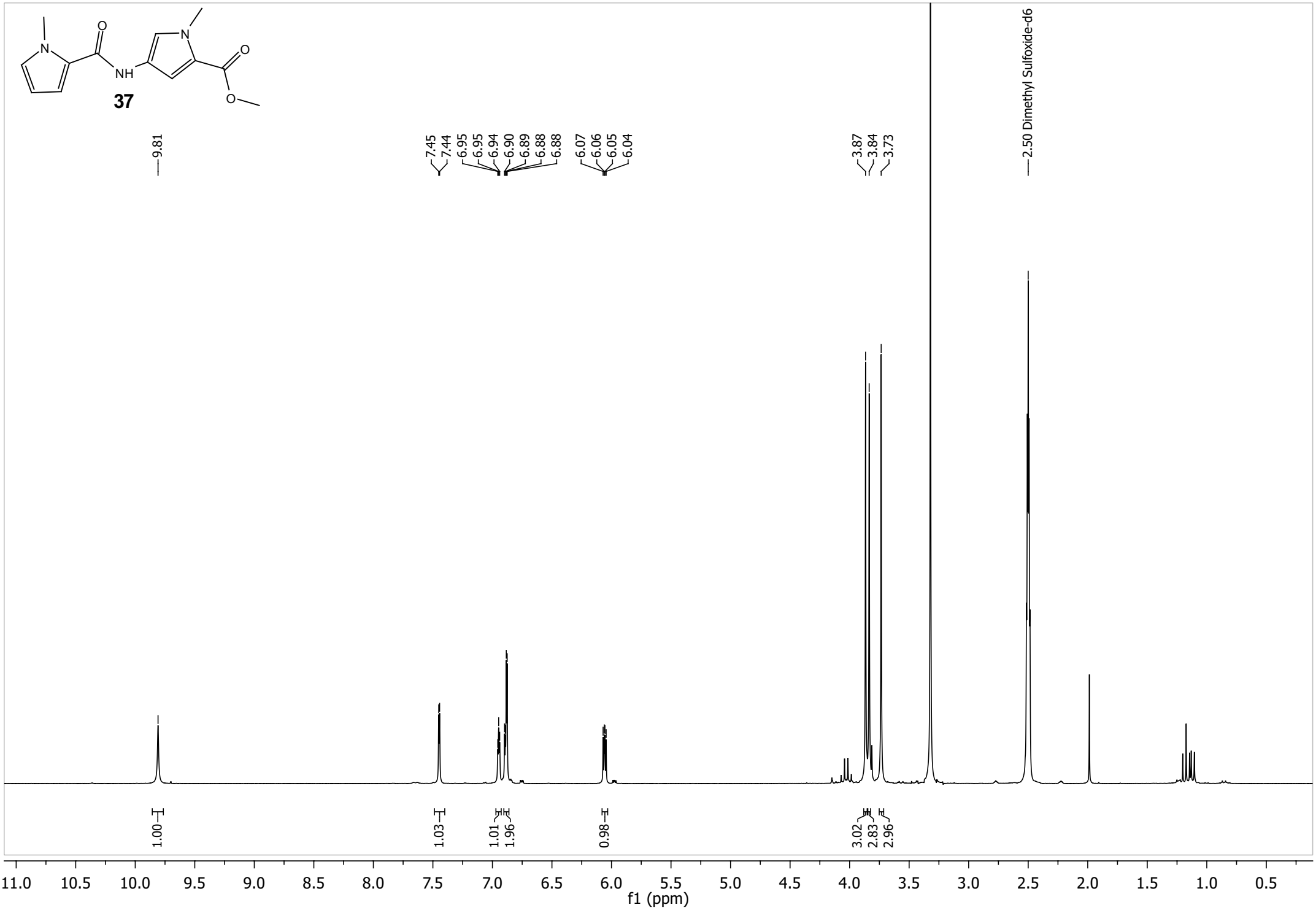
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

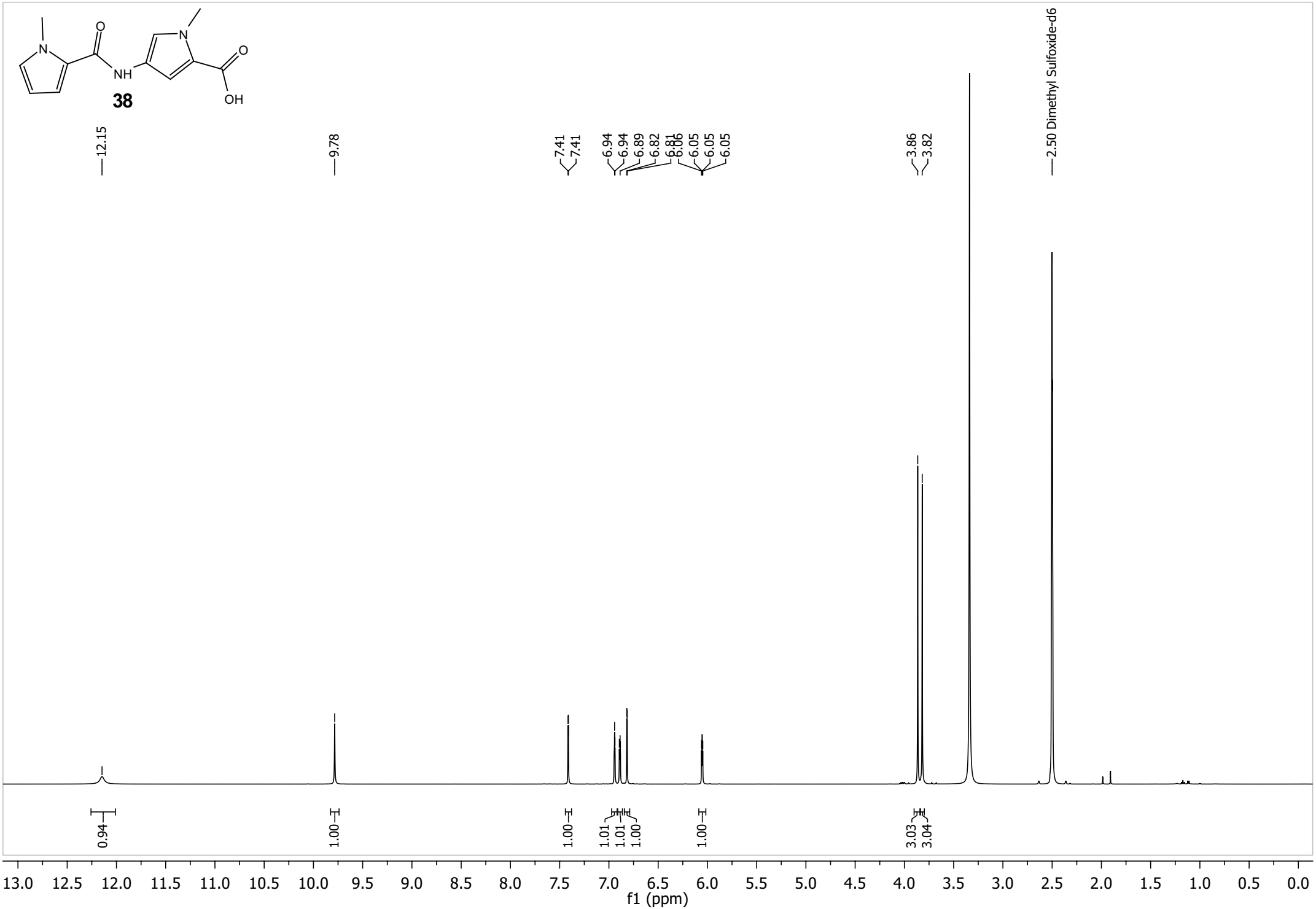

36
10.60
9.81
7.60
7.28
7.27
6.93
6.92
6.84
6.82
6.81
3.92
3.82
2.95
2.93
2.92
2.91
2.50 Dimethyl Sulfoxide-d6
2.23
2.21
2.20
1.68
1.66
1.65
1.63
1.62
1.37
0.86
0.85
0.87
0.85
0.84
0.85
2.77
2.72
2.14
1.99
2.00
8.79
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

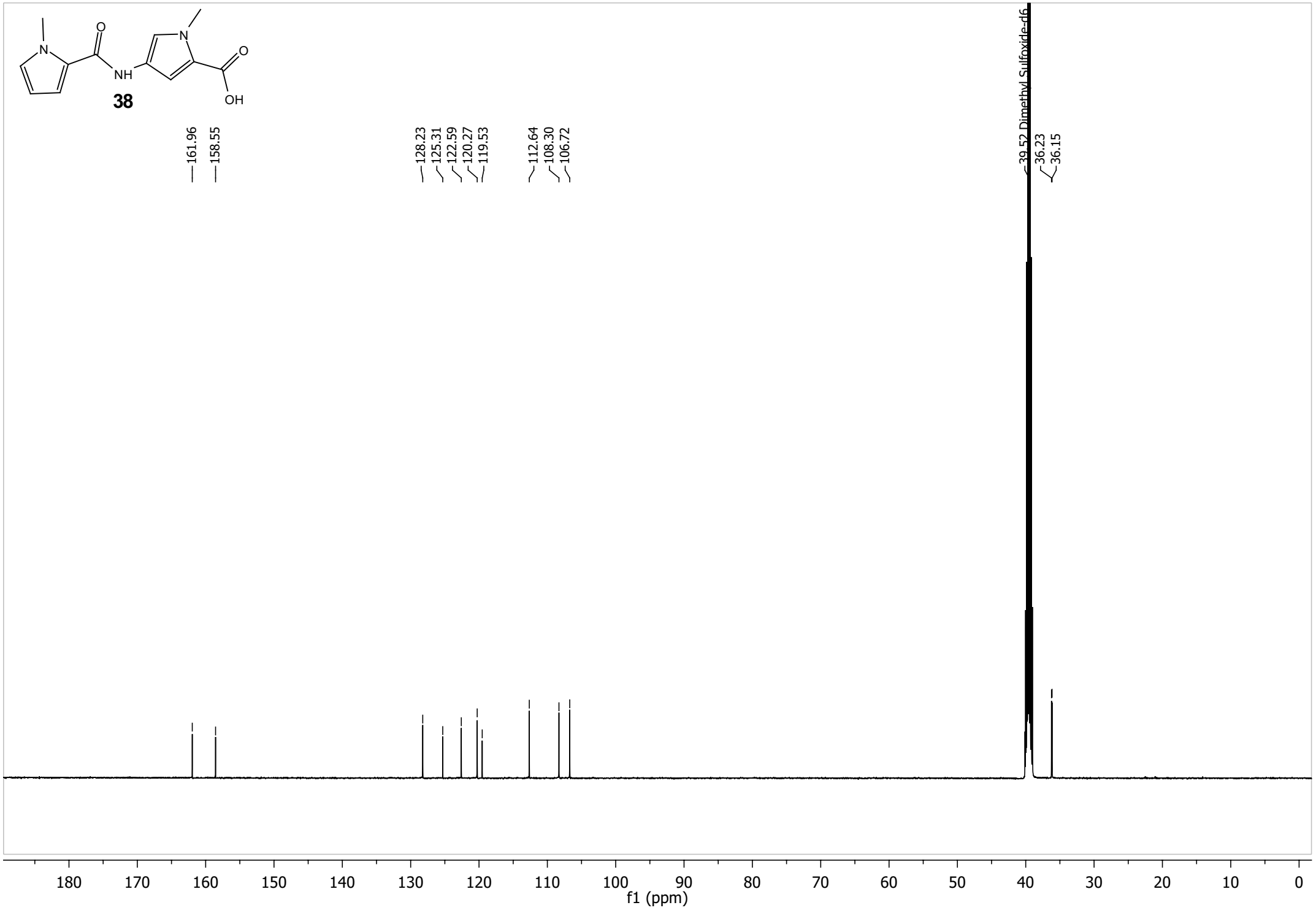


169.29
160.09
158.65
155.66
137.40
131.74
122.12
121.72
119.29
115.16
104.74
77.52
36.35
35.55
33.05
28.32
25.89

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


37
9.81
7.45
7.44
6.95
6.95
6.94
6.90
6.89
6.88
6.88
6.07
6.06
6.05
6.04
3.87
3.84
3.73
2.50 Dimethyl Sulfoxide-d6
1.00
1.03
1.01
1.96
0.98
3.02
2.83
2.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


38
12.15
9.78
7.41
7.41
6.94
6.94
6.89
6.82
6.81
6.06
6.05
6.05
6.05
3.86
3.82
2.50 Dimethyl Sulfoxide-d6
0.94
1.00
1.00
1.01
1.01
1.00
1.00
3.03
3.04
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


38
161.96
158.55
128.23
125.31
122.59
120.27
119.53
112.64
108.30
106.72
39.52 Dimethyl Sulfoxide-d6
36.23
36.15
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)