Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information for:

Access to Bicyclic Hydroxamate Macrocycles *Via* Intramolecular Aza-(4+3) Cyloaddition Reactions of Aza-Oxyallylic Cation Intermediates

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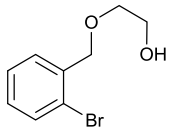
General Experimental:

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise specified. Hexafluoroisopropanol (HFIP) was purchased from SynQuest. All other reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used without any further purification. TLC information was recorded on Silicycle glass 60 F254 plates and developed by staining with $KMnO_4$ or ceric ammonium molybdate (CAM). Purification of reaction products was carried out by flash chromatography using Silicycle Siliaflash® P60 (230-400 mesh) or through a medium pressure liquid chromatography (MPLC), a Biotage® purification system equipped with 254 nm and 280 nm UV detectors and by using Biotage zip 10g Si gel column employing a hexane, ethyl acetate gradient for the mobile phase. The cartridges for Biotage purification system were purchased from Biotage®. ^1H NMR spectra were measured on Varian 400 (400 MHz), Varian MR400 (400 MHz), or Varian 500 (500 MHz) spectrometers and are reported in ppm (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad; integration; coupling constant(s) in Hz), using TMS as an internal standard (TMS at 0.00 ppm) in $CDCl_3$. ^{13}C NMR spectra were recorded on V400 or V500 spectrometer and reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm and CD_3OD at 49.86 ppm). Infrared (IR) spectra were recorded on a Nicolet 6700 FT-IR with a diamond ATR and data are reported as cm^{-1} (br = broad, s = strong). High-resolution mass spectra were obtained using an Agilent 6230 TOF LC/MS with an (atmospheric pressure photo-ionization (APPI) or electrospray (ESI) source with purine and HP-0921 as an internal calibrants.

General Procedure A: For the synthesis of alcohols (S1 and S2)[1]**:** To a mixture of sodium hydride (1.2 equiv.) in dry THF was added glycol (1 equiv.) at room temperature over 30 min and stirred for another 30 min. Then the solution was refluxed and benzyl bromide (1 equiv. was added over 2h. The mixture was refluxed overnight, cooled to room temperature, quenched with saturated ammonium chloride solution. The mixture was extracted with ethyl acetate (30 mL x 3). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified via flash column chromatography (3:7 to 1:1, hexanes: ethyl acetate) to provide the desired compounds.

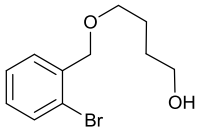
[1]*Journal of Med. Chem.* **2011**, 54, 525.

2-[(*O*-Bromophenyl)methoxy]ethanol (S1)



Prepared in 69% yield (1.92 g, 8.3 mmol) as a colorless oil from the reaction of *O*-bromo(bromomethyl)benzene (3.0 g, 12 mmol) with ethylene glycol (0.67 mL, 12 mmol) *via* general procedure **A**. R_f = 0.4 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (ddt, *J* = 7.7, 1.6, 0.8 Hz, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (dddt, *J* = 7.9, 7.3, 1.8, 0.6 Hz, 1H), 4.62 (s, 2H), 3.79 (br.s, 2H), 3.69 – 3.64 (m, 2H), 2.35 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.3, 132.6, 129.3, 129.1, 127.4, 122.9, 72.5, 71.9, 61.7; FT-IR (neat): 3366, 2921, 2863, 1592, 1568 cm^{-1}; HRESI-MS: calculated for $C_9H_{11}O_2BrNa$ $(M+Na)^+$ 252.9835, observed 252.9840.

4-[(*O*-Bromophenyl)methoxy]butanol (S2)



Prepared in 80% yield (1.66 g, 6.4 mmol) as a colorless oil from the reaction of *O*-bromo(bromomethyl)benzene (2.0 g, 8.0 mmol) with 1,4-butanediol (0.71 mL, 8.0 mmol) *via*

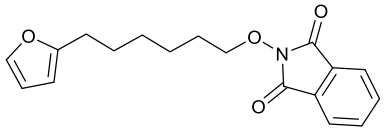
general procedure **A**. R_f = 0.30 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.17 – 7.11 (m, 1H), 4.58 (s, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 3.59 (t, *J* = 5.9 Hz, 2H), 2.15 (s, 1H), 1.79 – 1.66 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.6, 132.5, 129.0, 128.9, 127.4, 122.7, 72.3, 70.8, 62.7, 30.0, 26.5; FT-IR (neat): 3336, 2935, 2861, 1568 cm^{-1}; HRESI-MS: calculated for $C_{11}H_{15}O_2BrNa$ $(M+Na)^+$ 281.0148, observed 281.0154.

General Procedure B and C: For the synthesis of phthalimide derivatives.

Procedure B: A solution of furyl primary alkyl bromide (1 equiv.), *N*-hydroxyphthalimide (1.0 equiv.), and Et_3N (1.0 equiv.) in DMF (1M) was heated at 80°C for 3 - 12h. The reaction was monitored by TLC. DMF was removed with liquid-liquid extractions of ether and copious amounts of water. Ether was washed with brine and dried with $MgSO_4$, then filtered. The volatiles were removed under reduced pressure and the residue was purified via flash column chromatography (9:1 to 4:1, hexanes: ethyl acetate) to provide the desired compounds.

Procedure C: Diisopropyl azodicarboxylate (DIAD, 1.1 equiv.) was added dropwise to a homogeneous solution of furyl alkyl alcohol (1 equiv), N-hydroxyphthalimide (1 equiv.), and triphenylphosphine (1 equiv.) in THF (0.25 M). The mixture stirred for 24 h in a light protected round bottom flask until complete consumption of the alcohol was observed by TLC. The volatiles were removed under reduced pressure and the residue was purified via flash column chromatography (9:1 to 4:1, hexanes: ethyl acetate) to provide the desired compounds**.**

2-[6-(2-Furyl)hexyloxy]-2*H*-isoindole-1,3-dione (S3)

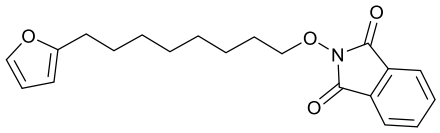


Prepared in 62% yield (2.52 g, 8.04 mmol) as a white solid from the reaction of 6-bromo-1-(2-furyl)hexane[2] (3 g, 12.97 mmol) with *N*-hydroxypthalimide (2.1 g, 13.47 mmol) *via* general procedure **B**. R_f = 0.45 (8:2, hexanes: ethyl acetate); mp 46.8 – 47.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 7.84 – 7.81 (m, 2H), 7.76 – 7.72 (m, 2H), 7.28 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.26 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (dq, *J* = 3.1, 0.9 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H) δ 2.63 (t, *J* = 7.5 Hz, 2H), 1.82 –

1.76 (m, 2H), 1.67 (pent *J* = 15.2 Hz, 2H), 1.53 (m, 2H), 1.42 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6, 156.3, 140.6, 134.4, 128.9, 123.4, 110.0, 104.6, 78.4, 28.8, 28.0, 27.8, 27.8, 25.3; FT-IR (neat): 2934, 2892, 2863, 1786, 1729, 1600 cm^{-1}; HRESI-MS: calculated for $C_{18}H_{19}NO_4Na$ $(M+Na)^+$ 336.1206, observed 336.1213.

[2]6-bromo-1-(2-furyl)hexane was prepared according to the procedure described in reference, *J. Nat. Prod.,* **2009,** 72, 857.

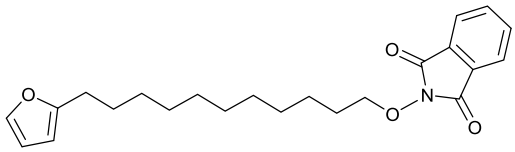
2-[8-(2-Furyl)octyloxy]-2*H*-isoindole-1,3-dione (S4)



Prepared in 68% yield (1.79 g, 5.25 mmol) as a white solid from the reaction of 8-bromo-1-(2-furyl)octane[3] (2.0 g, 7.72 mmol) with *N*-hydroxypthalimide (1.26 g, 7.72 mmol) *via* general procedure **B**. R_f = 0.28 (7:3, hexanes: ethyl acetate); mp 58.5 – 59.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 - 7.82 (m, 2H), 7.76-7.73 (m, 2H), 7.29 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (dq, *J* = 2.8, 0.8 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.48 (p, *J* = 7.4 Hz, 2H), 1.38-1.33 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.7, 156.5, 140.6, 134.4, 129.0, 123.5, 110.0, 104.5, 78.6, 29.2, 29.2, 29.1, 28.1, 28.0, 27.9, 25.5; FT-IR (neat): 2935, 2893, 2869, 1787, 1719, 1609 cm^{-1}; HRESI-MS: calculated for $C_{20}H_{23}NO_4Na$ $(M+Na)^+$ 364.1513, observed 364.1519.

[3]8-bromo-1-(2-furyl)octane was prepared according to the procedure described in reference, *J. Nat. Prod.,* **2009,** 72, 857.

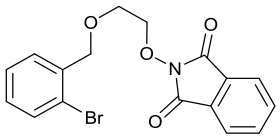
2-[11-(2-Furyl)undecyloxy]-2*H*-isoindole-1,3-dione (S5)



Prepared in 98% yield (4.7 g, 13.0 mmol) as a white solid from the reaction of 11-bromo-1-(2-furyl)undecane (4.0 g, 13.33 mmol) with *N*-hydroxypthalimide (2.18 g, 13.33 mmol) *via* general procedure **B**. R_f = 0.42 (7:3, hexanes: ethyl acetate); mp 83.3 – 85.2 °C; ^{1}H NMR (500 MHz,

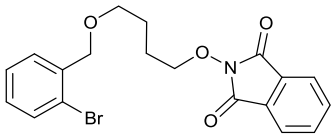
$CDCl_3$): δ 7.85 – 7.81 (m, 2H), 7.76 – 7.72 (m, 2H), 7.28 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.96 (dq, *J* = 3.1, 0.9 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.81 (p, *J* = 6.8 Hz, 2H), 1.63 (p, *J* = 7.7 Hz, 2H), 1.48 (p, *J* = 7.2 Hz, 2H), 1.40 – 1.24 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6, 156.6, 140.6, 134.4, 129.0, 123.4, 110.0, 104.5, 78.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 28.2, 28.0, 28.0, 25.5; FT-IR (neat): 2923, 2850, 1788, 1726 cm^{-1}; HRESI-MS: calculated for $C_{23}H_{30}NO_4$ $(M+H)^+$ 384.2169, observed 384.2177.

2-{2-[(*O*-Bromophenyl)methoxy]ethoxy}-2*H*-isoindole-1,3-dione (S6)



Prepared in 85% yield (1.79 g, 4.78 mmol) as a white solid from the reaction of 4-[(*O*-bromophenyl)methoxy]butanol **S1** (1.3 g, 5.63 mmol) with *N*-hydroxyphthalimide (0.92 g 5.64 mmol) *via* general procedure **C**. R_f = 0.52 (2:1, hexanes: ethyl acetate); mp 71.2 – 72.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.77 (m, 2H), 7.75 – 7.69 (m, , 2H), 7.48 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.17 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 (td, *J* = 7.7, 1.8 Hz, 1H), 4.61 (s, 2H), 4.47 – 4.45 (noform, 2H), 3.97 – 395 (noform, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.3, 137.1, 134.4, 132.3, 128.8, 128.8, 128.8, 127.3, 123.4, 122.3, 77.0, 72.4, 69.0; FT-IR (neat): 3076, 2984, 2928, 2863, 1785, 1722, 1603 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{14}NO_4BrNa$ $(M+Na)^+$ 397.9998, observed 398.0000.

2-{4-[(*O*-Bromophenyl)methoxy]butoxy}-2*H*-isoindole-1,3-dione (S7)



Prepared in 85% yield (2.38 g, 5.9 mmol) as a white solid from the reaction of **S2** (1.8 g, 6.95 mmol) with *N*-hydroxypthalimide (1.2 g, 7.3 mmol) *via* general procedure **C**. R_f = 0.52 (7:3, hexanes: ethyl acetate); mp 89.9 – 87.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 - 7.81 (m, 2H), 7.76 -7.72 (m, 2H), 7.51 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 4.56 (s, 2H), 4.26 (t, *J* = 6.3 Hz, 2H), 3.65 (t, *J* = 5.9 Hz, 2H), 1.97 – 1.86 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6, 137.8, 134.4, 132.4, 129.0, 129.0,

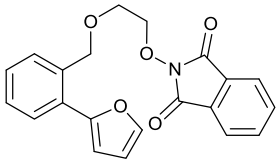
128.8, 127.4, 123.5, 122.6, 78.2, 72.1, 70.2, 25.9, 25.2; FT-IR (neat): 2958, 2923, 2860, 2796, 1782, 1734, 1612 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{18}NO_4BrNa$ $(M+Na)^+$ 426.0311, observed 426.0308.

General Procedure D: For Stille coupling reactions[4]

To a solution of *o*-bromobenzyl derivative (1.1 equiv.), $Pd(dba)_2$ (2 mol%), triphenyl phosphine (12.5 mol%) in dry toluene under nitrogen was added furylstannane (1equiv.) via syringe and the reaction was stirred for 30 min at rt then refluxed overnight at 110°C. The reaction mixture was cooled to room temperature, diluted with ether and saturated KF solution was added. The organic layer was separated, washed with water, HCl (1 M), water, brine and dried over sodium sulfate. The residue was purified via flash column chromatography (8:2, hexanes: ethyl acetate) to provide desired compounds.

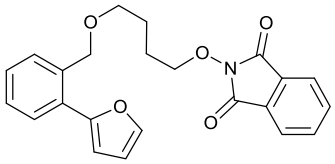
[4] *Tetrahedron lett.*, **1999**, 40,4769.

2-(2-{[*O*-(2-Furyl)phenyl]methoxy}ethoxy)-2*H*-isoindole-1,3-dione (S8)



Prepared in 50% yield (0.67 g, 1.86 mmol) as a white solid from the reaction of 2-{2-[(*O*-bromophenyl)methoxy]ethoxy}-2*H*-isoindole-1,3-dione **S6** (1.4 g, 3.72 mmol) with tributyl(2-furyl)stannane (0.12 mL, 3.72 mmol) *via* general procedure **D**. R_f = 0.50 (7:3, hexanes: ethyl acetate); mp 110.5 – 112.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.72 – 7.69 (m, 2H), 7.63 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.5, Hz, 1H), 7.29 (td, *J* = 7.6, 1.4 Hz, 1H), 7.19 (td, *J* = 7.5, 1.4 Hz, 1H), 6.61 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.69 (s, 2H), 4.44 – 4.42 (nofrom, 2H), 3.92 – 3.91 (nofrom, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.4, 152.3, 142.2, 134.3, 133.9, 129.9, 129.2, 128.9, 127.7, 127.4, 127.3, 123.4, 111.5, 109.1, 77.1, 71.6, 68.4; FT-IR (neat): 2948, 2891, 2863, 1786, 1724, 1606 cm^{-1}; HRESI-MS: calculated for $C_{21}H_{17}NO_5Na$ $(M+Na)^+$ 386.0999, observed 386.1010.

2-(4-{[*O*-(2-Furyl)phenyl]methoxy}butoxy)-2*H*-isoindole-1,3-dione (S9)

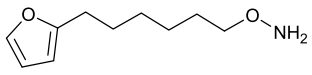


Prepared in 44% yield (0.98 g, 2.5 mmol) as a sticky liquid from the reaction of 2-{4-[(*O*-bromophenyl)methoxy]butoxy}-2***H***-isoindole-1,3-dione **S7** (2.3 g, 5.7 mmol) with tributyl(2-furyl)stannane (1.8 mL, 5.7 mmol) *via* general procedure D. R_f = 0.50 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.80 (m, 2H), 7.77 – 7.71 (m, 2H), 7.67 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.3 (td, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.3 (td, *J* = 7.4, 1.6 Hz, 1H), 6.62 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.65 (s, 2H), 4.22 (t, *J* = 6.1 Hz, 2H), 3.61 (t, *J* = 5.8 Hz, 2H), 1.92 – 1.85 (m, 4H), 1.38 – 1.35 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.6, 152.6, 142.2, 134.4, 134.4, 129.9, 129.3, 128.9, 127.7, 127.6, 127.4, 123.4, 111.6, 109.0, 78.2, 71.3, 69.7, 26.0, 25.2 cm^{-1}; FT-IR (neat): 2949, 2861, 1787, 1726, 1607 cm^{-1}; HRESI-MS: calculated for $C_{23}H_{21}NO_5Na$ $(M+Na)^+$ 414.1312, observed 414.1310.

General Procedure E: For the synthesis of alkylhydroxyl amines

To a solution of *O*-alkyl-*N*-hydroxyphthalimide (1 equiv.) in 10% MeOH in dichloromethane or chloroform was added hydrazine monohydrate ($N_2H_4{\cdot}H_2O$, 3 equiv.) dropwise with vigorous stirring at room temperature for 1-2 h. The completion of reaction was monitor by TLC. The white ppt was filtered. The volatiles of the filtrate were removed under reduced pressure and the residue was purified via flash column chromatography (4:1 to 1:1, hexanes: ethyl acetate) to provide *O*-alkyl hydroxylamines.

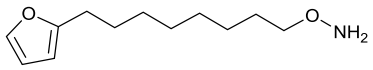
***O*-6-(2-Furyl)hexylhydroxylamine (S10)**



Prepared in 80% yield (0.56 g, 3.06 mmol) as a colorless oil from the reaction of 2-[6-(2-furyl)hexyloxy]-2*H*-isoindole-1,3-dione **S3** (1.2 g, 3.83 mmol) with hydrazine monohydrate (0.55 mL, 11.4 mmol) *via* general procedure **E**. R_f = 0.40 (6:4, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (dq, *J* = 3.0, 0.9 Hz, 1H), 5.34 (s, 2H), 3.65 (t, *J* = 6.7 Hz, 2H), 2.62 (t, *J* = 7.6 Hz,

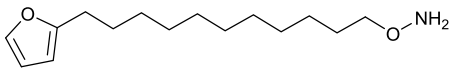
2H), 1.67 – 1.57 (m, 4H), 1.38 – 1.35 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 140.6, 110.0, 104.6, 76.0, 29.0, 28.3, 27.9, 27.9, 25.7; FT-IR (neat): 3314, 2931, 2857, 1592 cm^{-1}; HRESI-MS: calculated for $C_{10}H_{18}NO_2$ $(M+H)^+$ 184.1332, observed 184.1336.

***O*-8-(2-Furyl)octylhydroxylamine (S11)**



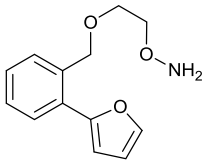
Prepared in 84% yield (0.52 g, 2.46 mmol) as a colorless oil from the reaction of 2-[8-(2-furyl)octyloxy]-2*H*-isoindole-1,3-dione **S4** (1.0 g, 2.93 mmol) with hydrazine monohydrate (0.42 mL, 8.8 mmol) *via* general procedure **E**. R_f = 0.4 (6:4, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.96 (dq, *J* = 2.8, 0.8 Hz, 1H), 5.34 (s, 2H), 3.65 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.59 – 1.54 (m, 2H), 1.31 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5, 140.6, 110.0, 104.5, 76.1, 29.4, 29.3, 29.1, 28.4, 28.0, 27.9, 26.0; FT-IR (neat): 2926, 2854, 1593 cm^{-1}; HRESI-MS: calculated for $C_{12}H_{22}NO_2$ $(M+H)^+$ 212.1645, observed 212.1652.

***O*-11-(2-Furyl)undecylhydroxylamine (S12)**



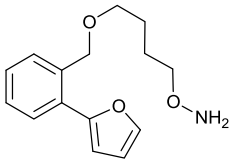
Prepared in 97% yield (3.2 g, 12.7 mmol) as a colorless oil from the reaction of 2-[11-(2-furyl)undecoxy]-2*H*-isoindole-1,3-dione **S5** (4.7 g, 13.08 mmol) with hydrazine monohydrate (1.9 mL, 39.2 mmol) *via* general procedure **E**. R_f = 0.46 (1:1, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.96 (dq, *J* = 3.1, 0.9 Hz, 1H), 5.34 (s, 2H), 3.65 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.53 (m, 4H), 1.34 – 1.25 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 140.5, 109.9, 104.4, 76.1, 29.5, 29.5, 29.5, 29.5, 29.3, 29.1, 28.4, 28.0, 27.9, 26.0 ; FT-IR (neat): 2923, 2853, 1594 cm^{-1}; HRESI-MS: calculated for $C_{15}H_{28}NO_2$ $(M+H)^+$ 254.2120, observed 254.2118.

***O*-2-{[*O*-(2-Furyl)phenyl]methoxy}ethylhydroxylamine (S13)**



Prepared in 78% yield (0.30 g, 1.28 mmol) as a colorless oil from the reaction of 2-{2-[(*O*-bromophenyl)methoxy]ethoxy}-2*H*-isoindole-1,3-dione **S8** (0.6 g, 1.65 mmol) with hydrazine monohydrate (0.26 mL, 4.95 mmol) *via* general procedure **E**. R_f = 0.38 (1:1, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.35 (td, *J* = 7.5, 1.6 Hz, 1H), 7.31 (td, *J* = 7.4, 1.6 Hz, 1H), 6.67 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.47 (s, 2H), 4.70 (s, 2H), 3.91 – 3.85 (noform, 2H), 3.72 – 3.67 (noform, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.6, 142.3, 134.3, 130.1, 129.5, 127.9, 127.6, 127.6, 111.6, 109.1, 74.8, 71.6, 68.5; FT-IR (neat): 3313, 3142, 3062, 2914, 2862, 1979, 1584 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{15}NO_3Na$ $(M+Na)^+$ 256.0944, observed 256.0944.

***O*-4-{[*O*-(2-Furyl)phenyl]methoxy}butylhydroxylamine (S14)**



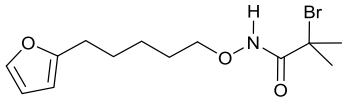
Prepared in 82% yield (0.26 g, 1.05 mmol) as colorless oil from the reaction of 2-(4-{[*O*-(2-furyl)phenyl]methoxy}butoxy)-2H-isoindole-1,3-dione **S9** (0.5 g, 1.28 mmol) with hydrazine monohydrate (0.2 mL, 3.84 mmol) *via* general procedure **E**. R_f = 0.27 (1:1, hexanes: ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.53– 7.51 (m 2H), 7.34 (td, *J* = 7.3, 1.7 Hz, 1H), 7.30 (td, *J* = 7.3, 1.6 Hz, 1H), 6.63 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.31 (s, 2H), 4.64 (s, 2H), 3.70 – 3.64 (noform, 2H), 3.57 – 3.50 (noform, 2H), 1.71 – 1.65 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 142.2, 134.7, 129.9, 129.2, 127.7, 127.5, 127.4, 111.5, 108.9, 75.8, 71.3, 70.1, 26.4, 25.2; FT-IR (neat): 3312, 3142, 3062, 2917, 2857, 1722, 1584 cm^{-1}; HRESI-MS: calculated for $C_{15}H_{19}NO_3Na$ $(M+Na)^+$ 284.1257, observed 284.1267.

General Procedure F: For the synthesis of α-haloamides.

To a solution of *O*-alkyl hydroxylamine (1 equiv.) in dichloromethane (0.25 M) was added triethylamine (1 equiv.) and acid chloride (1 equiv) dropwise at 0°C and stirred up to 1h at room temperature. The consumption of starting material was confirmed by TLC. The volatiles were removed under reduced pressure and the residue was purified *via* flash column chromatography (1:9 to 4:1, hexanes: ethyl acetate) to provide the desired compounds.

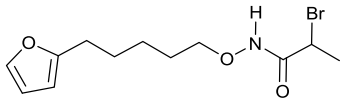
O-5-(2-furyl)pentylhydroxylamine has been prepared according to literature procedure.
[5]*Synthesis*, **2013**, 45,1825.

1-[*O*-5-(2-Furyl)pentyloxyamino]-2-bromo-2-methyl-1-propanone (S15)



Prepared in 66% yield (0.55 g, 1.72 mmol) as a colorless oil from the reaction of *O*-5-(2-furyl)pentylhydroxylamine (0.40 g, 2.61 mmol) with 2-bromo-2-methylpropionyl bromide (0.32 mL, 2.61 mmol) via general procedure **F**. R_f = 0.52 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.27 (s, 1H), 7.29 (dd, *J* =2.0, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9, 1H), 5.98 (dq, *J* = 3.0, 1.0 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 6H), 1.78 – 1.61 (m, 4H), 1.53 – 1.35 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 156.0, 140.7, 110.0, 104.8, 76.6, 59.4, 32.4, 30.6, 27.8, 27.7, 25.3; FT-IR (neat): 3230, 2935, 2862, 1735, 1662, 1596 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{20}BrNNaO_3$ $(M+Na)^+$ 340.0519, observed 340.0516.

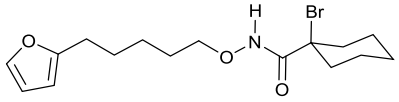
(±)-1-[*O*-5-(2-Furyl)pentyloxyamino]-2-bromo-1-propanone (S16)



Prepared in 62% yield (0.47 g, 1.56 mmol) as a colorless oil from the reaction of *O*-5-(2-furyl)pentylhydroxylamine (0.37 g, 2.48 mmol) with 2-bromopropionyl bromide (0.26 mL, 2.48 mmol) *via* general procedure **F**. R_f = 0.3 (7:3, hexanes: ethyl acetate); mp 52.7 – 55.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.29 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.98 (dq, *J* = 3.2, 0.9 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.86 (d, *J* = 6.9 Hz, 3H), 1.74 – 1.62 (m, 4H), 1.49 – 1.39 (m, 2H); ^{13}C NMR (126 MHz,

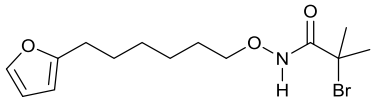
CD_3OD): δ 169.3, 157.3, 142.0, 111.2, 106.0, 77.2, 40.8, 29.1, 28.9, 28.8, 26.5, 22.2; FT-IR (neat): 3184, 3013, 2942, 2866, 1662, 1596 cm^{-1}; HRESI-MS: calculated for $C_{12}H_{18}NO_3BrNa$ $(M+Na)^+$ 326.0362, observed 362.0367.

[*O*-5-(2-Furyl)pentyloxyamino](1-bromocyclohexyl)formaldehyde (S17)



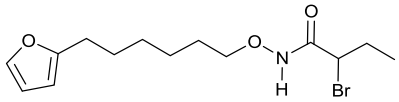
Prepared in 88% yield (0.37 g, 1.02 mmol) as a colorless oil from the reaction of *O*-5-(2-furyl)pentylhydroxylamine (0.2 g, 1.18 mmol) with 2-bromocyclohexanoyl chloride (0.27 g, 1.18 mmol) *via* general procedure **F**. R_f = 0.45 (8: 2, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (s, 1H), 7.29 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.98 (dq, *J* = 3.2, 0.9 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.15 (ddd, *J* = 14.8, 11.0, 4.0 Hz, 2H), 2.04 (br.d, *J* = 14.4 Hz, 2H), 1.79 – 1.64 (m, 9H), 1.50 – 1.42 (m, 2H), 1.38 – 1.30 (m, 1H); ^{13}C NMR (126 MHz, CD_3OD): δ 171.2, 157.9, 142.6, 111.8, 106.5, 77.5, 66.0, 39.5, 29.7, 29.6, 29.4, 27.2, 26.5, 25.3; FT-IR (neat): 3233, 2934, 2859, 1654, 1595 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{25}NO_3Br(M+H)^+$ 358.1012, observed 358.1001.

1-[*O*-6-(2-Furyl)hexyloxyamino]-2-bromo-2-methyl-1-propanone (S18)



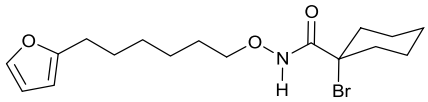
Prepared in 76% yield (0.27 g, 0.83 mmol) as a colorless oil from the reaction of *O*-6-(2-furyl)hexylhydroxylamine **S10** (0.2 g, 1.09 mmol) with 2-bromo-2-methylpropionyl bromide (0.14 mL, 1.1 mmol) *via* general procedure **F**. R_f = 0.74 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.29 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (dq, *J* = 2.3, 1.1 Hz, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H, 2H), 1.96 (s, 6H), 1.71 – 1.62 (m, 4H), 1.47 – 1.35 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7, 156.3, 140.6, 110.0, 104.6, 76.7, 32.3, 30.8, 28.8, 27.9, 27.8, 27.8, 25.5; FT-IR (neat): 3234, 2931, 2857, 1737, 1663, 1596 cm^{-1}; HRESI-MS: calculated for $C_{14}H_{23}NO_3Br$ $(M+H)^+$ 332.0856, observed 332.0855.

(±)-1-[*O*-6-(2-Furyl)hexyloxyamino]-2-bromo-1-butanone (S19)



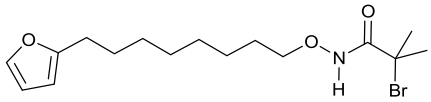
Prepared in 76% yield (0.55 g, 1.66 mmol) as a colorless oil from the reaction of *O*-6-(2-furyl)hexylhydroxylamine **S10** (0.4 g, 2.18 mmol) with 2-bromobutanoyl bromide (0.27 mL, 2.18 mmol) *via* general procedure **F**. R_f = 0.73 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.34 (s, 1H), 7.29 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.96 (br.d, *J* = 3.0, 1H), 4.19 (t, *J* = 6.5, 1H), 4.18 (t, *J* = 7.0 Hz, 1H), 3.93 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.15 (dq, *J* = 14.1, 7.1 Hz, 1H), 2.06 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.70 – 1.61 (m, 3H), 1.45 – 1.33 (m, 4H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.6, 156.3, 140.6, 110.1, 104.6, 76.8, 48.8, 28.8, 28.8, 27.9, 27.8, 27.8, 25.5, 11.7; FT-IR (neat): 3171, 29345, 2859, 1663, 1596 cm^{-1}; HRESI-MS: calculated for $C_{14}H_{23}NO_3Br$ $(M+H)^+$ 332.0856, observed 332.0858.

[*O*-6-(2-Furyl)hexyloxyamino](1-bromocyclohexyl)formaldehyde (S20)



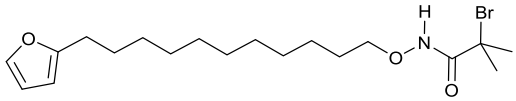
Prepared in 80% yield (0.32 g, 0.87 mmol) as a colorless oil from the reaction of *O*-6-(2-furyl)hexylhydroxylamine **S10** (0.2 g, 1.09 mmol) with 2-bromocyclohexanoyl chloride (0.25 g, 1.10 mmol) *via* general procedure **F**. R_f = 0.42 (8:2, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.29 (dd, *J* = 2.0, 0.7 Hz, 1H), 6.27 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.97 (dq, *J* = 3.1, 0.9 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.16 (ddd, *J* = 14.8, 10.9, 4.1 Hz, 2H), 2.04 (br.d, *J* = 14.3 Hz, 2H), 1.80 – 1.62 (m, 9H), 1.47 – 1.27 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7, 156.3, 140.7, 110.0, 104.6, 76.7, 69.0, 38.0, 28.9, 27.9, 27.9, 27.8, 25.6, 24.6, 22.4; FT-IR (neat): 3229, 2932, 2858, 1732, 1658, 1596 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{27}NO_3Br$ $(M+H)^+$ 372.1169, observed 372.1164.

1-[*O*-8-(2-Furyl)octyloxyamino]-2-bromo-2-methyl-1-propanone (S21)



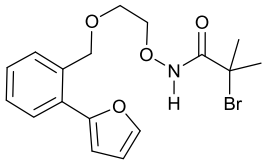
Prepared in 73% yield (0.37 g, 1.03 mmol) as a colorless oil from the reaction of *O*-8-(2-furyl)octylhydroxylamine **S11** (0.3 g, 1.42 mmol) with 2-bromo-2-methylpropionyl bromide (0.18 mL, 1.43 mmol) *via* general procedure **F**. R_f = 0.42 (7: 3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 1H), 7.29 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (dt, *J* = 3.2, 0.9 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 6H), 1.71 – 1.58 (m, 4H), 1.44 – 1.28 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7, 156.4, 140.6, 110.0, 104.5, 76.7, 59.3, 32.3, 30.8, 29.2, 29.2, 29.0, 28.0, 27.9, 25.7; FT-IR (neat): 3232, 2928, 2855, 1737, 1663, 1596 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{27}NO_3Br$ $(M+H)^+$ 360.1169, observed 360.1176.

1-[*O*-11-(2-Furyl)undecyloxyamino]-2-bromo-2-methyl-1-propanone (S22)



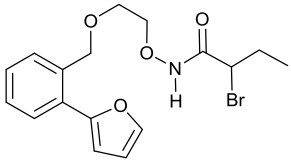
Prepared in 82% yield (0.65 g, 1.62 mmol) as a colorless oil from the reaction of *O*-11-(2-furyl)undecylhydroxylamine **S12** (0.5 g, 1.97 mmol) with 2-bromo-2-methylpropionyl bromide (0.16 mL, 1.97 mmol) *via* general procedure **F**. R_f = 0.64 (7: 3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.29 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.26 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.96 (dq, *J* = 3.3, 0.8 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.96 (s, 6H), 1.71 – 1.57 (m, 4H), 1.43 – 1.25 (m, 14H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.8, 156.6, 140.6, 110.0, 104.5, 76.9, 59.5, 32.4, 30.8, 29.5, 29.5, 29.4, 29.4, 29.2, 28.1, 28.0, 28.0, 25.8; FT-IR (neat): 3285, 2926, 2848, 1737, 1667 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{33}NO_3Br$ $(M+H)^+$ 402.1638, observed 402.1639.

1-{*O*-2-[*O*-(2-Furyl)phenoxy]ethoxyamino}-2-bromo-2-methyl-1-propanone (S23)



Prepared in 85% yield (0.14 g, 0.36 mmol) as a colorless oil from the reaction of *O*-2-{[*O*-(2-furyl)phenyl]methoxy}ethylhydroxylamine **S13** (0.1 g, 0.43 mmol) with 2-bromo-2-methylpropionyl bromide (54 µL 0.43 mmol) *via* general procedure **F**. R_f = 0.38 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.69 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.53 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.51 (dd, *J* = 7.5 , 0.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 6.66 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.51 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.73 (s, 2H), 4.14 – 4.11 (noform, 2H), 3.82 – 3.79 (noform, 2H), 1.87 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9, 152.4, 142.2, 133.5, 130.1, 129.7, 128.0, 127.6, 127.5, 111.4, 108.8, 74.9, 71.8, 69.1, 58.8, 32.1; FT-IR (neat): 3207, 3000, 2935, 2882, 1663, 1513, 1503 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{20}NO_4BrNa$ $(M+Na)^+$ 404.0468, observed 404.0467.

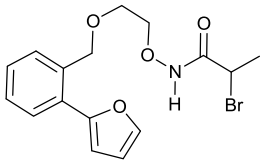
(±)-1-{*O*-2-[*O*-(2-Furyl)phenoxy]ethoxyamino}-2-bromo-1-butanone (S24)



Prepared in 82% yield (0.13 g, 0.35 mmol) as a colorless oil from the reaction of *O*-2-{[*O* -(2-furyl)phenyl]methoxy}ethylhydroxylamine **S13** (0.1 g, 0.43 mmol) with 2-bromobutanoyl bromide (52 µL 0.43 mmol) *via* general procedure **F**. R_f = 0.52 (6:4, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.5 Hz,1H), 7.36 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.70 (s, 2H), 4.10 (t, *J* = 4.1 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 1H), 3.76 (t,*J* = 7.3, 4.1 Hz, 2H), 2.11 – 2.03 (m, 1H), 1.96 (dq, *J* = 14.7, 7.3 Hz, 1H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.2, 152.5, 142.4, 133.7, 130.2, 129.8, 128.2, 127.7, 127.7, 111.6, 109.0, 75.2, 71.9, 68.9, 48.6, 28.7, 11.7; FT-IR (neat): 3165, 2970, 2934, 2874,

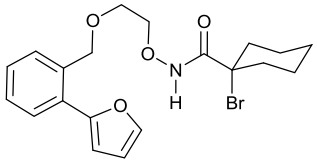
1664, 1501 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{20}NO_4BrNa$ $(M+Na)^+$ 404.0468, observed 404.0472.

(±)-1-{*O*-2-[*O*-(2-Furyl)phenoxy]ethoxyamino}-2-bromo-1-propanone (S25)



Prepared in 88% yield (0.14 g, 0.38 mmol) as a colorless oil from the reaction of *O*-2-{[*O*-(2-furyl)phenyl]methoxy}ethylhydroxylamine **S13** (0.1 g, 0.43 mmol) with 2-bromopripionyl bromide (45 µL 0.43 mmol) *via* general procedure **F**. R_f = 0.28 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.35 (td, *J* = 7.6, 1.4 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.69 (s, 2H), 4.20 (q, *J* = 6.6 Hz, 1H), 4.09 (t, *J* = 4.5 Hz, 2H), 3.74 (t,*J* = 4.4 Hz, 2H), 1.76 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 152.5, 142.4, 133.7, 130.2, 129.8, 128.2, 127.7, 127.7, 111.7, 109.0, 75.1, 71.9, 68.9, 40.6, 22.2; FT-IR (neat): 3173, 2974, 2926, 2866, 1666, 1501 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{18}NO_4BrNa$ $(M+Na)^+$ 390.0311, observed 390.0309.

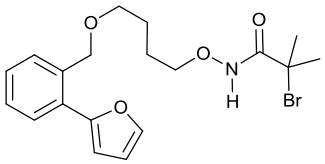
{*O*-2-[*O*-(2-Furyl)phenoxy]ethoxyamino}(1-bromocyclohexyl)formaldehyde (S26)



Prepared in 62% yield (0.11 g, 0.26 mmol) as a colorless oil from the reaction of *O*-2-{[*O*-(2-furyl)phenyl]methoxy}ethylhydroxylamine **S13** (0.1 g, 0.43 mmol) with 1-bromocyclohexanecarbonyl chloride (97 mg, 0.43 mmol) *via* general procedure **F**. R_f = 0.50 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.51 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.36 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 6.65 (dd, *J* = 3.3, 0.9 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.71 (s, 2H), 4.13 (t, *J* = 4.4 Hz, 2H), 3.80 (t, *J* = 4.4 Hz, 2H), 2.02 (ddd, *J* = 14.3, 10.6, 3.7 Hz, 2H), 1.94 (dt, = 14.4, 4.5 Hz, 2H), 1.71 – 1.53 (m, 5H), 1.33 – 1.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.1, 152.5,

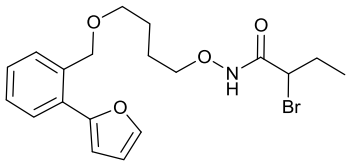
142.4, 133.6, 130.3, 129.9, 128.2, 127.7, 127.7, 111.6, 109.0, 74.9, 72.0, 69.3, 67.6, 37.7, 24.6, 22.5; FT-IR (neat): 3230, 2933, 2859, 1661, 1501 cm^{-1}; HRESI-MS: calculated for $C_{20}H_{24}NO_4BrNa$ $(M+Na)^+$ 444.0781, observed 444.0782.

1-{*O*-4-[*O*-(2-Furyl)phenoxy]butoxyamino}-2-bromo-2-methyl-1-propanone (S27)



Prepared in 85% yield (0.18 g, 0.44 mmol) as a colorless oil from the reaction of *O*-4-{[*O*-(2-furyl)phenyl]methoxy}butylhydroxylamine **S14** (0.13 g, 0.52 mmol) with 2-bromo-2-methylpropionyl bromide (65 µL 0.52 mmol) *via* general procedure **F**. R_f = 0.43 (7:3, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.63 – 6.62 (m, 1H), 6.50 (m,1H), 4.65 (s, 2H), 3.96 (t, *J* = 5.5 Hz, 2H), 3.58 (t, *J* = 5.7 Hz, 2H), 1.94 (s, 6H), 1.82 – 1.72 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 152.6, 142.2, 134.6, 129.9, 129.3, 127.8, 127.6, 127.5, 111.5, 108.9, 76.4, 71.3, 69.8, 59.5, 32.4, 26.2, 24.8; FT-IR (neat): 3238, 2925, 2855, 1663, 1501 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{24}NO_4BrNa$ $(M+Na)^+$ 432.0781, observed 432.0781.

(±)-1-{*O*-4-[*O*-(2-Furyl)phenoxy]butoxyamino}-2-bromo-1-butanone (S28)



Prepared in 91% yield (0.19 g, 0.47 mmol) as a colorless oil from the reaction of *O*-4-{[*O*-(2-furyl)phenyl]methoxy}butylhydroxylamine **S14** (0.13 g, 0.52 mmol) with 2-bromobutanoyl bromide (63 µL 0.52 mmol) *via* general procedure **F**. R_f = 0.52 (6:4, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.69 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.6 Hz, 1H), 7.32 (td, *J* = 7.4, 1.6 Hz, 1H), 6.62 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.65 (s, 2H), 4.02 (t, *J* = 6.2 Hz, 1H), 3.97 – 3.94 (m, 2H), 3.59 (t, *J* = 5.6 Hz, 2H), 2.12 (ddq, *J* = 14.6, 7.3, 5.7 Hz, 1H), 2.01 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.82 – 1.72 (m, 4H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.1, 152.6, 142.3,

134.5, 130.0, 129.4, 127.9, 127.6, 127.6, 111.5, 109.0, 76.5, 71.4, 69.9, 49.4, 28.9, 26.1, 24.6, 11.6; FT-IR (neat): 3168, 2968, 2934, 2873, 1663 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{24}NO_4BrNa$ $(M+Na)^+$ 432.0781, observed 432.0783.

General Procedure G: For macrocyclization reactions

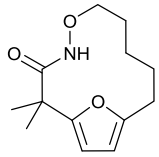
To a solution of haloamide (1 equiv.) in hexafluoroisopropanol [$(CF_3)_2CHOH$, 0.1 M] was added triethylamine (2 equiv.) in hexafluroisopropanol (2 M) was added,

-slowly over 3 h at room temperature *via* syringe pump and stirred additional 30 min to 2h at room temperature (**5**, **7-c**, **7e**-**h** and **7k**).

-at room temperature and stirred for 8 hours (**7k**), 6 days (**7a**) or refluxed at 70 °C for 6 hr (**7d**), overnight (**7i**, **7j** and **7m**).

The consumption of halo amide was monitored by TLC (3:1, hexanes : ethyl acetate). The volatiles were removed under reduced pressure and the residue was purified *via* flash column chromatography or medium pressure liquid chromatography (MPLC), a Biotage® purification system equipped with 254 nm and 280 nm UV detectors and by using Biotage zip 10g Si gel column employing a hexane:ethyl acetate gradient for the mobile phase (9:1 to 1:1, hexanes : ethyl acetate) to provide the macrocycles.

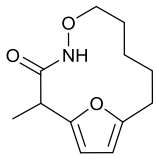
2,2-Dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one (5)



Prepared in 58% yield (49 mg, 0.19 mmol) from 1-[*O*-5-(2-furyl)pentyloxyamino]-2-bromo-2-methyl-1-propanone **S15** (108 mg, 0.34 mmol) via general procedure **G**. R_f = 0.43 (1:1, hexanes : ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 6.11 (d, *J* = 3.1 Hz, 1H), 5.96 (dt, *J* = 3.0, 0.8 Hz, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 2.68 (t, *J* = 6.3, 2H), 1.78 – 1.73 (m, 2H), 1.53 (s, 6H), 1.39 (pent. *J* = 6.4 Hz, 2H), 1.25 (pent., *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 157.2, 156.1, 106.3, 106.0, 73.4, 43.2, 27.8, 25.0, 24.2, 24.0, 23.5; FT-IR (neat): 3266, 2929, 2851,

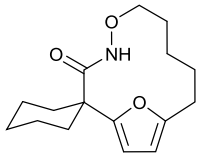
1661, 1555 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{20}NO_3$ $(M+H)^+$ 238.1438, observed 238.1429.

(±)-2-Methyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one (7a)



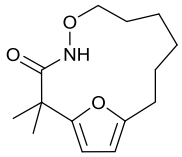
Prepared in 35% yield (25 mg, 0.11 mmol) as a white solid from the reaction of 1-[*O*-5-(2-furyl) pentyloxyamino]-2-bromo-1-propanone **S16** (0.1 g, 0.33 mmol) with triethyl amine (92 µL, 0.66 mmol) *via* general procedure **G**. R_f = 0.42 (1:1, hexanes: ethyl acetate); mp 128.5 – 130.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 6.11 (dd, *J* = 3.0, 0.6 Hz, 1H), 5.95 (dt, *J* = 3.1, 0.8 Hz, 1H), 4.04 (br.s, 1H), 3.80 (br.s, 1H), 3.69 (br.s, 1H), 2.72 (ddd, *J* = 15.2, 7.2, 3.5 Hz, 1H), 2.63 (ddd, *J* = 15.0, 9.2, 3.8 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.64 – 1.51 (m, 2H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.46 – 1.29 (m, 2H), 1.17 (s, 1H); ^{13}C NMR (126 MHz, CD_3OD): δ 172.0, 158.0, 154.7, 108.5, 107.9, 75.1, 40.2, 28.8, 27.1, 26.9, 26.6, 13.3; FT-IR (neat): 3221, 2973, 2937, 2880, 2858, 1708, 1657, 1601 cm^{-1}; HRESI-MS: calculated for $C_{12}H_{18}NO_3$ $(M+H)^+$ 224.1281, observed 224.1281.

2-(Spirocyclohexane)-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one (7b)



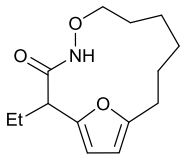
Prepared in 52% yield (41 mg, 0.15 mmol) as a white solid from the reaction of [*O*-5-(2-furyl)pentyloxyamino](1-bromocyclohexyl)formaldehyde **S17** (0.1 g, 0.28 mmol) with triethyl amine (78 µL 0.56 mmol) *via* general procedure **G**. R_f = 0.33 (7:3, hexanes: ethyl acetate); mp 129.6 – 132.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 5.97 (dt, *J* = 3.1, 0.8 Hz, 1H), 3.92 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.14 (ddd, *J* = 13.1, 8.8, 3.8 Hz, 2H), 1.91 (ddd, *J* = 13.0, 6.2, 2.4 Hz, 2H), 1.71 (ddq, *J* = 8.7, 6.0, 3.9 Hz, 2H), 1.69 – 1.65 (m, 4H), 1.62 – 1.51 (m, 2H), 1.49 – 1.43 (m, 2H), 1.42 – 1.38 (m, 2H), 1.18 – 1.13 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 156.0, 155.9, 107.4, 106.3,72.8, 47.9, 32.0, 27.9, 25.7, 24.7, 24.5, 24.3, 22.6; FT-IR (neat): 3242, 2923, 2851, 1653, 1546 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{24}NO_3$ $(M+H)^+$ 278.1751, observed 278.1754.

2,2-Dimethyl-5.15-dioxa-4-azabicyclo[10.2.1]pentadeca-1(14),12-dien-3-one (7c)



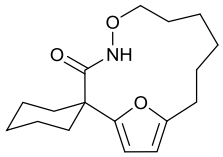
Prepared in 47% yield (36 mg, 0.14 mmol) as a white solid from the reaction of 1-[*O*-6-(2-furyl)hexyloxyamino]-2-bromo-1-propanone **S18** (0.1 g, 0.3 mmol) with triethyl amine (84 µL 0.6 mmol) *via* general procedure **G**. R_f = 0.50 (1:1, hexanes: ethyl acetate); mp 141.2 – 142.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 5.95 (dt, *J* = 3.2, 0.8 Hz, 1H), 3.82 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.3 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.67 – 1.62 (m, 2H), 1.54 (s, 6H), 1.31 – 1.19 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.0, 156.1, 155.5, 106.4, 106.3 75.0, 42.5, 27.2, 26.7, 26.6, 25.2, 24.8, 23.9; FT-IR (neat): 3284, 2968, 2938, 2913, 2867, 2852, 1650, 1609, 1557 cm^{-1}; HRESI-MS: calculated for $C_{14}H_{21}NO_3Na$ $(M+Na)^+$ 274.1414, observed 274.1414.

(±)-2-Ethyl-5.15-dioxa-4-azabicyclo[10.2.1]pentadeca-1(14),12-dien-3-one (7d)



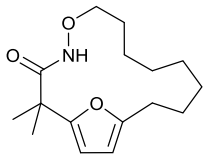
Prepared in 30% yield (23 mg, 0.09 mmol) as a white solid from the reaction of 1-[*O*-6-(2-furyl)hexyloxyamino]-2-bromo-1-butanone **S19** (0.1 g, 0.3 mmol) with triethyl amine (84 µL 0.6 mmol) *via* general procedure **G**. R_f = 0.48 (1:1, hexanes: ethyl acetate); mp 127.0 – 129.2 °C; ^{1}H NMR (500 MHz, CD_3OD): δ 6.08 (dd, *J* = 3.2, 0.7 Hz, 1H), 5.94 (br.d, *J* = 3.0 Hz, 1H), 3.71 (ddd, *J* = 12.4, 8.7, 7.1 Hz, 1H), 3.60 (ddd, *J* = 12.4, 9.4, 4.5 Hz, 1H), 3.32 (m, 1H), 2.73 (ddd, *J* = 15.3, 6.8, 4.2 Hz, 1H), 2.60 (ddd, *J* = 15.2, 10.7, 3.9 Hz, 1H), 2.09 – 1.79 (m, 4H), 1.68 (dddt, *J* = 17.2, 10.5, 7.1, 3.5 Hz, 1H), 1.59 (dddd, *J* = 16.0, 9.4, 6.3, 3.2 Hz, 1H), 1.34 (dtt, *J* = 14.5, 7.7, 3.9 Hz, 2H), 1.23 (dqd, *J* = 12.1, 6.1, 3.3 Hz, 1H), 1.21 – 1.13 (m, 1H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CD_3OD): δ 170.9, 156.6, 152.9, 108.7, 76.0, 47.7, 28.7, 27.4, 26.9, 26.5, 25.4, 22.5, 13.1(one carbon missing due to overlapping); FT-IR (neat): 3195, 2933, 2864, 1659, 1557 cm^{-1}; HRESI-MS: calculated for $C_{14}H_{21}NO_3Na$ $(M+Na)^+$ 274.1414, observed 274.1407.

2-(Spirocyclohexane)-5.15-dioxa-4-azabicyclo[10.2.1]pentadeca-1(14),12-dien-3-one (7e)



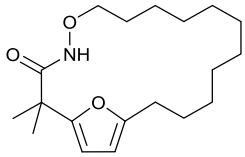
Prepared in 38% yield (30 mg 0.1 mmol) as a white solid from the reaction of [*O*-6-(2-furyl)hexyloxyamino](1-bromocyclohexyl)formaldehyde **S20** (0.1 g, 0.27 mmol) with triethyl amine (75 µL 0.54 mmol) *via* general procedure **G**. R_f = 0.40 (6:4, hexanes: ethyl acetate); mp 167.2 – 169.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H), 6.13 (d, *J* = 3.1 Hz, 1H), 5.96 (dt, *J* = 3.0, 0.9 Hz, 1H), 3.77 (t, *J* = 6.6 Hz, 2H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.15 (ddd, *J* = 13.4, 9.2, 3.7 Hz, 2H), 1.98 (ddq, , *J* = 13.3, 6.6, 3.0 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.67 – 1.60 (m, 4H), 1.55 – 1.42 (m, 4H), 1.24 – 1.17 (m, 4H); ^{13}C NMR (126 MHz, CD_3OD): δ 173.2, 156.9, 156.8, 108.7, 108.6, 76.2, 49.1, 33.6, 29.0, 27.8, 27.6, 27.4, 26.6, 25.8, 24.7; FT-IR (neat): 3282, 2932, 2851, 2451, 1644, 1554 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{25}NO_3Na$ $(M+Na)^+$ 314.1727, observed 314.1733.

2,2-Dimethyl-5.17-dioxa-4-azabicyclo[12.2.1]heptadeca-1(16),14-dien-3-one (7f)



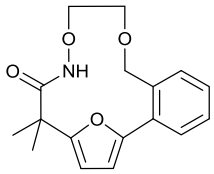
Prepared in 20% yield (28 mg, 0.1 mmol) as a white solid from the reaction of 1-[*O*-8-(2-furyl)octyloxyamino]-2-bromo-2-methyl-1-propanone **S21** (0.2 g, 0.55 mmol) with triethyl amine (0.15 mL, 1.1 mmol) *via* general procedure **G**. R_f = 0.55 (1:1, hexanes: ethyl acetate); mp 167.3 – 169.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 6.08 (d, *J* = 3.1 Hz, 1H), 5.93 (dt, *J* = 3.2, 0.8 Hz, 1H), 3.81 (t, *J* = 6.7 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.54 (m, 4H), 1.52 (s, 6H), 1.31 – 1.27 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$): 172.8, 156.3, 154.9, 106.8, 105.9, 76.5, 42.5, 29.4, 29.3, 28.9, 28.5, 27.9, 27.7, 25.9, 24.6; FT-IR (neat): 3176, 2909, 2846, 1655, 1561 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{25}NO_3Na$ $(M+Na)^+$ 302.1732, observed 302.1733.

2,2-Dimethyl-5.20-dioxa-4-azabicyclo[15.2.1]heptadeca-1(19),17-dien-3-one (7g)



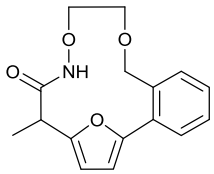
Prepared in 31% yield (25 mg, 0.08 mmol) as a white solid from the reaction of 1-[*O*-11-(2-furyl)undecyloxyamino]-2-bromo-2-methyl-1-propanone **S22** (0.1 g, 0.25 mmol) with triethyl amine (70 µL 0.5 mmol) *via* general procedure **G**. R_f = 0.62 (1:1, hexanes: ethyl acetate); mp 135.5 –136.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 6.10 (d, *J* = 3.1 Hz, 1H), 5.94 (br.d, *J* = 3.1, Hz, 1H), 3.82 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.57 (m, 4H), 1.53 (s, 6H), 1.33 – 1.25 (m, 14H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 156.5, 154.8, 106.9, 105.7, 76.5, 42.5, 29.7, 29.7, 29.6, 29.5, 29.5, 29.2, 28.5, 28.0, 27.8, 25.8, 24.6; FT-IR (neat): 3196, 2915, 2850, 1664, 1562 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{32}NO_3$ $(M+H)^+$ 322.2377, observed 322.2374.

15,15-Dimethyl-9.12.19-trioxa-13-azatricyclo[14.2.1.0^{2,7}]nonadeca-1(18),2(7),3,5,16-pentaen-14-one (7h)



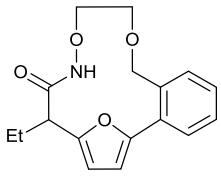
Prepared in 75% yield (57.2 mg, 0.19 mmol) as a white solid from the reaction of 1-{*O*-2-[*O*-(2-furyl)phenoxy]ethoxyamino}-2-bromo-2-methyl-1-propanone **S23** (0.1 g, 0.26 mmol) with triethyl amine (72.5 µL 0.52 mmol) via general procedure **G**. Rf = 0.25 (3:7, hexanes: ethyl acetate); mp 118.6 – 120.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.52 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.35-7.33 (m, 2H), 6.48 (d, *J* = 3.3 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 4.71 (s, 2H), 4.10 – 4.09 (noform, 2H), 4.01 – 3.99 (noform, 2H), 1.59 (s, 6H); ^{13}C NMR (126 MHz,$CDCl_3$): δ 171.3, 156.8, 154.0, 134.2, 132.1, 130.4, 128.9, 128.8, 128.7, 108.5, 107.8, 74.2, 73.7, 72.2, 42.9, 24.7; FT-IR (neat): 3246, 2970, 2947, 2904, 2877, 2838, 1655 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{19}NO_4Na$ $(M+Na)^+$ 324.1206, observed 324.1216.

(±)-15-Methyl-9.12.19-trioxa-13-azatricyclo[14.2.1.0^{2,7}]nonadeca-1(18),2(7),3,5,16-pentaen-14-one (7i)



Prepared in 77% yield (57.5 mg, 0.20 mmol) as a white solid from the reaction of 1-{*O*-2-[*O*-(2-furyl)phenoxy]ethoxyamino}-2-bromo-1-propanone **S24** (96 mg, 0.26 mmol) with triethyl amine (73 µL, 0.52 mmol) *via* general procedure **G**. R_f = 0.23 (3:7, hexanes: ethyl acetate); mp 161.4 – 162.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.32 (m, 3H), 6.46 (d, *J* = 3.3 Hz, 1H), 6.28 (dd, *J* = 3.3, 1.1 Hz, 1H), 4.59 (d, *J* = 9.3 Hz, 1H), 4.51 (d, *J* = 9.2 Hz, 1H), 4.20 – 4.06 (m, 3H), 4.05 – 3.97 (m, 1H), 3.70 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 153.8, 152.8, 134.3, 132.5, 130.9, 128.9, 128.9, 128.8, 108.6, 108.1, 74.3, 73.3, 72.4, 38.7, 14.5; FT-IR (neat): 3167, 2981, 2936, 2917, 2878, 1687, 1658 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{17}NO_4Na$ $(M+Na)^+$ 310.1050, observed 310.1063.

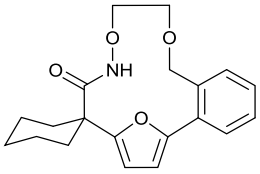
(±)-15-Ethyl-9.12.19-trioxa-13-azatricyclo[14.2.1.0^{2,7}]nonadeca-1(18),2(7),3,5,16-pentaen-14-one (7j)



Prepared in 77% yield (60.3 mg, 0.20 mmol) as a white solid from the reaction of 1-{*O*-2-[*O*-(2-furyl)phenoxy]ethoxyamino}-2-bromo-1-butanone **S25** (0.1 g, 0.26 mmol) with triethyl amine (72.5 µL, 0.52 mmol) *via* general procedure **G**. R_f = 0.41 (3:7, hexanes: ethyl acetate); mp 174.2 – 175.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.49-7.47 (m, 1H), 7.43 – 7.33 (m, 3H), 6.45 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 4.56 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.2 Hz, 1H),4.27 – 3.93 (m, 4H), 3.49 (t, *J* = 7.4 1H), 2.15 (dp, *J* = 14.1, 7.2 Hz, 1H), 1.95 – 1.86 (m, 1H),1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6, 153.8, 151.4, 134.4, 132.5, 131.0, 129.0, 128.9, 128.8, 109.3, 108.6, 74.3, 73.2, 72.4, 47.0, 24.0, 12.1; FT-IR (neat): 3128, 2964, 2926, 2868,

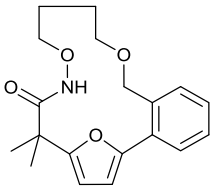
2815, 2777, 1679, 1655 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{19}NO_4Na$ $(M+Na)^+$ 324.1206, observed 324.1221.

15-(Spirocyclohexane)-9.12.19-trioxa-13-azatricyclo[14.2.1.$0^{2,7}$]nonadeca-1(18),2(7),3,5,16-pentaen-14-one (7k)



Prepared in 89% yield (54.6 mg, 0.16 mmol) as a white solid from the reaction of {*O*-2-[*O*-(2-furyl)phenoxy]ethoxyamino}(1-bromocyclohexyl)formaldehyde **S26** (76 mg, 0.18 mmol) with triethyl amine (50.2 µL, 0.36 mmol) *via* general procedure **G**. R_f = 0.25 (3:7, hexanes: ethyl acetate); mp 132.7 – 134.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00 (s, 1H), 7.50 (dt, *J* = 7.5, 0.9, Hz, 1H), 7.43 – 7.28 (m, 3H), 6.48 (d, *J* = 3.3 Hz, 1H), 6.36 (d, *J* = 3.3 Hz, 1H), 4.66 (s, 2H), 4.08 – 4.02 (m, 2H), 3.97(m, 2H), 2.19 (ddd, *J* = 14.1, 1 0.8, 3.9 Hz, 2H), 2.08 (dt, *J* = 14.6, 3.8 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.57 – 1.54 (m, 1H), 1.45 – 1.40 (m, Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 154.6, 153.7, 134.7, 131.9, 130.6, 129.1, 128.9, 128.7, 110.0, 108.6, 74.0, 73.5, 72.3, 47.9, 31.9, 25.5, 22.2; FT-IR (neat): 3263, 2933, 2861, 2850, 2831, 1688, 1650 cm^{-1}; HRESI-MS: calculated for $C_{20}H_{24}NO_4$ $(M+H)^+$ 342.1690, observed 234.1692.

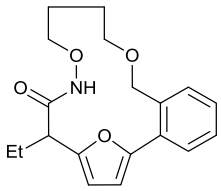
17,17-Dimethyl-9.14.21-trioxa-15-azatricyclo[16.2.1.$0^{2,7}$]henicosa-1(20),2(7),3,5,18-pentaen-16-one (7l)



Prepared in 27% yield (19.8 mg, 0.06 mmol) as a white solid from the reaction of 1-{*O*-4-[*O*-(2-furyl)phenoxy]butoxyamino}-2-bromo-2-methyl-1-propanone **S27** (0.1 g, 0.24 mmol) with triethyl amine (67 µL, 0.48 mmol) *via* general procedure **G**. R_f = 0.31 (1: 1, hexanes: ethyl acetate); mp 134.0 – 136.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.61 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.37 (ddd, *J* = 7.8, 6.8, 2.1 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.27 (d, *J* = 3.4 Hz, 1H), 4.93 (s, 2H), 3.83 (t, *J* = 5.7 Hz, 2H), 3.43 (t, *J* = 5.5 Hz, 2H), 1.71 (p, *J* = 5.8 Hz, 2H),

1.62 (s, 6H), 1.48 (p, *J* = 5.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 157.4, 153.8, 133.0, 132.3, 129.9, 128.8, 127.7, 127.6, 108.6, 107.3, 75.0, 73.7, 69.9, 42.4, 24.7, 24.2, 22.9; FT-IR (neat): 3264, 2928, 2865, 1681, 1600 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{23}NO_4Na$ $(M+Na)^+$ 352.1519, observed 352.1514.

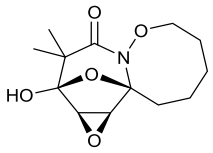
(±)-17-Ethyl-9.14.21-trioxa-15-azatricyclo[16.2.1.0^{2,7}]henicosa-1(20),2(7),3,5,18-pentaen-16-one (7m)



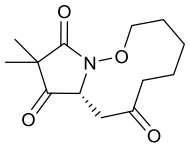
Prepared in 30% yield (23 mg, 0.07 mmol) as a white solid from the reaction of 1-{*O*-4-[*O*-(2-furyl)phenoxy]butoxyamino}-2-bromo-1-butanone **S28** (0.1 g, 0.24 mmol) with triethyl amine (67 µL, 0.48 mmol) *via* general procedure **G**. R_f = 0.36 (1:1, hexanes: ethyl acetate); mp 140.2 – 142.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.19 (s, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.37 (ddd, *J* = 7.8, 6.7, 2.1 Hz, 1H), 7.31 – 7.24 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 5.21 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 12.1 Hz, 1H), 3.91 – 3.79 (m, 2H), 3.53 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.47 – 3.37 (m, 2H), 2.18(dqd, *J* = 13.6, 7.5, 6.0 Hz, 1H), 1.97 (ddq, *J* = 14.6, 9.5, 7.3 Hz, 1H), 1.80 – 1.67 (m, 2H), 1.56 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 153.9, 151.8, 132.7, 132.5, 129.9, 128.9, 127.5, 127.4, 109.4, 108.5, 74.9, 73.7, 69.8, 47.9, 24.4, 24.3, 22.8, 12.3; FT-IR (neat): 3124, 2921, 2850, 1656 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{23}NO_4Na$ $(M+Na)^+$ 352.1519, observed 352.1526

(±)-(1*S*,11*R*,12*S*,14*S*)-11-Hydroxy-10,10-dimethyl-7,13,15-trioxa-8-azatetracyclo[9.3.1.$0^{1,8}$.$0^{12,14}$]pentadecan-9-one (9) and (±)-12,1-dimethyl-2-oxa-1-azabicyclo[8,3,0]tridecane-8,11,13-trione (10)

To a solution of 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (90 mg, 0.38 mmol) in dichloromethane (2.0 mL) was added *m*-CPBA (97 mg, 1.52 mmol) at 0°C and the reaction mixture was stirred for 3 hours at room temperature. The complete consumption of **5** was confirmed by TLC (1:1, hexanes: ethyl acetate). The white ppt was filtered, the filtrate was washed with aqueous sodium bicarbonate (5 mL) and brine solution (5 mL) and then the organic layer was dried over sodium sulfate. The volatiles are removed under reduced pressure and purified by flash column chromatography (3:1 to 3:2, hexanes: ethyl acetate) to afford **9 and 10.**



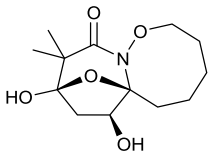
9: Yield = 52% (54 mg, 0.20 mmol), white solid, mp 189.0 – 191.2°C; R_f = 0.40 (1:1, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.29 (ddd, *J* = 11.7, 5.7, 3.9 Hz, 1H), 3.87 (ddd, *J* = 12.0, 8.2, 4.1 Hz, 1H), 3.77 (d, *J* = 3.0 Hz, 1H), 3.63 (d, *J* = 3.0 Hz, 1H), 3.42 (s, 1H), 2.23 (ddd, *J* = 14.9, 10.4, 4.1 Hz, 1H), 2.03 (ddd, *J* = 15.3, 5.7, 3.0 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.81 – 1.67 (m, 4H), 1.52 – 1.46 (m, 1H), 1.39 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.1, 102.8, 92.4, 75.2, 58.0, 52.5, 49.7, 28.6, 27.4, 26.0, 22.3, 21.6, 18.0 ; FT-IR (neat): 3277, 2978, 2930, 2850, 1701, 1653 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{19}NO_5Na$ $(M+Na)^+$ 292.1155, observed 292.1143.



10: Yield = 22% (21 mg, 0.08 mmol), white solid, mp 170.1 – 172.2 °C; R_f = 0.39 (1:1, hexanes: ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.22 (ddd, *J* = 9.4, 7.2, 3.2 Hz, 1H), 4.11 (ddd, *J* = 9.4, 7.2, 3.3 Hz, 1H), 2.88 – 2.80 (m, 2H), 2.74 (ddd, *J* = 13.9, 7.7, 3.7

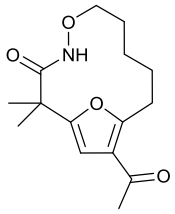
Hz, 1H), 2.46 (ddd, *J* = 14.1, 9.7, 4.8 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.80 – 1.68 (m, 3H), 1.68 – 1.53 (m, 2H), 1.31 (d, *J* = 5.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.9, 208.2, 172.4, 76.1, 63.5, 48.4, 43.2, 41.7, 26.7, 22.8, 22.5, 21.8, 19.6, ; FT-IR (neat): 3277, 2980, 2959, 2930, 2869, 2849, 1766, 1697 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{19}NO_4Na$ $(M+Na)^+$ 276.1206, observed 276.1218.

(±)-(1*R*,11*R*,12*S*)-1,12-Dihydroxy-2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradecan-3-one (11)



To a solution 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (50 mg, 0.21 mmol) in CH_3CN:H_2O:acetone (0.5 mL:0.5 mL:1 mL) was added NMO (49.2 mg, 0.42 mmol), and OsO_4 (0.3 mL, 1% in H_20) and stirred at room temperature for overnight. The complete consumption of **5** was confirmed by TLC (1:1, hexanes : ethyl acetate). To the reaction mixture was added sodium hydrosulfite (0.50 g) and stirred the reaction mixture for one hour. The reaction mixture was filtered and the filtrate was neutralized to pH 7 with 1N H_2SO_4 and the solvents were removed under rotary vapor and the pH was further adjusted to 2. The solution was extracted with ethyl acetate (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure to obtain product **11** in 67% yield as a white solid (38.2 mg, 0.14 mmol). R_f = 0.62 (1:1, hexanes: ethyl acetate); mp 172.0 – 174.1 °C; ^{1}H NMR (400 MHz, CD_3OD): δ 4.18 (dt, *J* = 11.6, 4.8 Hz, 1H), 3.91 (dd, *J* = 7.4, 2.5 Hz, 1H), 3.77 – 3.66 (m, 1H), 3.2 (pent *J* = 1.6, Hz, 1H). 2.65 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.98 – 1.90 (m, 1H), 1.85 – 1.74 (m, 1H), 1.73 – 1.59 (m, 6H), 1.45 – 1.33 (m, 1H), 1.24 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD): δ 176.6, 107.5, 99.6, 76.5, 76.0, 51.4, 43.6, 29.0, 29.0, 28.0, 24.1, 22.8, 18.9; FT-IR (neat): 3435, 3344, 2984, 2948, 2928, 2911, 2484, 1720, 1620 cm^{-1}; HRESI-MS: calculated for $C_{13}H_{21}NO_5Na$ $(M+Na)^+$ 294.1312, observed 294.1307.

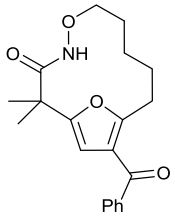
12-Acetyl-2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one (12)



Acetyl chloride (10 µL, 0.16 mmol) was added to a suspension of $AlCl_3$ (28 mg, 0.022 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C under nitrogen followed by dropwise addition of 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (25 mg, 0.105 mmol) and stirred for 6h at 0 °C. The reaction was quenched with water (1mL). The organic layer was separated and the aqueous layer was extracted twice with dichloromethane (5mL). The organic extract was washed with saturated $NaHCO_3$ solution (5 mL) and dried with anhydrous sodium sulfate. Volatiles were removed under reduced pressure and purified by column chromatography to obtain **12** as a white solid; 65% yield (19 mg, 0.068 mmol). mp 131.8 – 132.8 °C; R_f = 0.40 (3:7, hexanes: ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 6.46 (s, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 3.12 – 3.08 (noform, 2H), 2.42 (s, 3H), 1.86 – 1.80 (m, 2H), 1.56 (s, 6H), 1.41 –1.35 (m, *J* = 6.6 Hz, 2H), 1.27 – 1.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6, 171.6, 162.0, 156.8, 122.2, 106.0, 73.2, 42.9, 29.3, 27.8, 25.4, 24.5, 23.1, 23.4; FT-IR (neat): 2851, 1663, 1589, 1555 cm^{-1}; HRESI-MS: calculated

for $C_{15}H_{21}NO_4Na$ $(M+Na)^+$ 302.1363, observed 302.1353.

12-Benzoyl-2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one (13)



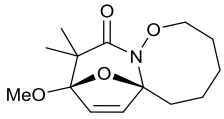
Benzoyl chloride (18 µL, 0.16 mmol) was added to a suspension of $AlCl_3$ (28 mg, 0.022 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C under nitrogen followed by dropwise addition of 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (25 mg, 0.105 mmol) and stirred for 10 h at 0 °C. The reaction was quenched with water (1 mL). The organic layer was separated and the aqueous layer was extracted twice with dichloromethane (5 mL). The organic extract

was washed with saturated $NaHCO_3$ solution (5 mL) and dried with anhydrous sodium sulfate. Volatiles were removed under reduced pressure and purified by column chromatography to obtain **13** as a white solid in 48% yield (17 mg, 0.05 mmol). R_f = 0.41 (3:7, hexanes: ethyl acetate); mp 132.8 – 135.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.83 – 7.77 (m, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.47 (m, 2H), 6.45 (s, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 2.94 (t, *J* = 6.1 Hz, 2H), 1.84 (p, *J* = 6.2 Hz, 2H), 1.58 (s, 6H), 1.38 (p, *J* = 6.7 Hz, 2H), 1.30 (p, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.8, 162.7, 156.9, 138.8, 132.5, 129.0, 128.5, 121.7, 110.0, 107.3, 73.3, 43.0, 27.8, 25.6, 24.3, 24.1, 23.4; FT-IR (neat): 3259, 2933, 2869, 1643, 1598, 1553 cm^{-1}; HRESI-MS: calculated for $C_{20}H_{23}NO_4Na$ $(M+Na)^+$ 364.1519, observed 364.1513.

General Procedure H: For the synthesis of lactams (16-21)

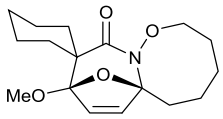
To a solution of macrocycle (1equiv.) in methanol (0.25 M) added $PhI(OAc)_2$ (1 equiv.) and stirred at room temperature for 10 min. The volatiles were removed in vacuo and the crude mixture was purified by column chromatography (1:9 to 3:7 ethylacetate : hexane) to afford the desired compounds.

(±)-(1*S*,11*R, Z*)-11-Methoxy-10,10-dimethyl-7.14-dioxa-8-azatricyclo[9.2.1.0^{1,8}]tetradec-12-en-9-one (16)



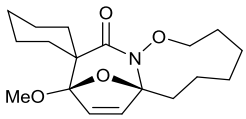
Prepared in 82% yield (23 mg, 0.086 mmol) as a white solid from the reaction of 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (25 mg, 0.105 mmol) with (diacetoxyiodo)benzene (35.8 mg, 0.105 mmol) *via* general procedure **H**. R_f = 0.5 (7:3, hexanes: ethyl acetate); mp 107.1 – 109.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.17 (d, *J* = 5.8 Hz, 1H), 5.92 (d, *J* = 5.8 Hz, 1H), 4.19 (dddd, *J* = 12.3, 5.0, 2.7, 0.8 Hz, 1H), 3.98 (ddd, *J* = 12.3, 10.2, 2.1 Hz, 1H), 3.16 (s, 3H), 2.33 – 2.21 (m, 1H), 2.11 – 2.05 (m, 1H), 1.87 – 1.83 (m, 1H), 1.67 – 1.47 (m, 4H), 1.45 – 1.40 (m, 1H), 1.39 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.8, 135.9, 130.1, 116.4, 105.2, 80.8, 54.0, 50.0, 36.9, 29.7, 25.1, 20.7, 19.0, 18.2; FT-IR (neat): 3083, 2961, 2982, 2929, 2910, 2893, 2846, 2823, 1770 cm^{-1}; HRESI-MS: calculated for $C_{14}H_{21}NO_4Na$ $(M+Na)^+$ 290.1363, observed 290.1371.

(±)-(1*S*,11*R, Z*)-11-Methoxy-10-(spirocyclohexane)-7.14-dioxa-8-azatricyclo[9.2.1.0^{1,8}]tetradec-12-en-9-one (17)



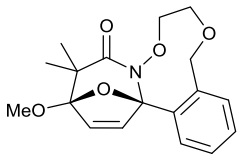
Prepared in 90% yield (9.8 mg, 0.032 mmol) as a white solid from the reaction of **7b** (10 mg, 0.036 mmol) with (diacetoxyiodo)benzene (11.6 mg mL 0.036 mmol) *via* general procedure **H**. R_f = 0.5 (7:3, hexanes: ethyl acetate); mp 137.6 – 140.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.14 (d, *J* = 5.8 Hz, 1H), 5.92 (d, *J* = 5.8 Hz, 1H), 4.19 (ddd, *J* = 12.3, 5.0, 2.6 Hz, 1H), 3.97 (ddd, *J* = 12.3, 10.2, 2.0 Hz, 1H), 3.21 (s, 3H), 2.30 – 2.22 (m, 1H), 2.11 – 2.01 (m, 2H), 1.94 (dt, *J* = 13.2, 4.3 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.79 – 1.52 (m, 9H), 1.46 – 1.35 (m, 2H), 1.28 – 1.14 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8, 135.8, 130.0, 116.2, 104.8, 80.7, 57.8, 50.3, 36.8, 30.0, 29.8, 29.2, 25.5, 25.1, 23.3, 22.9, 20.7, ; FT-IR (neat): 3079, 2936, 2921, 2854, 2826, 1756, 1626 cm^{-1}; HRESI-MS: calculated for $C_{17}H_{26}NO_4$ $(M+H)^+$ 308.1856, observed 308.1863.

(±)-(1*S*,11*R, Z*)-11-Methoxy-11,11-dimethyl-7.14-dioxa-9-azatricyclo[10.2.1.0^{1,9}]pentadec-12-en-10-one (18)



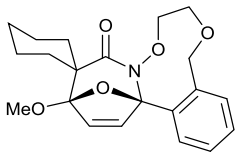
Prepared in 88% yield (4.8 mg, 0.015 mmol) as a white solid from the reaction of **7e** (5.0 mg, 0.017 mmol) with (diacetoxyiodo)benzene (5.7 mg 0.017 mmol) *via* general procedure **H**. R_f = 0.7 (2:1, hexanes: ethyl acetate); mp 157.5 – 159.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.04 (d, *J* = 5.8 Hz, 1H), 6.02 (d, *J* = 5.8 Hz, 1H), 4.13 – 4.08 (m, 2H), 3.21 (s, 3H), 2.09 – 2.00 (m, 1H), 1.97 – 1.87 (m, 3H), 1.86 – 1.78 (m, 2H), 1.77 – 1.52 (m, 8H), 1.51 – 1.42 (m, 4H), 1.43 – 1.36 (m, 1H), 1.27 – 1.14 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.6, 136.7, 128.2, 115.3, 105.0, 78.0, 57.9, 50.5, 34.7, 29.9, 29.1, 26.1, 25.5, 24.9, 23.6, 23.3, 22.9, 19.6; FT-IR (neat): 3089, 2933, 2857, 1759, 1633 cm^{-1}; HRESI-MS: calculated for $C_{18}H_{27}NO_4Na$ $(M+Na)^+$ 344.1832, observed 344.1848.

(±)-(1*S*,16*S*, *Z*)-16-Methoxy-15,15-Dimethyl-9,12,19-trioxa-13-azatetracyclo[14.2.1.0^{1,13}.0^{2,7}]octadeca-2(7),3,5,17-tetraen-14-one (19)



Prepared in 85% yield (9.3 mg, 0.028 mmol) as a white solid from the reaction of **7h** (10.0 mg, 0.033 mmol) with (diacetoxyiodo)benzene (10.7 mg 0.033 mmol) *via* general procedure **H**. R_f = 0.51 (1:1, hexanes: ethyl acetate); mp 175.0 – 176.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.39 (ddd, *J* = 7.9, 6.5, 2.2 Hz, 1H), 7.35 – 7.26 (m, 2H), 6.39 (d, *J* = 5.7 Hz, 1H), 6.10 (s, 1H), 5.04 (d, *J* = 8.5 Hz, 1H), 4.35 (d, *J* = 8.5 Hz, 1H), 4.27 (dt, *J* = 1.1, 2.7 Hz, 1H), 4.11 (ddd, *J* = 12.1, 10.3, 3.1 Hz, 1H), 3.94 (ddd, *J* = 11.5, 10.3, 2.9 Hz, 1H), 3.79 (dt, *J* = 11.5, 2.9 Hz, 1H), 3.16 (s, 3H), 1.45 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 138.9, 137.4, 135.5, 132.8, 129.3, 129.0, 128.7, 126.8, 114.3, 108.5, 74.3, 73.5, 67.3, 55.0, 50.4, 19.7, 18.3; FT-IR (neat): 3100, 2963, 2922, 2904, 2873, 28501, 2832, 2814, 1781, 1634 cm^{-1}; HRESI-MS: calculated for $C_{18}H_{21}NO_5Na$ $(M+Na)^+$ 354.1312, observed 354.1330.

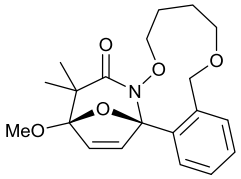
(±)-(1*S*,16*S*, *Z*)-16-Methoxy-15-(spiroclohexane)-9,12,19-trioxa-13-azatetracyclo[14.2.1.0^{1,13}.0^{2,7}]octadeca-2(7),3,5,17-tetraen-14-one (20)



Prepared in 92% yield (6.7 mg, 0.018 mmol) as a white solid from the reaction of **7k** (7.0 mg, 0.02 mmol) with (diacetoxyiodo)benzene (6.8 mg 0.02 mmol) *via* general procedure **H**. R_f = 0.6 (1:1, hexanes: ethyl acetate); mp 165.5 – 167.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.39 (ddd, *J* = 7.9, 6.6, 2.1 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.41 (d, *J* = 5.8 Hz, 1H), 6.09 (d, *J* = 5.7 Hz, 1H), 5.02 (d, *J* = 8.4 Hz, 1H), 4.35 (d, *J* = 8.4 Hz, 1H), 4.27 (ddd, *J* = 12.0, 2.9, 2.0 Hz, 1H), 4.08 (ddd, *J* = 11.9, 10.7, 3.1 Hz, 1H), 3.97 (td, *J* = 11.0, 2.9 Hz, 1H), 3.77 (ddd, *J* = 11.3, 3.0, 2.0 Hz, 1H), 3.13 (s, 3H), 2.09 (dd, *J* = 9.6, 5.1 Hz, 1H), 1.88 – 1.70 (m, 5H), 1.69 – 1.61 (m, 2H), 1.54 – 1.50 (m, 1H), 1.34 – 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 138.8, 137.5, 135.5, 132.7, 129.3, 129.0, 128.5, 126.7, 114.4, 108.4, 73.9, 73.6, 67.2, 58.8, 50.5, 30.2, 29.0,

25.3, 23.2, 22.8; FT-IR (neat): 2968, 2925, 2855, 1768 cm^{-1}; HRESI-MS: calculated for $C_{21}H_{26}NO_5$ $(M+H)^+$ 372.1805, observed 372.1822.

(±)-(1*S*,18*S*, *Z*)-18-Methoxy-17,17-dimethyl-9,14,21-trioxa-15-azatetracyclo[16.2.1.0^{1,15}.0^{2,7}]icosan-2(7),3,5,19-tetraen-16-one (21)

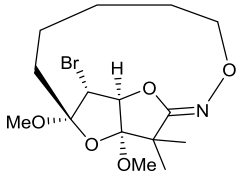


Prepared in 82% yield (4.3 mg, 0.012 mmol) as a white solid from the reaction of **7l** (5.0 mg, 0.015 mmol) with (diacetoxyiodo)benzene (4.8 mg 0.015 mmol) *via* general procedure **H**. R_f = 0.48 (1:1, hexanes: ethyl acetate); mp 176.0 – 179.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.39 (m, 2H), 7.39 – 7.24 (m, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.27 (d, *J* = 5.9 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 4.45 (d, *J* = 11.1 Hz, 1H), 4.02 (dt, *J* = 10.0, 5.9 Hz, 1H), 3.88 (dt, *J* = 10.1, 6.9 Hz, 1H), 3.69 (ddd, *J* = 10.9, 6.7, 4.5 Hz, 1H), 3.48 (ddd, *J* = 10.8, 7.2, 4.4 Hz, 1H), 3.20 (s, 3H), 1.79 – 1.74 (m, 2H), 1.66 – 1.48 (m, 2H), 1.46 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 69.2, 136.8, 136.8, 136.7, 132.5, 128.9, 128.7, 127.9, 127.8, 113.8, 107.6, 75.2, 70.1, 69.3, 55.0, 50.7, 25.2, 24.3, 19.2, 18.6; FT-IR (neat): 2929, 2870, 1771, 1694, 1601 cm^{-1}; HRESI-MS: calculated for $C_{20}H_{25}NO_5Na$ $(M+Na)^+$ 382.1625, observed 382.1633.

General Procedure I: For the synthesis of lactones (24-27)

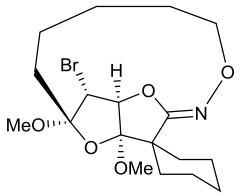
To a solution of macrocycle (1equiv.) in methanol (0.25 M) at 0 °C added bromine dropwise (2 equiv.) and stirred at room temperature for 10 min to 1h and quenched with brine solution. The organic phase was separated and aqueous phase was extracted with dichloromethane (3 times) The organic phases were washed with brine solution and dried over anhydrous sodium sulfate and volatiles were removed under reduced pressure. The crude mixture was purified by column chromatography to afford the desired compounds.

(±)-(1S,11S,13R,14R,Z)-14-Bromo-11,13-dimethoxy-15,15-dimethyl-2.5.12-trioxa-4-azatricyclo[9.2.1.1^{3,13}]pentadec-3-ene (24)



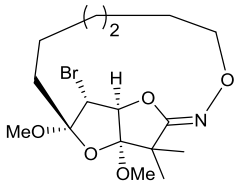
Prepared in 59% yield (14 mg, 0.037 mmol) as a white solid from the reaction of 2,2-dimethyl-5.14-dioxa-4-azabicyclo[9.2.1]tetradeca-1(13),11-dien-3-one **5** (15 mg, 0.06 mmol) with bromine (3 µL 0.12 mmol) *via* general procedure **I**. R_f = 0.74 (3:7, hexanes: ethyl acetate); mp 89.5 – 92.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 1H), 4.61 (s, 1H), 4.20 – 4.04 (m, 2H), 3.51 (s, 3H), 3.47 (s, 3H), 2.05 – 1.98 (m, 1H), 1.88 – 1.80 (m, 2H), 1.70 – 1.47(m, 5H), 1.42 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 113.6, 110.5, 91.6, 74.4, 52.9, 51.9, 51.4, 46.8, 34.1, 29.6, 24.9, 24.3, 21.9, 18.6; FT-IR (neat): 3708, 2934, 2905, 2874, 2857, 2839, 1793, 1678 cm^{-1}; HRESI-MS: calculated for $C_{15}H_{24}NO_5BrNa$ $(M+Na)^+$ 400.0730, observed 400.0742.

(±)-(1S,11S,13R,14R,Z)-14-Bromo-11,13-dimethoxy-15-(spirocyclohexane)-2.5.12-trioxa-4-azatricyclo[9.2.1.1^{3,13}]pentadec-3-ene (25)



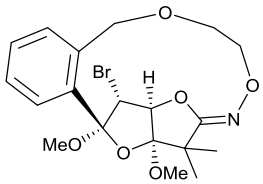
Prepared in 84% yield (19 mg, 0.045 mmol) as a white solid from the reaction of **7b** (15 mg, 0.054 mmol) with bromine (3 µL 0.12 mmol) *via* general procedure **I**. R_f = 0.54 (3:7, hexanes: ethyl acetate); mp 148.6 – 151.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.92 (s, 1H), 4.59 (s, 1H), 4.18 – 4.12 (m, 2H), 3.56 (s, 3H), 3.47 (s, 3H), 2.20 – 2.13 (m, 1H), 2.09 – 1.96 (m, 2H), 1.94 – 1.88 (m, 1H), 1.87 – 1.79 (m, 1H), 1.75 – 1.43 (m, 13H), 1.22 – 1.13 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 113.7, 110.4, 90.9, 74.7, 53.0, 52.3, 51.5, 51.4, 34.2, 29.7, 29.4, 27.7, 25.7, 25.2, 24.2, 22.2, 22.0; FT-IR (neat): 2930, 2846, 1737, 1660 cm^{-1}; HRESI-MS: calculated for $C_{18}H_{29}NO_5Br$ $(M+H)^+$ 418.1224, observed 418.1223.

(±)-(1S,12S,14R,15R,Z)-15-Bromo-12,14-dimethoxy-16,16-dimethyl-2.5.13-trioxa-4-azatricyclo[10.2.1.1^{3,14}]hexadec-3-ene (26)



Prepared in 52% yield (21 mg, 0.054 mmol) as a white solid from the reaction of **7c** (25 mg, 0.104 mmol) with bromine (6 µL 0.2 mmol) *via* general procedure **I**. R_f = 0.45 (1:9, hexanes: ethyl acetate); mp 121.2 – 124.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.97 (s, 1H), 4.52 (s, 1H), 4.19 (dt, *J* = 11.9, 2.9 Hz, 1H), 3.82 (td, *J* = 11.8, 1.9 Hz, 1H), 3.52 (s, 3H), 3.49 (s, 3H), 1.89 (ddd, *J* = 14.7, 9.7, 5.3 Hz, 1H), 1.81 (ddd, *J* = 14.4, 10.1, 5.5 Hz, 1H), 1.72 – 1.35 (m, 8H), 1.42 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8, 113.6, 110.7, 91.5, 75.3, 53.0, 51.8, 51.8, 47.0, 35.2, 27.6, 26.5, 24.3, 22.7, 22.2, 18.8; FT-IR (neat): 2974, 2936, 2853, 1677 cm^{-1}; HRESI-MS: calculated for $C_{16}H_{27}NO_5Br$ $(M+H)^+$ 392.1067, observed 392.1047.

(±)-(1S,16S,18R,19R,Z)-19-Bromo-16,18-dimethoxy-20,20-dimethyl-2.5.8.17-tetraoxa-4-azatetracyclo[12.2.1.1^{3,18}.0^{10,15}]icosa-3,10(15),11,13-tetraene (27)



Prepared in 46% yield (10 mg, 0.022 mmol) as a white solid from the reaction of **7h** (15 mg, 0.049 mmol) with bromine (3 µL 0.1 mmol) *via* general procedure **I**. R_f = 0.52 (7:3, hexanes: ethyl acetate); mp 127.8 – 130.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (m, 1H), 7.49 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 – 7.25 (m, 1H), 5.11 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 12.9 Hz, 1H), 4.47 (br.d, *J* = 12.9, Hz, 1H), 4.40 (d, *J* = 0.8 Hz, 1H), 4.26 (ddd, *J* = 12.5, 3.0, 2.0 Hz, 1H), 4.19 (ddd, *J* = 12.4, 10.2, 3.1 Hz, 1H), 4.04 (ddd, *J* = 13.2, 10.3, 3.0 Hz, 1H), 3.79 (ddd, *J* = 13.0, 3.1, 2.0 Hz, 1H), 3.67 (s, 3H), 3.36 (s, 3H), 1.57 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6, 136.9, 133.9, 129.1, 128.1, 128.1, 127.2, 116.2, 110.6, 90.9, 74.2, 71.4, 68.7, 57.6, 53.7, 52.4, 47.5, 22.6, 18.5; FT-IR (neat): 2973, 2939, 2850, 1672 cm^{-1}; HRESI-MS: calculated for $C_{19}H_{24}NO_6BrNa$ $(M+Na)^+$ 464.0679, observed 464.0674.

Crystallography

Single crystal X-ray diffraction was performed at 100 K on a Bruker SMART Apex CCD instrument using graphite-monochromated Mo K_α radiation. The crystals of **9-12** and **24** were grown by slow evaporation in a dichloromethane/hexanes mixture. The crystals were covered in Paratone oil and mounted on glass fibers. Lorentz and polarization effects were corrected using SAINT[6] and absorption corrections were applied using SADABS.[7] The structures were solved by direct or Patterson methods using OLEX2.[8] Tables S1-S18 summarizes the crystallographic data and parameters.

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[6]*SAINT: Program for data reduction, Version 7.68A; Bruker AXS: Madison, WI,* **2009.**
[7]Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008,** *64*, 112.
[8]Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009,** *42*, 339.

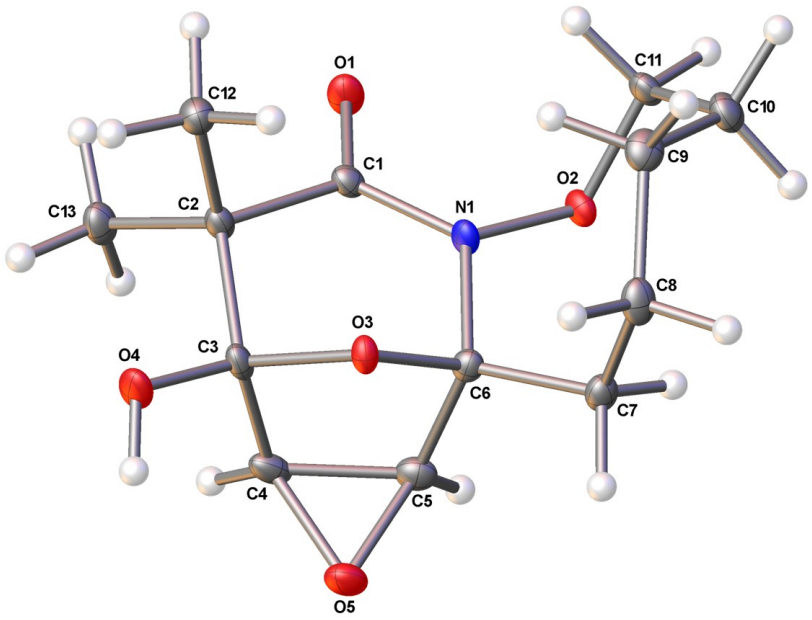


Figure S1. Thermal ellipsoid (50%) plot of **9**. Hydrogen atoms are shown as spheres of arbitrary radius.

Table S1. Crystal data and structure refinement for **9**.

Identification code	aa006_0m	
CCDC no.	1429958	
Empirical formula	$C_{13}H_{19}NO_5$	
Formula weight	269.29	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.9816(5) Å	α = 90°.
	b = 9.2222(4) Å	β = 107.6889(8)°.
	c = 13.0751(6) Å	γ = 90°.
Volume	1261.57(10) $Å^3$	
Z	4	
Density (calculated)	1.418 Mg/m^3	

Absorption coefficient	0.109 mm^{-1}
F(000)	576
Crystal size	0.253 x 0.071 x 0.067 mm^3
Theta range for data collection	2.128 to 27.531°.
Index ranges	-14<=h<=14, -11<=k<=11, -16<=l<=16
Reflections collected	21450
Independent reflections	2898 [R(int) = 0.0452]
Completeness to theta = 25.242°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2898 / 0 / 175
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1239
R indices (all data)	R1 = 0.0605, wR2 = 0.1382
Extinction coefficient	n/a
Largest diff. peak and hole	0.401 and -0.240 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [°] for **9**.

C(1)-C(2)	1.5442(19)	C(4)-C(5)	1.458(2)
C(1)-N(1)	1.3658(18)	C(4)-O(5)	1.4506(18)
C(1)-O(1)	1.2301(17)	C(5)-C(6)	1.531(2)
C(2)-C(3)	1.5462(19)	C(5)-O(5)	1.4381(18)
C(2)-C(12)	1.540(2)	C(6)-C(7)	1.5085(19)
C(2)-C(13)	1.5318(19)	C(6)-N(1)	1.4854(17)
C(3)-C(4)	1.519(2)	C(6)-O(3)	1.4090(17)
C(3)-O(3)	1.4567(17)	C(7)-C(8)	1.528(2)
C(3)-O(4)	1.3736(18)	C(8)-C(9)	1.534(2)

C(9)-C(10)	1.541(2)	O(3)-C(6)-C(7)	110.89(12)
C(10)-C(11)	1.516(2)	O(3)-C(6)-N(1)	105.56(11)
C(11)-O(2)	1.4547(17)	C(6)-C(7)-C(8)	116.17(13)
N(1)-O(2)	1.4020(15)	C(7)-C(8)-C(9)	116.59(12)
N(1)-C(1)-C(2)	116.09(12)	C(8)-C(9)-C(10)	114.52(13)
O(1)-C(1)-C(2)	121.33(13)	C(11)-C(10)-C(9)	115.55(13)
O(1)-C(1)-N(1)	122.32(13)	C(1)-N(1)-C(6)	122.02(11)
C(1)-C(2)-C(3)	109.78(12)	C(1)-N(1)-O(2)	116.21(11)
C(12)-C(2)-C(1)	106.70(11)	O(2)-N(1)-C(6)	115.86(11)
C(12)-C(2)-C(3)	109.86(12)	N(1)-O(2)-C(11)	109.58(10)
C(13)-C(2)-C(1)	109.63(12)	C(6)-O(3)-C(3)	105.49(11)
C(13)-C(2)-C(3)	111.00(12)	C(5)-O(5)-C(4)	60.63(10)
C(13)-C(2)-C(12)	109.77(13)		
C(4)-C(3)-C(2)	111.44(12)		
O(3)-C(3)-C(2)	106.36(11)		
O(3)-C(3)-C(4)	102.55(12)		
O(4)-C(3)-C(2)	109.96(12)		
O(4)-C(3)-C(4)	116.74(12)		
O(4)-C(3)-O(3)	109.04(12)		
C(5)-C(4)-C(3)	106.46(12)		
O(5)-C(4)-C(3)	111.88(12)		
O(5)-C(4)-C(5)	59.26(9)		
C(4)-C(5)-C(6)	104.84(13)		
O(5)-C(5)-C(4)	60.11(9)		
O(5)-C(5)-C(6)	112.49(12)		
C(7)-C(6)-C(5)	116.35(13)		
N(1)-C(6)-C(5)	106.38(11)		
N(1)-C(6)-C(7)	113.04(12)		
O(3)-C(6)-C(5)	103.67(12)		

Table S3. Torsion angles [°] for **9**.

		C(7)-C(6)-O(3)-C(3)	-166.42(11)
C(1)-C(2)-C(3)-C(4)	-59.70(15)	C(7)-C(8)-C(9)-C(10)	-48.93(18)
C(1)-C(2)-C(3)-O(3)	51.31(15)	C(8)-C(9)-C(10)-C(11)	97.59(16)
C(1)-C(2)-C(3)-O(4)	169.24(11)	C(9)-C(10)-C(11)-O(2)	-67.18(18)
C(1)-N(1)-O(2)-C(11)	91.21(14)	C(10)-C(11)-O(2)-N(1)	77.68(15)
C(2)-C(1)-N(1)-C(6)	23.5(2)	C(12)-C(2)-C(3)-C(4)	-176.74(12)
C(2)-C(1)-N(1)-O(2)	175.26(11)	C(12)-C(2)-C(3)-O(3)	-65.73(14)
C(2)-C(3)-C(4)-C(5)	91.37(14)	C(12)-C(2)-C(3)-O(4)	52.19(15)
C(2)-C(3)-C(4)-O(5)	154.26(11)	C(13)-C(2)-C(3)-C(4)	61.66(16)
C(2)-C(3)-O(3)-C(6)	-77.64(14)	C(13)-C(2)-C(3)-O(3)	172.67(12)
C(3)-C(4)-C(5)-C(6)	-1.66(15)	C(13)-C(2)-C(3)-O(4)	-69.40(16)
C(3)-C(4)-C(5)-O(5)	106.05(12)	N(1)-C(1)-C(2)-C(3)	-25.70(18)
C(3)-C(4)-O(5)-C(5)	-96.69(14)	N(1)-C(1)-C(2)-C(12)	93.30(15)
C(4)-C(3)-O(3)-C(6)	39.46(13)	N(1)-C(1)-C(2)-C(13)	-147.88(14)
C(4)-C(5)-C(6)-C(7)	147.79(12)	N(1)-C(6)-C(7)-C(8)	69.47(16)
C(4)-C(5)-C(6)-N(1)	-85.28(13)	N(1)-C(6)-O(3)-C(3)	70.82(13)
C(4)-C(5)-C(6)-O(3)	25.78(14)	O(1)-C(1)-C(2)-C(3)	160.08(14)
C(5)-C(6)-C(7)-C(8)	-166.97(13)	O(1)-C(1)-C(2)-C(12)	-80.92(17)
C(5)-C(6)-N(1)-C(1)	64.36(17)	O(1)-C(1)-C(2)-C(13)	37.9(2)
C(5)-C(6)-N(1)-O(2)	-87.54(14)	O(1)-C(1)-N(1)-C(6)	-162.39(14)
C(5)-C(6)-O(3)-C(3)	-40.84(13)	O(1)-C(1)-N(1)-O(2)	-10.6(2)
C(6)-C(5)-O(5)-C(4)	94.69(14)	O(3)-C(3)-C(4)-C(5)	-22.04(14)
C(6)-C(7)-C(8)-C(9)	-58.36(18)	O(3)-C(3)-C(4)-O(5)	40.85(14)
C(6)-N(1)-O(2)-C(11)	-115.23(13)	O(3)-C(6)-C(7)-C(8)	-48.84(17)
C(7)-C(6)-N(1)-C(1)	-166.75(13)	O(3)-C(6)-N(1)-C(1)	-45.38(17)
C(7)-C(6)-N(1)-O(2)	41.35(17)	O(3)-C(6)-N(1)-O(2)	162.73(10)

O(4)-C(3)-C(4)-C(5)	-141.15(13)	O(5)-C(5)-C(6)-C(7)	84.42(16)
O(4)-C(3)-C(4)-O(5)	-78.26(16)	O(5)-C(5)-C(6)-N(1)	-148.65(12)
O(4)-C(3)-O(3)-C(6)	163.83(12)	O(5)-C(5)-C(6)-O(3)	-37.59(15)
O(5)-C(4)-C(5)-C(6)	-107.71(12)		

Table S4. Hydrogen bonds for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(1)#1	0.84	1.98	2.8055(15)	166.9

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2

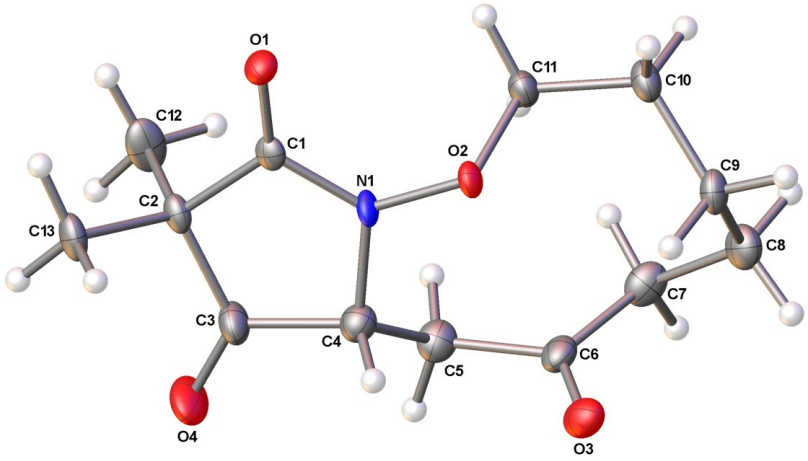


Figure S2. Thermal ellipsoid (50%) plot of **10**. Hydrogen atoms are shown as spheres of arbitrary radius.

Table S5. Crystal data and structure refinement for **10**.

Identification code	aa004_0m
CCDC no.	1429956
Empirical formula	$C_{13}H_{19}NO_4$
Formula weight	253.29
Temperature	100 K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.3134(5) Å	α= 90°.
	b = 9.4290(4) Å	β= 110.9907(8)°.
	c = 12.7345(6) Å	γ = 90°.
Volume	1268.29(10) $Å^3$	
Z	4	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	544	
Crystal size	0.284 x 0.254 x 0.158 mm^3	
Theta range for data collection	2.070 to 27.590°.	
Index ranges	-14<=h<=14, -12<=k<=12, -16<=l<=16	
Reflections collected	21397	
Independent reflections	2947 [R(int) = 0.0433]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6943	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2947 / 0 / 165	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.2501	
R indices (all data)	R1 = 0.0791, wR2 = 0.2774	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.427 and -0.386 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for **10**.

C(1)-C(2)	1.523(3)	C(1)-C(2)-C(12)	109.64(17)
C(1)-N(1)	1.348(2)	C(1)-C(2)-C(13)	112.73(16)
C(1)-O(1)	1.226(2)	C(3)-C(2)-C(12)	109.40(18)
C(2)-C(3)	1.522(3)	C(3)-C(2)-C(13)	111.00(17)
C(2)-C(12)	1.532(3)	C(13)-C(2)-C(12)	110.87(18)
C(2)-C(13)	1.528(3)	C(4)-C(3)-C(2)	110.90(17)
C(3)-C(4)	1.521(3)	O(4)-C(3)-C(2)	125.95(19)
C(3)-O(4)	1.208(3)	O(4)-C(3)-C(4)	123.1(2)
C(4)-C(5)	1.515(3)	C(5)-C(4)-C(3)	113.52(18)
C(4)-N(1)	1.472(3)	N(1)-C(4)-C(3)	99.53(16)
C(5)-C(6)	1.536(3)	N(1)-C(4)-C(5)	112.02(17)
C(6)-C(7)	1.492(3)	C(4)-C(5)-C(6)	109.98(17)
C(6)-O(3)	1.226(3)	C(7)-C(6)-C(5)	116.35(18)
C(7)-C(8)	1.512(3)	O(3)-C(6)-C(5)	121.9(2)
C(8)-C(9)	1.535(3)	O(3)-C(6)-C(7)	121.7(2)
C(9)-C(10)	1.539(3)	C(6)-C(7)-C(8)	114.85(18)
C(10)-C(11)	1.515(3)	C(7)-C(8)-C(9)	116.98(18)
C(11)-O(2)	1.461(2)	C(8)-C(9)-C(10)	117.52(17)
N(1)-O(2)	1.391(2)	C(11)-C(10)-C(9)	117.16(18)
		O(2)-C(11)-C(10)	107.96(16)
N(1)-C(1)-C(2)	106.98(16)	C(1)-N(1)-C(4)	117.27(16)
O(1)-C(1)-C(2)	126.99(18)	C(1)-N(1)-O(2)	123.08(16)
O(1)-C(1)-N(1)	125.96(18)	O(2)-N(1)-C(4)	116.69(15)
C(1)-C(2)-C(3)	102.89(16)	N(1)-O(2)-C(11)	109.90(14)

Table S7. Torsion angles [°] for **10**.

C(1)-C(2)-C(3)-C(4)	-5.1(2)	C(9)-C(10)-C(11)-O(2)	49.0(2)
C(1)-C(2)-C(3)-O(4)	175.5(2)	C(10)-C(11)-O(2)-N(1)	-165.31(15)
C(1)-N(1)-O(2)-C(11)	-84.4(2)	C(12)-C(2)-C(3)-C(4)	111.4(2)
C(2)-C(1)-N(1)-C(4)	-17.3(2)	C(12)-C(2)-C(3)-O(4)	-68.0(3)
C(2)-C(1)-N(1)-O(2)	-177.18(15)	C(13)-C(2)-C(3)-C(4)	-125.91(19)
C(2)-C(3)-C(4)-C(5)	-122.85(19)	C(13)-C(2)-C(3)-O(4)	54.7(3)
C(2)-C(3)-C(4)-N(1)	-3.7(2)	N(1)-C(1)-C(2)-C(3)	12.72(19)
C(3)-C(4)-C(5)-C(6)	-173.32(18)	N(1)-C(1)-C(2)-C(12)	-103.6(2)
C(3)-C(4)-N(1)-C(1)	13.3(2)	N(1)-C(1)-C(2)-C(13)	132.36(18)
C(3)-C(4)-N(1)-O(2)	174.44(15)	N(1)-C(4)-C(5)-C(6)	74.9(2)
C(4)-C(5)-C(6)-C(7)	-131.33(19)	O(1)-C(1)-C(2)-C(3)	-170.25(19)
C(4)-C(5)-C(6)-O(3)	48.5(3)	O(1)-C(1)-C(2)-C(12)	73.4(2)
C(4)-N(1)-O(2)-C(11)	115.67(18)	O(1)-C(1)-C(2)-C(13)	-50.6(3)
C(5)-C(4)-N(1)-C(1)	133.60(19)	O(1)-C(1)-N(1)-C(4)	165.59(18)
C(5)-C(4)-N(1)-O(2)	-65.3(2)	O(1)-C(1)-N(1)-O(2)	5.8(3)
C(5)-C(6)-C(7)-C(8)	148.0(2)	O(3)-C(6)-C(7)-C(8)	-31.9(3)
C(6)-C(7)-C(8)-C(9)	-50.0(3)	O(4)-C(3)-C(4)-C(5)	56.6(3)
C(7)-C(8)-C(9)-C(10)	-61.7(3)	O(4)-C(3)-C(4)-N(1)	175.8(2)
C(8)-C(9)-C(10)-C(11)	70.3(3)		

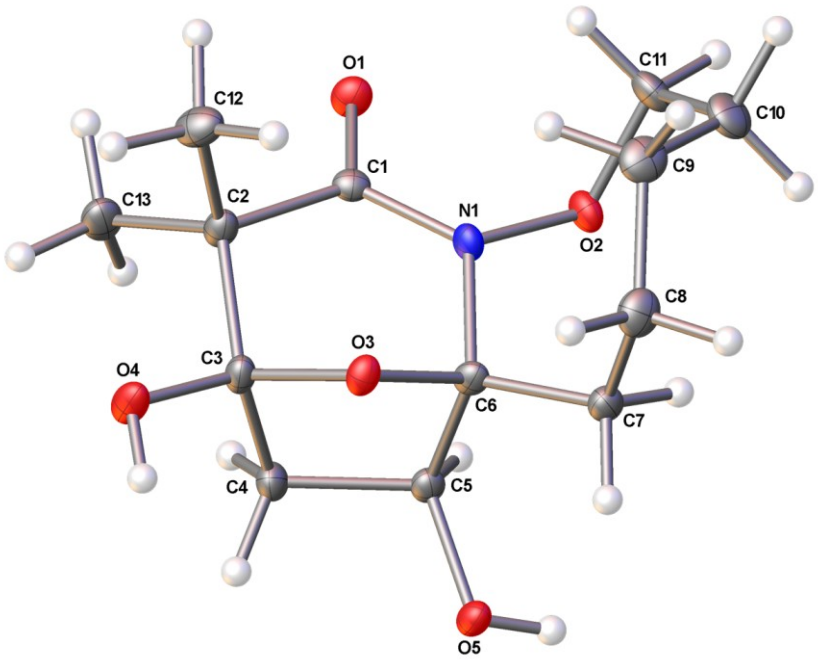


Figure S3. Thermal ellipsoid (50%) plot of **11**. Hydrogen atoms are shown as spheres of arbitrary radius.

Table S8. Crystal data and structure refinement for **11**.

Identification code	aa002_0m	
CCDC no.	1429955	
Empirical formula	$C_{14}H_{23}Cl_2NO_5$	
Formula weight	356.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.7775(8) Å	α = 90°.
	b = 8.7429(6) Å	β = 105.8523(13)°.
	c = 16.8595(12) Å	γ = 90°.
Volume	1670.0(2) $Å^3$	
Z	4	
Density (calculated)	1.417 Mg/m^3	

Absorption coefficient	0.410 mm^{-1}
F(000)	752
Crystal size	0.453 x 0.294 x 0.062 mm^3
Theta range for data collection	1.891 to 25.497°.
Index ranges	-14<=h<=14, -10<=k<=10, -20<=l<=20
Reflections collected	23957
Independent reflections	3102 [R(int) = 0.0652]
Completeness to theta = 25.242°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6725
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3102 / 0 / 203
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.1167
R indices (all data)	R1 = 0.0550, wR2 = 0.1240
Extinction coefficient	n/a
Largest diff. peak and hole	0.320 and -0.425 e.$Å^{-3}$

Table S9. Bond lengths [Å] and angles [°] for **11**.

C(1)-C(2)	1.531(3)	C(4)-C(5)	1.537(3)
C(1)-N(1)	1.361(3)	C(5)-C(6)	1.551(3)
C(1)-O(1)	1.232(2)	C(5)-O(5)	1.416(2)
C(2)-C(3)	1.548(3)	C(6)-C(7)	1.509(3)
C(2)-C(12)	1.540(3)	C(6)-N(1)	1.495(2)
C(2)-C(13)	1.527(3)	C(6)-O(3)	1.417(2)
C(3)-C(4)	1.534(3)	C(7)-C(8)	1.535(3)
C(3)-O(3)	1.459(2)	C(8)-C(9)	1.524(3)
C(3)-O(4)	1.381(2)	C(9)-C(10)	1.536(3)

C(10)-C(11)	1.518(3)	C(4)-C(5)-C(6)	102.15(15)
C(11)-O(2)	1.457(2)	O(5)-C(5)-C(4)	109.09(15)
N(1)-O(2)	1.405(2)	O(5)-C(5)-C(6)	113.44(16)
N(1)-C(1)-C(2)	115.78(16)	C(7)-C(6)-C(5)	115.90(16)
O(1)-C(1)-C(2)	121.86(17)	N(1)-C(6)-C(5)	107.09(15)
O(1)-C(1)-N(1)	122.14(18)	N(1)-C(6)-C(7)	111.60(16)
C(1)-C(2)-C(3)	108.53(16)	O(3)-C(6)-C(5)	104.94(15)
C(1)-C(2)-C(12)	106.90(16)	O(3)-C(6)-C(7)	111.19(16)
C(12)-C(2)-C(3)	110.68(16)	O(3)-C(6)-N(1)	105.39(15)
C(13)-C(2)-C(1)	109.33(16)	C(6)-C(7)-C(8)	116.40(17)
C(13)-C(2)-C(3)	111.76(17)	C(9)-C(8)-C(7)	117.12(17)
C(13)-C(2)-C(12)	109.50(17)	C(8)-C(9)-C(10)	114.71(18)
C(4)-C(3)-C(2)	114.59(16)	C(11)-C(10)-C(9)	116.06(18)
O(3)-C(3)-C(2)	107.62(15)	O(2)-C(11)-C(10)	114.89(17)
O(3)-C(3)-C(4)	102.53(15)	C(1)-N(1)-C(6)	122.52(16)
O(4)-C(3)-C(2)	107.36(15)	C(1)-N(1)-O(2)	115.29(15)
O(4)-C(3)-C(4)	115.57(16)	O(2)-N(1)-C(6)	114.39(14)
O(4)-C(3)-O(3)	108.71(15)	N(1)-O(2)-C(11)	109.82(14)
C(3)-C(4)-C(5)	105.63(15)	C(6)-O(3)-C(3)	104.64(14)

Table S10. Torsion angles [°] for **11**.

C(1)-C(2)-C(3)-C(4)	-59.1(2)	C(2)-C(3)-O(3)-C(6)	-77.61(18)
C(1)-C(2)-C(3)-O(3)	54.2(2)	C(3)-C(4)-C(5)-C(6)	0.45(19)
C(1)-C(2)-C(3)-O(4)	171.05(15)	C(3)-C(4)-C(5)-O(5)	120.79(17)
C(1)-N(1)-O(2)-C(11)	91.89(18)	C(4)-C(3)-O(3)-C(6)	43.58(17)
C(2)-C(1)-N(1)-C(6)	27.2(2)	C(4)-C(5)-C(6)-C(7)	149.11(17)
C(2)-C(1)-N(1)-O(2)	174.67(15)	C(4)-C(5)-C(6)-N(1)	-85.62(17)
C(2)-C(3)-C(4)-C(5)	90.55(19)	C(4)-C(5)-C(6)-O(3)	26.06(18)

C(5)-C(6)-C(7)-C(8)	-170.03(17)	N(1)-C(1)-C(2)-C(3)	-29.4(2)
C(5)-C(6)-N(1)-C(1)	64.8(2)	N(1)-C(1)-C(2)-C(12)	90.05(19)
C(5)-C(6)-N(1)-O(2)	-82.97(18)	N(1)-C(1)-C(2)-C(13)	-151.50(17)
C(5)-C(6)-O(3)-C(3)	-44.20(17)	N(1)-C(6)-C(7)-C(8)	67.0(2)
C(6)-C(7)-C(8)-C(9)	-58.9(3)	N(1)-C(6)-O(3)-C(3)	68.69(17)
C(6)-N(1)-O(2)-C(11)	-117.97(17)	O(1)-C(1)-C(2)-C(3)	155.83(18)
C(7)-C(6)-N(1)-C(1)	-167.42(17)	O(1)-C(1)-C(2)-C(12)	-84.8(2)
C(7)-C(6)-N(1)-O(2)	44.8(2)	O(1)-C(1)-C(2)-C(13)	33.7(2)
C(7)-C(6)-O(3)-C(3)	-170.24(15)	O(1)-C(1)-N(1)-C(6)	-158.01(18)
C(7)-C(8)-C(9)-C(10)	-49.1(3)	O(1)-C(1)-N(1)-O(2)	-10.5(3)
C(8)-C(9)-C(10)-C(11)	96.5(2)	O(3)-C(3)-C(4)-C(5)	-25.73(19)
C(9)-C(10)-C(11)-O(2)	-64.1(2)	O(3)-C(6)-C(7)-C(8)	-50.3(2)
C(10)-C(11)-O(2)-N(1)	75.6(2)	O(3)-C(6)-N(1)-C(1)	-46.6(2)
C(12)-C(2)-C(3)-C(4)	-176.15(16)	O(3)-C(6)-N(1)-O(2)	165.66(13)
C(12)-C(2)-C(3)-O(3)	-62.8(2)	O(4)-C(3)-C(4)-C(5)	-143.80(16)
C(12)-C(2)-C(3)-O(4)	54.0(2)	O(4)-C(3)-O(3)-C(6)	166.41(15)
C(13)-C(2)-C(3)-C(4)	61.5(2)	O(5)-C(5)-C(6)-C(7)	31.9(2)
C(13)-C(2)-C(3)-O(3)	174.82(16)	O(5)-C(5)-C(6)-N(1)	157.12(15)
C(13)-C(2)-C(3)-O(4)	-68.3(2)	O(5)-C(5)-C(6)-O(3)	-91.20(18)

Table S11. Hydrogen bonds for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4)...O(5)#1	0.84	1.96	2.7262(19)	150.3
O(5)-H(5)...O(1)#2	0.84	1.93	2.7065(19)	152.4
O(5)-H(5)...O(2)#2	0.84	2.52	3.1735(19)	134.9

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y-1,-z #2 -x-3/2,y-1/2,-z-1/2

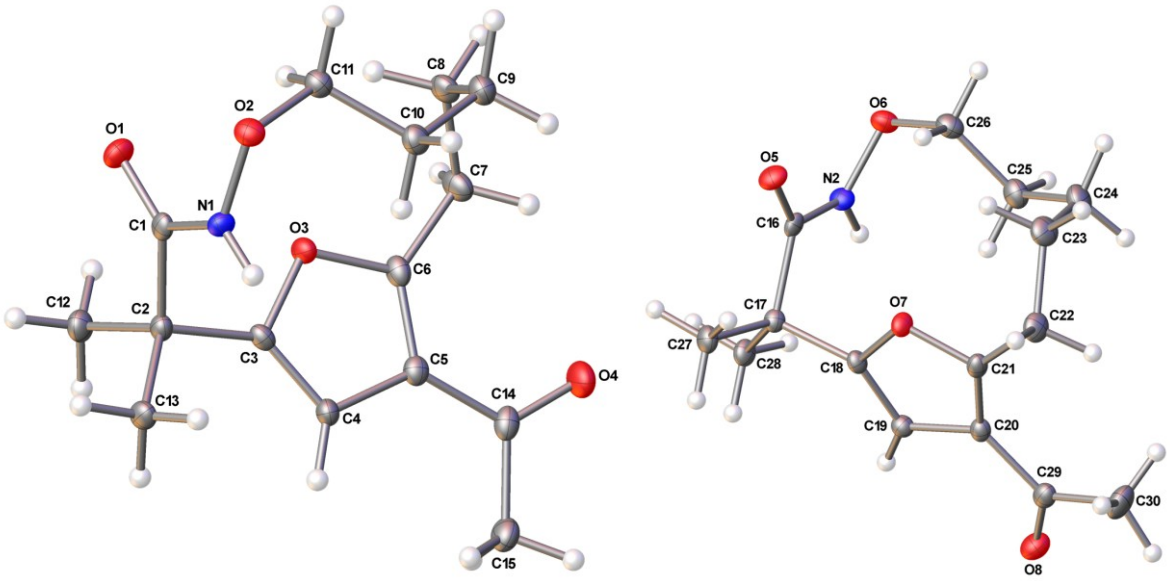


Figure S4. Thermal ellipsoid (50%) plots of **12**. Both molecules appear in the asymmetric unit. Hydrogen atoms are shown as spheres of arbitrary radius.

Table S12. Crystal data and structure refinement for **12**.

Identification code	aa005_0ma	
CCDC no.	1429957	
Empirical formula	$C_{15}H_{21}NO_4$	
Formula weight	558.65	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.0197(5) Å	α = 90°.
	b = 16.2710(5) Å	β = 99.0774(5)°.
	c = 10.1414(3) Å	γ = 90°.
Volume	2773.26(14) $Å^3$	
Z	4	
Density (calculated)	1.338 Mg/m^3	

Absorption coefficient	0.097 mm^{-1}
F(000)	1200
Crystal size	0.256 x 0.2 x 0.155 mm^3
Theta range for data collection	1.742 to 25.498°.
Index ranges	-19<=h<=20, -19<=k<=19, -12<=l<=12
Reflections collected	41363
Independent reflections	5170 [R(int) = 0.0413]
Completeness to theta = 25.242°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7038
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5170 / 0 / 375
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.1193
R indices (all data)	R1 = 0.0470, wR2 = 0.1275
Extinction coefficient	n/a
Largest diff. peak and hole	0.299 and -0.203 e.$Å^{-3}$

Table S13. Bond lengths [Å] and angles [°] for **12**.

C(1)-C(2)	1.5508(19)	C(5)-C(6)	1.3680(19)
C(1)-N(1)	1.3421(17)	C(5)-C(14)	1.4704(19)
C(1)-O(1)	1.2263(15)	C(6)-C(7)	1.4868(19)
C(2)-C(3)	1.5062(18)	C(6)-O(3)	1.3655(16)
C(2)-C(12)	1.5393(18)	C(7)-C(8)	1.5345(19)
C(2)-C(13)	1.5341(18)	C(8)-C(9)	1.5348(19)
C(3)-C(4)	1.3463(18)	C(9)-C(10)	1.5347(19)
C(3)-O(3)	1.3837(16)	C(10)-C(11)	1.5218(19)
C(4)-C(5)	1.4426(19)	C(11)-O(2)	1.4557(16)

C(14)-C(15)	1.501(2)	O(1)-C(1)-N(1)	122.95(13)
C(14)-O(4)	1.2277(17)	C(3)-C(2)-C(1)	105.48(10)
N(1)-H(1)	0.865(15)	C(3)-C(2)-C(12)	110.63(11)
N(1)-O(2)	1.4028(15)	C(3)-C(2)-C(13)	109.61(11)
C(16)-C(17)	1.5499(19)	C(12)-C(2)-C(1)	109.18(10)
C(16)-N(2)	1.3478(17)	C(13)-C(2)-C(1)	112.37(11)
C(16)-O(5)	1.2253(15)	C(13)-C(2)-C(12)	109.51(11)
C(17)-C(18)	1.5009(18)	C(4)-C(3)-C(2)	134.73(12)
C(17)-C(27)	1.5371(18)	C(4)-C(3)-O(3)	109.27(11)
C(17)-C(28)	1.5313(18)	O(3)-C(3)-C(2)	115.90(11)
C(18)-C(19)	1.3465(18)	C(3)-C(4)-C(5)	107.14(12)
C(18)-O(7)	1.3875(15)	C(4)-C(5)-C(14)	127.75(12)
C(19)-C(20)	1.4438(19)	C(6)-C(5)-C(4)	106.29(11)
C(20)-C(21)	1.3663(19)	C(6)-C(5)-C(14)	125.93(13)
C(20)-C(29)	1.4695(19)	C(5)-C(6)-C(7)	134.44(13)
C(21)-C(22)	1.4933(18)	O(3)-C(6)-C(5)	109.30(11)
C(21)-O(7)	1.3626(16)	O(3)-C(6)-C(7)	116.26(12)
C(22)-C(23)	1.533(2)	C(6)-C(7)-C(8)	115.57(12)
C(23)-C(24)	1.537(2)	C(9)-C(8)-C(7)	116.07(11)
C(24)-C(25)	1.538(2)	C(10)-C(9)-C(8)	117.34(11)
C(25)-C(26)	1.516(2)	C(11)-C(10)-C(9)	111.57(11)
C(26)-O(6)	1.4520(17)	O(2)-C(11)-C(10)	113.53(11)
C(29)-C(30)	1.506(2)	C(5)-C(14)-C(15)	117.71(12)
C(29)-O(8)	1.2195(17)	O(4)-C(14)-C(5)	122.38(13)
N(2)-H(2)	0.888(16)	O(4)-C(14)-C(15)	119.85(13)
N(2)-O(6)	1.4022(15)	C(1)-N(1)-H(1)	124.4(10)
		C(1)-N(1)-O(2)	119.21(11)
N(1)-C(1)-C(2)	114.29(11)	O(2)-N(1)-H(1)	115.2(10)
O(1)-C(1)-C(2)	122.61(11)	N(1)-O(2)-C(11)	109.55(9)

C(6)-O(3)-C(3)	107.93(10)	C(20)-C(21)-C(22)	136.59(13)
N(2)-C(16)-C(17)	113.93(11)	O(7)-C(21)-C(20)	109.59(12)
O(5)-C(16)-C(17)	123.26(11)	O(7)-C(21)-C(22)	113.69(11)
O(5)-C(16)-N(2)	122.62(13)	C(21)-C(22)-C(23)	113.56(12)
C(18)-C(17)-C(16)	104.70(10)	C(22)-C(23)-C(24)	115.51(12)
C(18)-C(17)-C(27)	111.04(11)	C(25)-C(24)-C(23)	116.88(12)
C(18)-C(17)-C(28)	109.09(11)	C(26)-C(25)-C(24)	111.78(12)
C(27)-C(17)-C(16)	108.90(10)	O(6)-C(26)-C(25)	114.40(11)
C(28)-C(17)-C(16)	113.06(11)	C(20)-C(29)-C(30)	120.60(12)
C(28)-C(17)-C(27)	109.95(11)	O(8)-C(29)-C(20)	119.54(13)
C(19)-C(18)-C(17)	135.12(12)	O(8)-C(29)-C(30)	119.84(13)
C(19)-C(18)-O(7)	109.36(12)	C(16)-N(2)-H(2)	122.7(10)
O(7)-C(18)-C(17)	115.40(11)	C(16)-N(2)-O(6)	119.38(11)
C(18)-C(19)-C(20)	107.00(12)	O(6)-N(2)-H(2)	115.9(10)
C(19)-C(20)-C(29)	122.84(12)	N(2)-O(6)-C(26)	109.96(10)
C(21)-C(20)-C(19)	106.29(12)	C(21)-O(7)-C(18)	107.73(10)
C(21)-C(20)-C(29)	130.80(13)		

Table S14. Torsion angles [°] for **12**.

C(1)-C(2)-C(3)-C(4)	139.45(15)	C(4)-C(5)-C(6)-C(7)	177.35(15)
C(1)-C(2)-C(3)-O(3)	-36.54(14)	C(4)-C(5)-C(6)-O(3)	-1.98(14)
C(1)-N(1)-O(2)-C(11)	-69.89(14)	C(4)-C(5)-C(14)-C(15)	8.4(2)
C(2)-C(1)-N(1)-O(2)	162.72(11)	C(4)-C(5)-C(14)-O(4)	-174.28(13)
C(2)-C(3)-C(4)-C(5)	-174.97(14)	C(5)-C(6)-C(7)-C(8)	-139.94(15)
C(2)-C(3)-O(3)-C(6)	174.53(11)	C(5)-C(6)-O(3)-C(3)	2.75(14)
C(3)-C(4)-C(5)-C(6)	0.46(15)	C(6)-C(5)-C(14)-C(15)	-169.32(13)
C(3)-C(4)-C(5)-C(14)	-177.64(13)	C(6)-C(5)-C(14)-O(4)	8.0(2)
C(4)-C(3)-O(3)-C(6)	-2.45(14)	C(6)-C(7)-C(8)-C(9)	65.89(17)

C(7)-C(6)-O(3)-C(3)	-176.71(11)	C(19)-C(20)-C(21)-C(22)	-173.68(15)
C(7)-C(8)-C(9)-C(10)	-78.69(16)	C(19)-C(20)-C(21)-O(7)	1.67(14)
C(8)-C(9)-C(10)-C(11)	-65.24(16)	C(19)-C(20)-C(29)-C(30)	-173.32(13)
C(9)-C(10)-C(11)-O(2)	175.43(11)	C(19)-C(20)-C(29)-O(8)	5.0(2)
C(10)-C(11)-O(2)-N(1)	-63.93(13)	C(20)-C(21)-C(22)-C(23)	127.86(17)
C(12)-C(2)-C(3)-C(4)	-102.60(17)	C(20)-C(21)-O(7)-C(18)	-1.67(14)
C(12)-C(2)-C(3)-O(3)	81.41(14)	C(21)-C(20)-C(29)-C(30)	3.4(2)
C(13)-C(2)-C(3)-C(4)	18.3(2)	C(21)-C(20)-C(29)-O(8)	-178.26(13)
C(13)-C(2)-C(3)-O(3)	-157.73(11)	C(21)-C(22)-C(23)-C(24)	-60.99(17)
C(14)-C(5)-C(6)-C(7)	-4.5(2)	C(22)-C(21)-O(7)-C(18)	174.84(11)
C(14)-C(5)-C(6)-O(3)	176.16(12)	C(22)-C(23)-C(24)-C(25)	81.49(17)
N(1)-C(1)-C(2)-C(3)	-69.78(14)	C(23)-C(24)-C(25)-C(26)	66.81(16)
N(1)-C(1)-C(2)-C(12)	171.31(11)	C(24)-C(25)-C(26)-O(6)	-175.40(11)
N(1)-C(1)-C(2)-C(13)	49.60(15)	C(25)-C(26)-O(6)-N(2)	59.28(14)
O(1)-C(1)-C(2)-C(3)	105.74(14)	C(27)-C(17)-C(18)-C(19)	110.64(17)
O(1)-C(1)-C(2)-C(12)	-13.17(18)	C(27)-C(17)-C(18)-O(7)	-73.93(14)
O(1)-C(1)-C(2)-C(13)	-134.88(13)	C(28)-C(17)-C(18)-C(19)	-10.7(2)
O(1)-C(1)-N(1)-O(2)	-12.78(19)	C(28)-C(17)-C(18)-O(7)	164.74(11)
O(3)-C(3)-C(4)-C(5)	1.21(15)	C(29)-C(20)-C(21)-C(22)	9.2(3)
O(3)-C(6)-C(7)-C(8)	39.35(17)	C(29)-C(20)-C(21)-O(7)	-175.48(13)
C(16)-C(17)-C(18)-C(19)	-131.99(16)	N(2)-C(16)-C(17)-C(18)	71.06(13)
C(16)-C(17)-C(18)-O(7)	43.45(14)	N(2)-C(16)-C(17)-C(27)	-170.11(11)
C(16)-N(2)-O(6)-C(26)	67.12(14)	N(2)-C(16)-C(17)-C(28)	-47.57(15)
C(17)-C(16)-N(2)-O(6)	-161.31(11)	O(5)-C(16)-C(17)-C(18)	-103.99(14)
C(17)-C(18)-C(19)-C(20)	175.67(14)	O(5)-C(16)-C(17)-C(27)	14.84(18)
C(17)-C(18)-O(7)-C(21)	-175.60(11)	O(5)-C(16)-C(17)-C(28)	137.38(13)
C(18)-C(19)-C(20)-C(21)	-1.04(15)	O(5)-C(16)-N(2)-O(6)	13.77(19)
C(18)-C(19)-C(20)-C(29)	176.39(12)	O(7)-C(18)-C(19)-C(20)	0.04(14)
C(19)-C(18)-O(7)-C(21)	0.99(14)	O(7)-C(21)-C(22)-C(23)	-47.36(16)

Table S15. Hydrogen bonds for **12** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(1)	0.888(16)	2.000(16)	2.8561(14)	161.4(14)

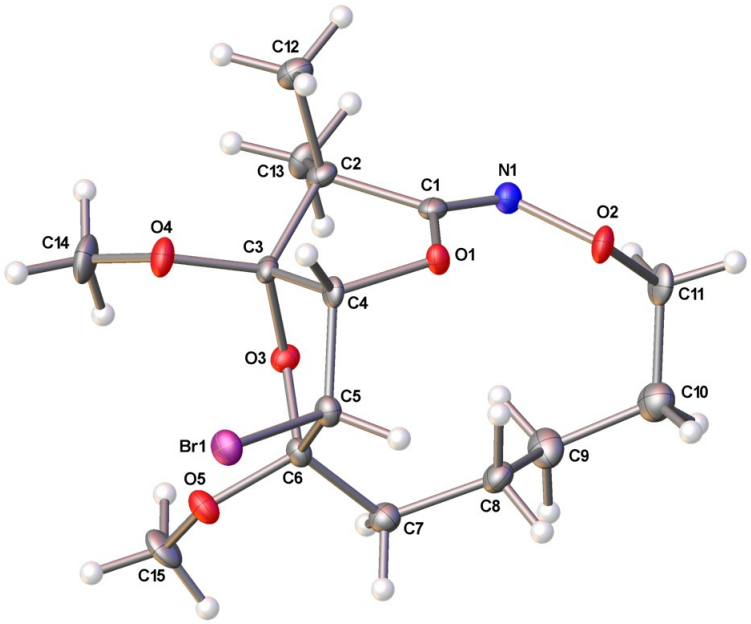


Figure S5. Thermal ellipsoid (50%) plot of **24**. Hydrogen atoms are shown as spheres of arbitrary radius.

Table S16. Crystal data and structure refinement for **24**.

Identification code	aa001_0m
CCDC no.	1429954
Empirical formula	$C_{15}H_{24}BrNO_5$
Formula weight	378.26
Temperature	99.65 K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 8.8508(8) Å	α = 116.0658(15)°.
	b = 10.0352(8) Å	β = 107.1142(16)°.
	c = 10.7879(9) Å	γ = 90.5266(17)°.
Volume	811.83(12) $Å^3$	
Z	2	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	2.555 mm^{-1}	
F(000)	392	
Crystal size	0.142 x 0.129 x 0.082 mm^3	
Theta range for data collection	2.228 to 25.496°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=13	
Reflections collected	14678	
Independent reflections	3029 [R(int) = 0.0794]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6440	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3029 / 0 / 203	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0694	
R indices (all data)	R1 = 0.0483, wR2 = 0.0722	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.396 and -0.384 $e.Å^{-3}$	

Table S17. Bond lengths [Å] and angles [°] for **24**.

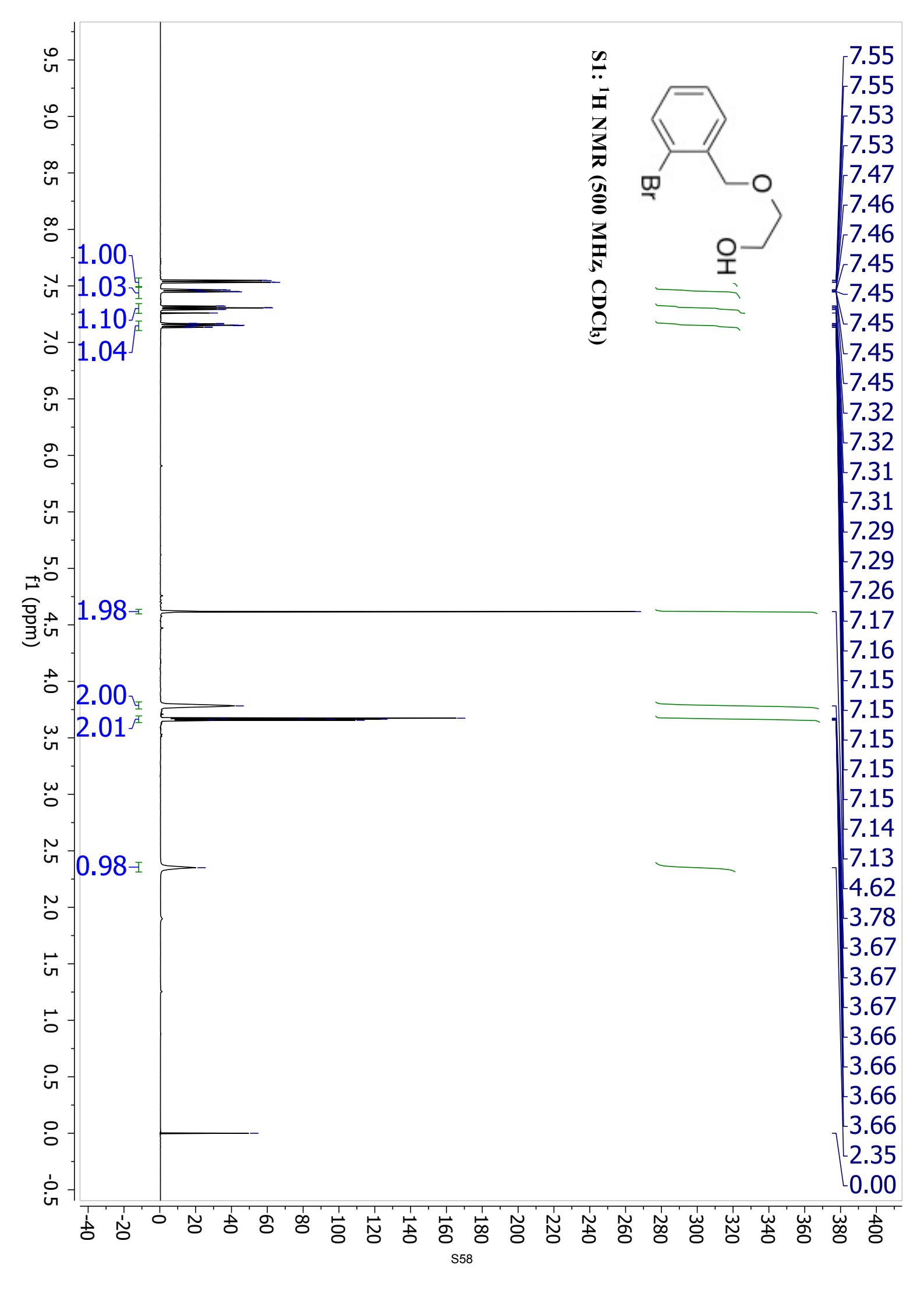
Br(1)-C(5)	1.946(3)	C(4)-C(5)-Br(1)	109.21(19)
O(5)-C(6)	1.400(3)	C(4)-C(5)-C(6)	104.9(2)
O(5)-C(15)	1.434(3)	C(1)-N(1)-O(2)	111.3(2)
C(5)-C(6)	1.558(4)	C(1)-O(1)-C(4)	108.7(2)
C(5)-C(4)	1.524(4)	C(3)-O(3)-C(6)	111.2(2)
N(1)-O(2)	1.436(3)	N(1)-O(2)-C(11)	107.3(2)
N(1)-C(1)	1.266(4)	O(5)-C(6)-C(5)	108.6(2)
O(1)-C(1)	1.369(3)	O(5)-C(6)-O(3)	109.8(2)
O(1)-C(4)	1.449(3)	O(5)-C(6)-C(7)	111.9(2)
O(3)-C(6)	1.445(3)	O(3)-C(6)-C(5)	104.4(2)
O(3)-C(3)	1.420(3)	O(3)-C(6)-C(7)	107.4(2)
O(2)-C(11)	1.445(3)	C(7)-C(6)-C(5)	114.5(2)
C(6)-C(7)	1.530(4)	C(1)-C(2)-C(3)	96.0(2)
C(2)-C(1)	1.514(4)	C(1)-C(2)-C(12)	110.2(2)
C(2)-C(3)	1.546(4)	C(1)-C(2)-C(13)	112.0(2)
C(2)-C(12)	1.528(4)	C(12)-C(2)-C(3)	110.2(2)
C(2)-C(13)	1.525(4)	C(13)-C(2)-C(3)	116.9(3)
C(4)-C(3)	1.524(4)	C(13)-C(2)-C(12)	110.7(2)
C(7)-C(8)	1.535(4)	N(1)-C(1)-O(1)	125.8(3)
C(3)-O(4)	1.401(3)	N(1)-C(1)-C(2)	122.5(3)
C(8)-C(9)	1.544(4)	O(1)-C(1)-C(2)	111.5(2)
C(11)-C(10)	1.498(4)	O(1)-C(4)-C(5)	110.5(2)
C(9)-C(10)	1.528(4)	O(1)-C(4)-C(3)	104.1(2)
O(4)-C(14)	1.425(3)	C(3)-C(4)-C(5)	104.0(2)
		C(6)-C(7)-C(8)	117.3(3)
C(6)-O(5)-C(15)	116.3(2)	O(3)-C(3)-C(2)	107.3(2)
C(6)-C(5)-Br(1)	114.07(19)	O(3)-C(3)-C(4)	103.4(2)

C(4)-C(3)-C(2)	104.5(2)	O(2)-C(11)-C(10)	112.6(3)
O(4)-C(3)-O(3)	114.1(2)	C(10)-C(9)-C(8)	113.3(3)
O(4)-C(3)-C(2)	117.7(2)	C(11)-C(10)-C(9)	115.1(3)
O(4)-C(3)-C(4)	108.5(2)	C(3)-O(4)-C(14)	116.5(2)
C(7)-C(8)-C(9)	113.3(3)		

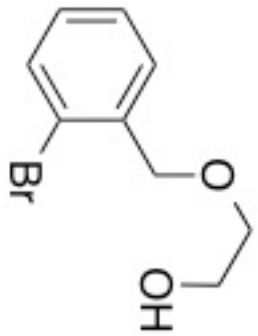
Table S18. Torsion angles [°] for **24**.

Br(1)-C(5)-C(6)-O(5)	-0.2(3)	C(6)-O(3)-C(3)-C(4)	33.9(3)
Br(1)-C(5)-C(6)-O(3)	116.9(2)	C(6)-O(3)-C(3)-O(4)	-83.7(3)
Br(1)-C(5)-C(6)-C(7)	-126.0(2)	C(6)-C(7)-C(8)-C(9)	-116.3(3)
Br(1)-C(5)-C(4)-O(1)	147.85(18)	C(2)-C(3)-O(4)-C(14)	75.5(3)
Br(1)-C(5)-C(4)-C(3)	-100.9(2)	C(1)-N(1)-O(2)-C(11)	146.9(3)
O(5)-C(6)-C(7)-C(8)	-167.9(2)	C(1)-O(1)-C(4)-C(5)	119.4(2)
C(5)-C(6)-C(7)-C(8)	-43.8(4)	C(1)-O(1)-C(4)-C(3)	8.2(3)
C(5)-C(4)-C(3)-O(3)	-33.5(3)	C(1)-C(2)-C(3)-O(3)	-72.4(2)
C(5)-C(4)-C(3)-C(2)	-145.6(2)	C(1)-C(2)-C(3)-C(4)	37.0(3)
C(5)-C(4)-C(3)-O(4)	88.1(3)	C(1)-C(2)-C(3)-O(4)	157.3(2)
N(1)-O(2)-C(11)-C(10)	-106.0(3)	C(4)-C(5)-C(6)-O(5)	-119.7(2)
O(1)-C(4)-C(3)-O(3)	82.4(2)	C(4)-C(5)-C(6)-O(3)	-2.6(3)
O(1)-C(4)-C(3)-C(2)	-29.8(3)	C(4)-C(5)-C(6)-C(7)	114.5(3)
O(1)-C(4)-C(3)-O(4)	-156.1(2)	C(4)-O(1)-C(1)-N(1)	-157.0(3)
O(3)-C(6)-C(7)-C(8)	71.6(3)	C(4)-O(1)-C(1)-C(2)	17.7(3)
O(3)-C(3)-O(4)-C(14)	-51.6(3)	C(4)-C(3)-O(4)-C(14)	-166.3(2)
O(2)-N(1)-C(1)-O(1)	-1.1(4)	C(7)-C(8)-C(9)-C(10)	176.7(3)
O(2)-N(1)-C(1)-C(2)	-175.1(2)	C(15)-O(5)-C(6)-C(5)	178.8(2)
O(2)-C(11)-C(10)-C(9)	58.2(4)	C(15)-O(5)-C(6)-O(3)	65.2(3)
C(6)-C(5)-C(4)-O(1)	-89.5(3)	C(15)-O(5)-C(6)-C(7)	-53.9(3)
C(6)-C(5)-C(4)-C(3)	21.7(3)	C(3)-O(3)-C(6)-O(5)	96.4(3)
C(6)-O(3)-C(3)-C(2)	144.0(2)	C(3)-O(3)-C(6)-C(5)	-19.8(3)

C(3)-O(3)-C(6)-C(7)	-141.8(2)	C(12)-C(2)-C(3)-C(4)	-77.1(3)
C(3)-C(2)-C(1)-N(1)	140.5(3)	C(12)-C(2)-C(3)-O(4)	43.2(3)
C(3)-C(2)-C(1)-O(1)	-34.3(3)	C(13)-C(2)-C(1)-N(1)	18.3(4)
C(8)-C(9)-C(10)-C(11)	-91.9(3)	C(13)-C(2)-C(1)-O(1)	-156.5(2)
C(12)-C(2)-C(1)-N(1)	-105.4(3)	C(13)-C(2)-C(3)-O(3)	46.0(3)
C(12)-C(2)-C(1)-O(1)	79.8(3)	C(13)-C(2)-C(3)-C(4)	155.4(2)
C(12)-C(2)-C(3)-O(3)	173.5(2)	C(13)-C(2)-C(3)-O(4)	-84.3(3)


S1: ¹H NMR (500 MHz, CDCl₃)
Br
O
OH
1.00
1.03
1.10
1.04
1.98
2.00
2.01
0.98
f1 (ppm)
7.55
7.55
7.53
7.53
7.47
7.46
7.46
7.45
7.45
7.45
7.45
7.45
7.32
7.32
7.31
7.31
7.29
7.29
7.26
7.17
7.16
7.15
7.15
7.15
7.15
7.15
7.14
7.13
4.62
3.78
3.67
3.67
3.67
3.66
3.66
3.66
3.66
2.35
0.00

S1: ^{13}C NMR (101 MHz, $CDCl_3$)

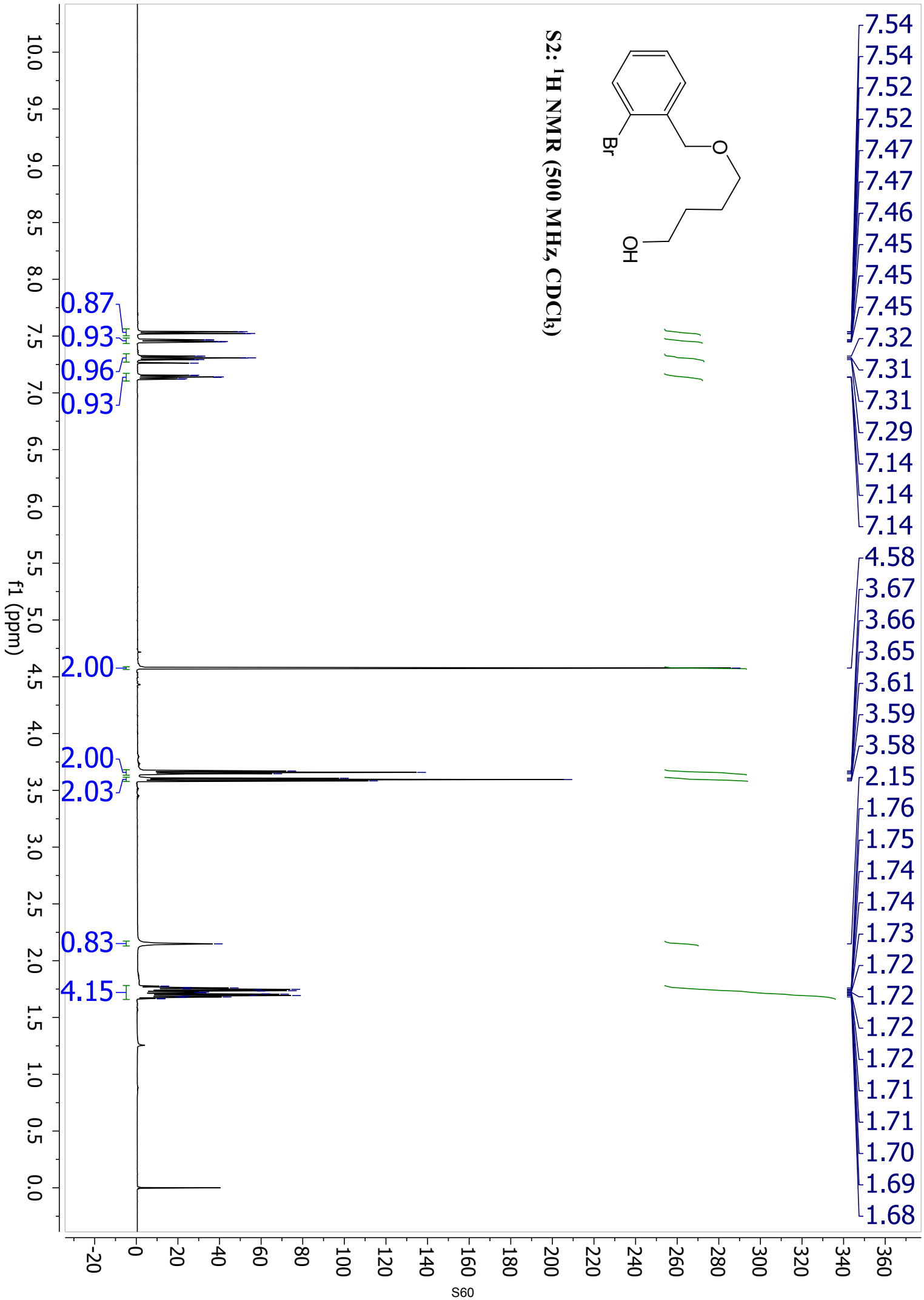


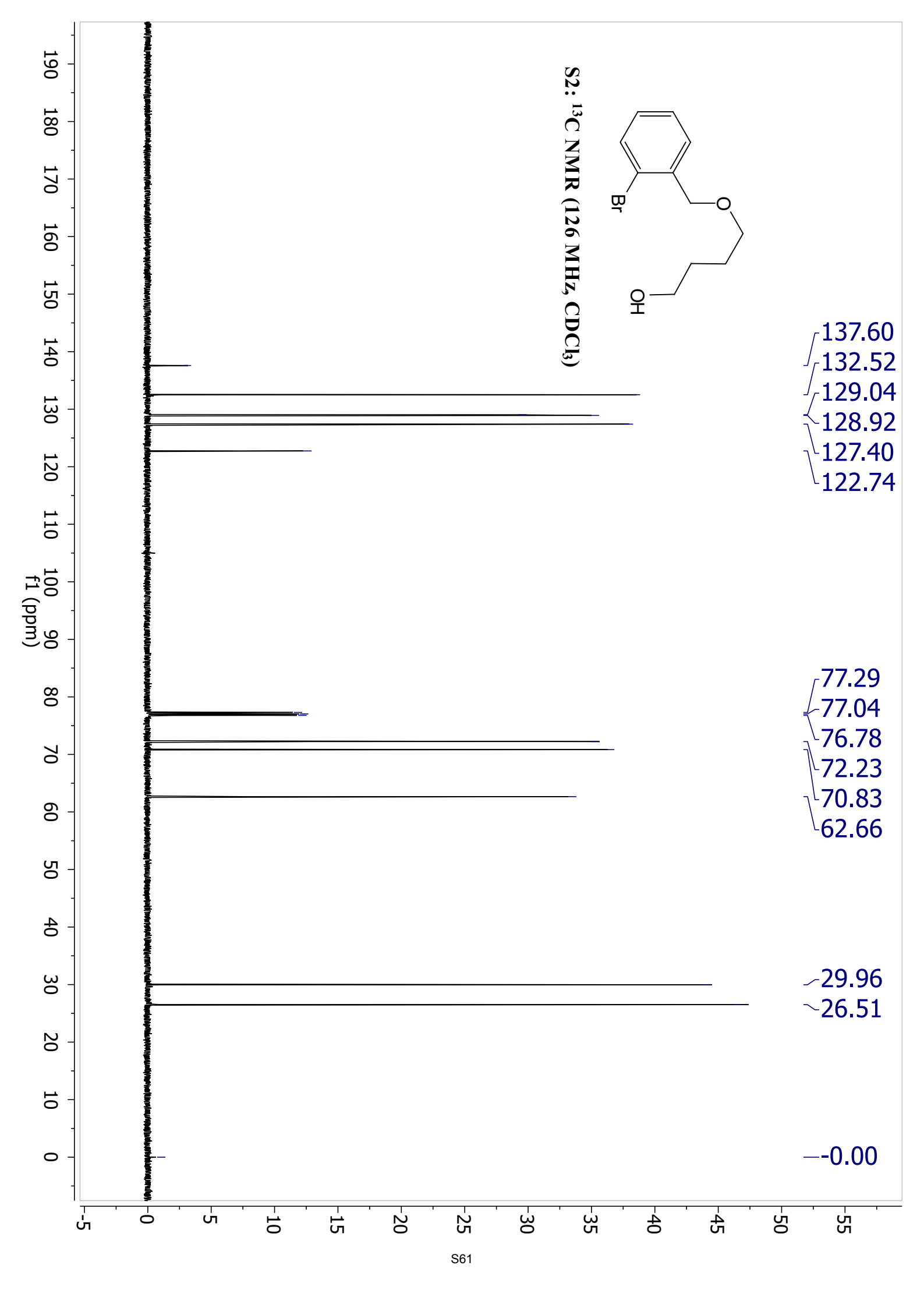
137.26
132.61
129.30
129.13
127.43
122.94

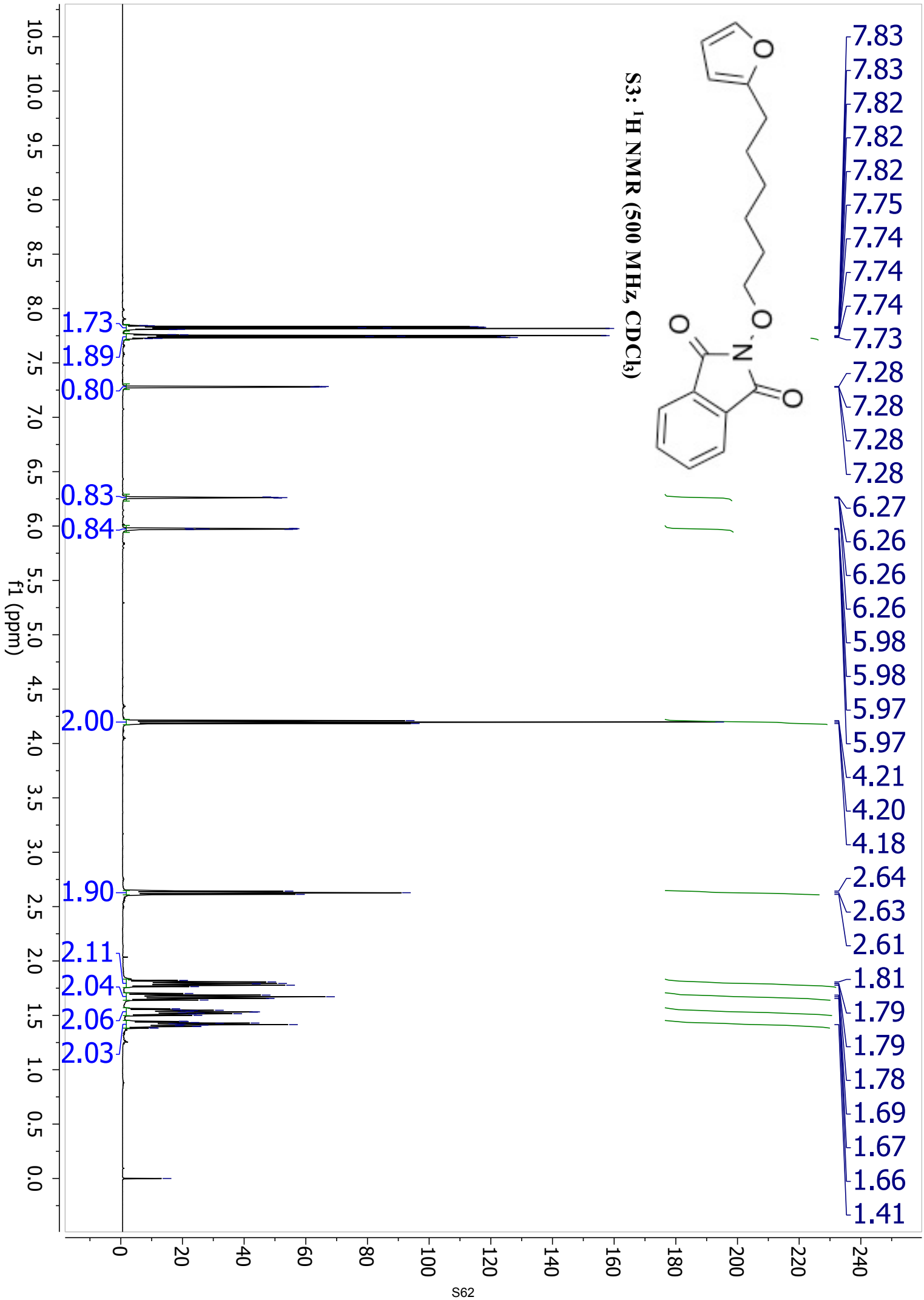
77.45
77.12
76.80
72.49
71.93
61.75

−0.03

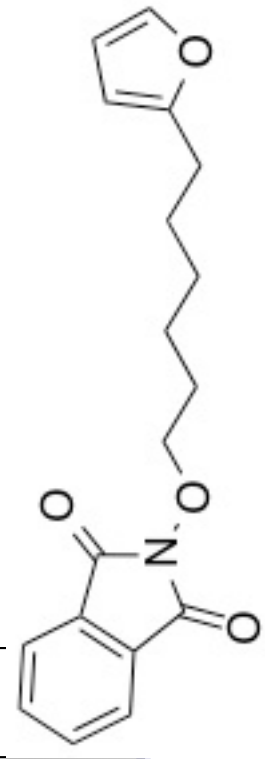
f1 (ppm)


S2: ^{1}H NMR (500 MHz, CDCl$_3$)
Br
O
OH
0.87
0.93
0.96
0.93
2.00
2.00
2.03
0.83
4.15
7.54
7.54
7.52
7.52
7.47
7.47
7.46
7.45
7.45
7.45
7.32
7.31
7.31
7.29
7.14
7.14
7.14
4.58
3.67
3.66
3.65
3.61
3.59
3.58
2.15
1.76
1.75
1.74
1.74
1.73
1.72
1.72
1.72
1.72
1.71
1.71
1.70
1.69
1.68
f1 (ppm)


S2: ^{13}C NMR (126 MHz, $CDCl_3$)
Br
O
OH
137.60
132.52
129.04
128.92
127.40
122.74
77.29
77.04
76.78
72.23
70.83
62.66
29.96
26.51
-0.00
f1 (ppm)

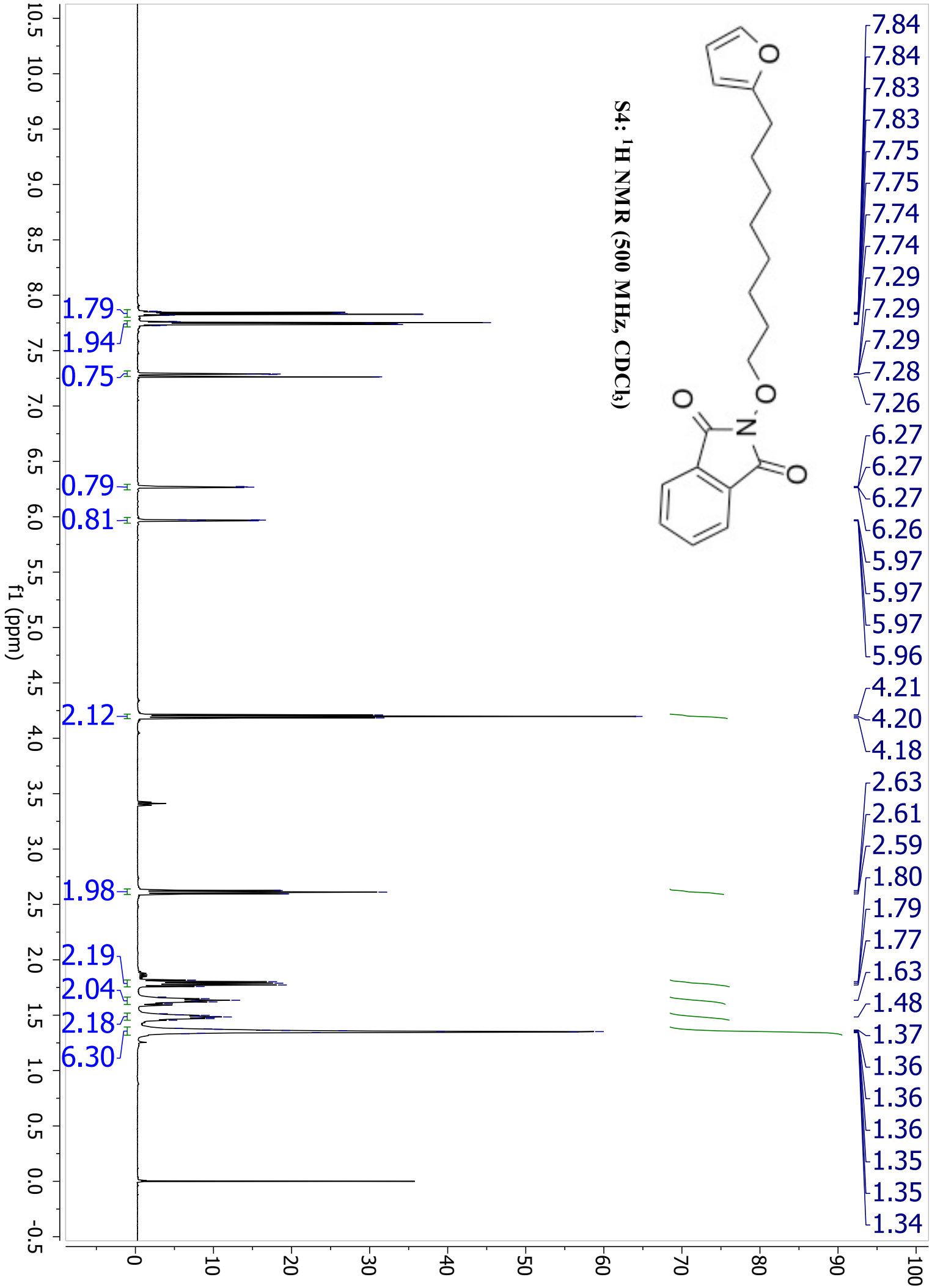

S3: ^{1}H NMR (500 MHz, $CDCl_3$)
1.73
1.89
0.80
0.83
0.84
2.00
1.90
2.11
2.04
2.06
2.03
7.83
7.83
7.82
7.82
7.82
7.75
7.74
7.74
7.74
7.73
7.28
7.28
7.28
7.28
6.27
6.26
6.26
6.26
5.98
5.98
5.97
5.97
4.21
4.20
4.18
2.64
2.63
2.61
1.81
1.79
1.79
1.78
1.69
1.67
1.66
1.41
f1 (ppm)

S3: ^{13}C NMR (126 MHz, $CDCl_3$)

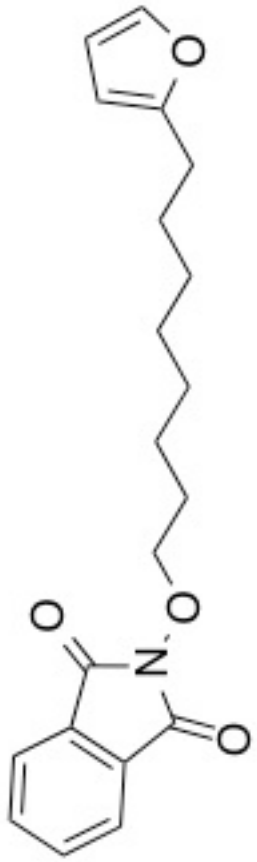


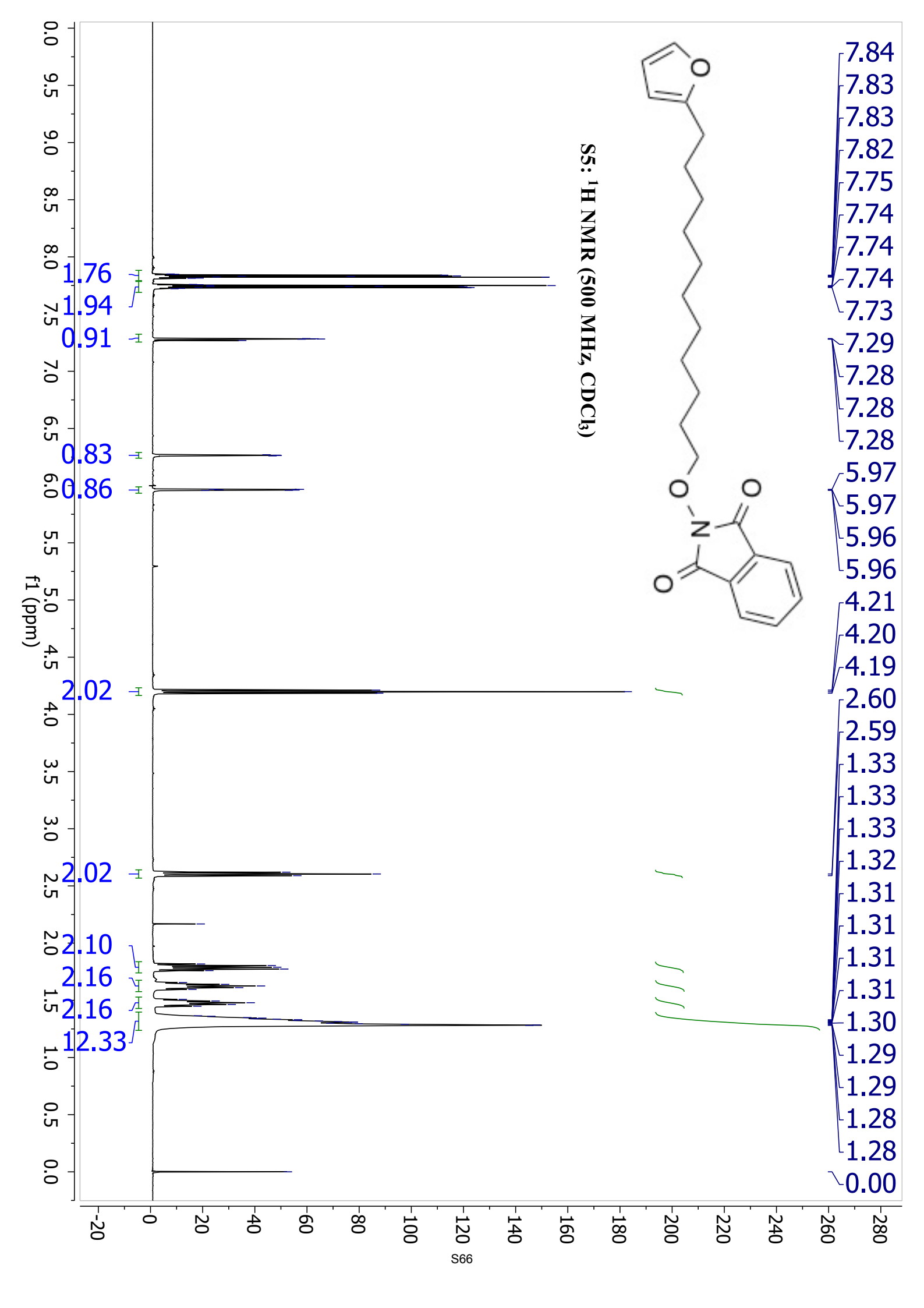
163.61
156.26
140.64
134.41
128.94
123.42
110.02
104.64
78.44
77.36
77.11
76.85
28.77
28.05
27.83
27.81
25.28

f1 (ppm)

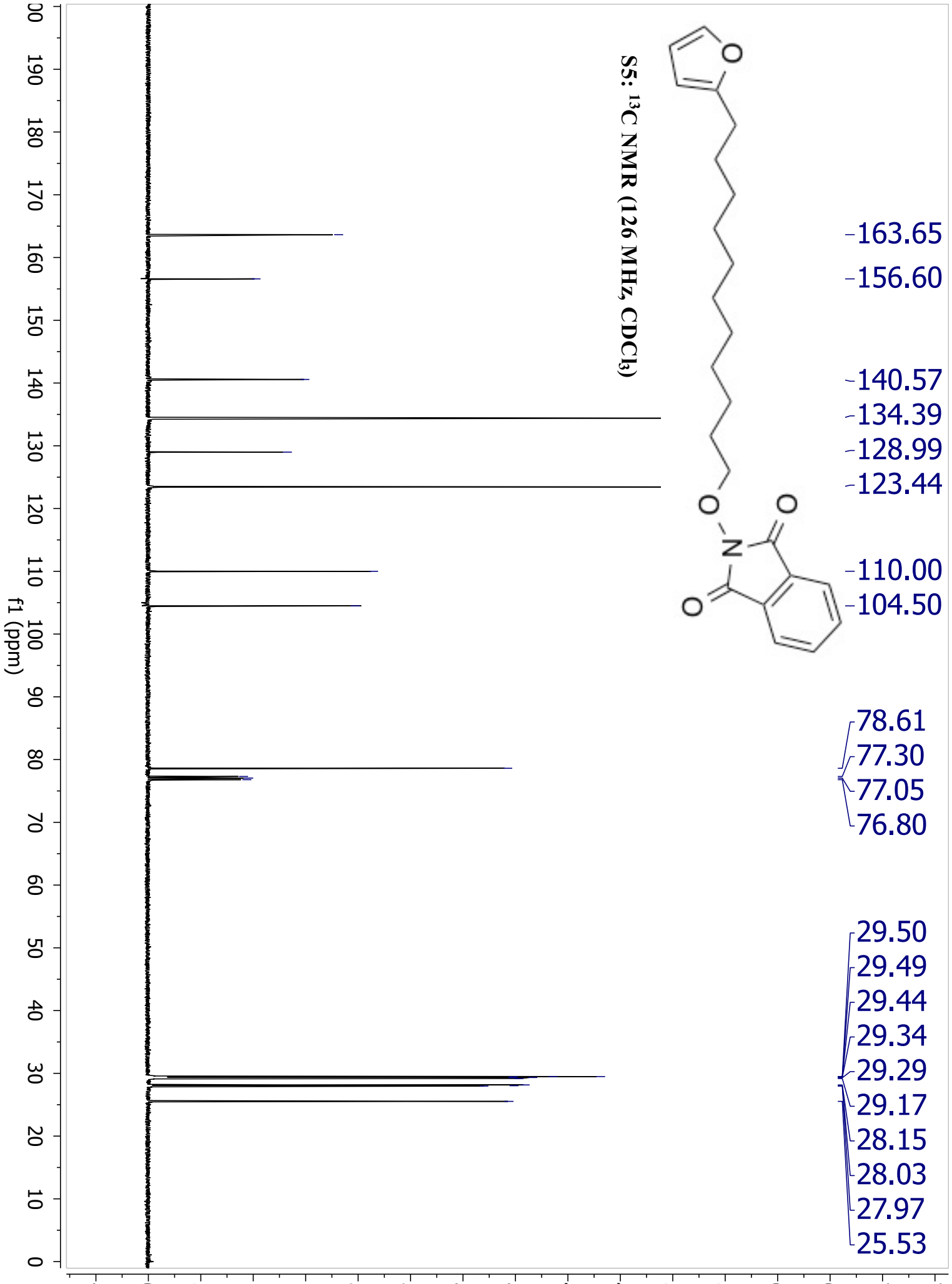

S4: ¹H NMR (500 MHz, CDCl₃)
f1 (ppm)
1.79
1.94
0.75
0.79
0.81
2.12
1.98
2.19
2.04
2.18
6.30
7.84
7.84
7.83
7.83
7.75
7.75
7.74
7.74
7.29
7.29
7.29
7.28
7.26
6.27
6.27
6.27
6.26
5.97
5.97
5.97
5.96
4.21
4.20
4.18
2.63
2.61
2.59
1.80
1.79
1.77
1.63
1.48
1.37
1.36
1.36
1.36
1.35
1.35
1.34

S4: ^{13}C NMR (126 MHz, $CDCl_3$)

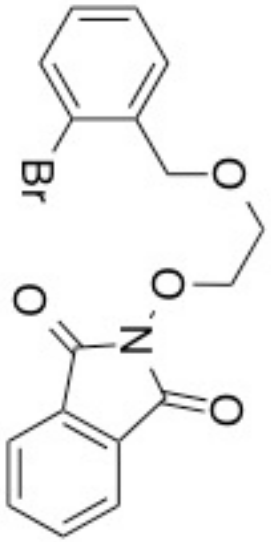


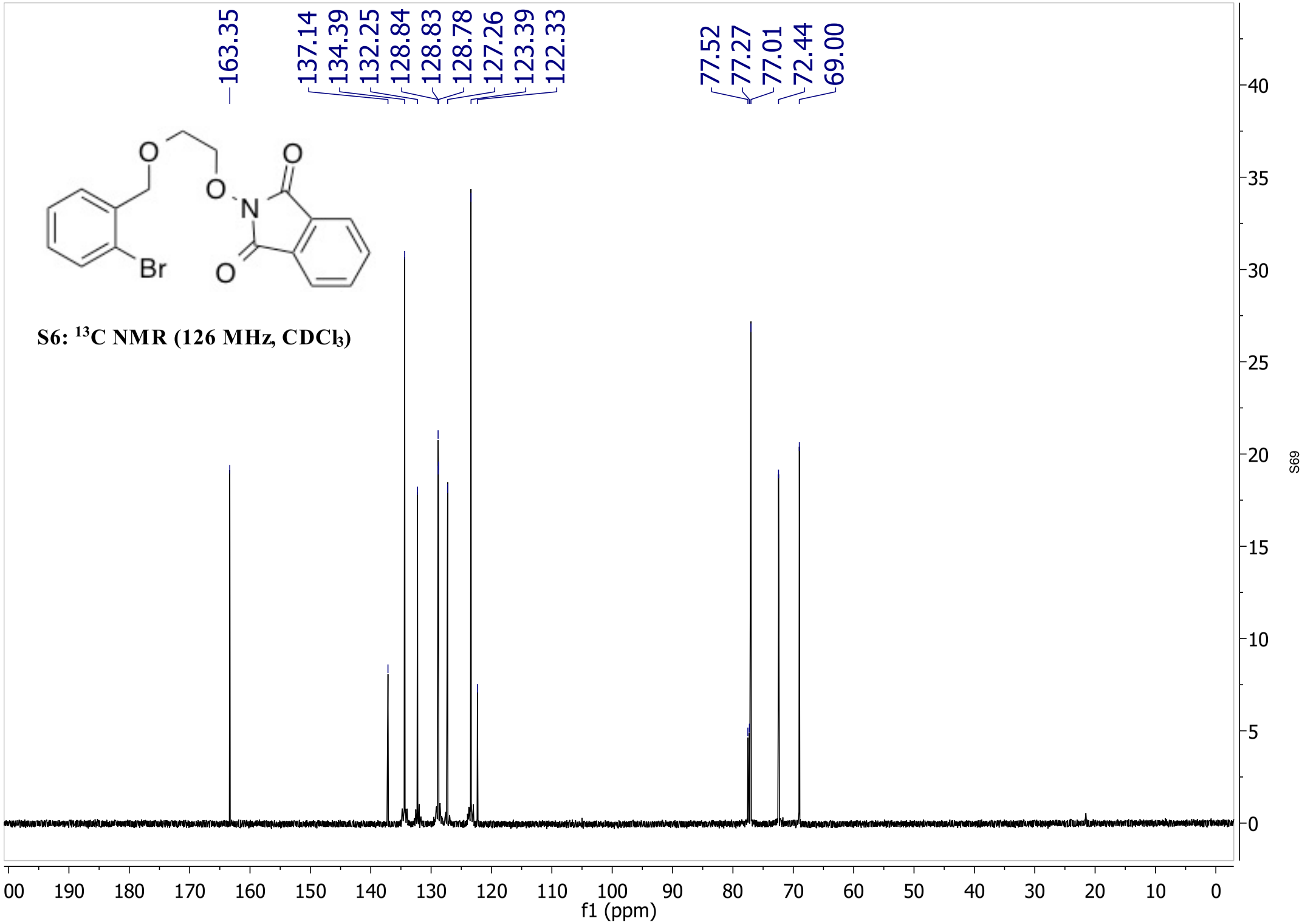

S5: ^{1}H NMR (500 MHz, CDCl$_3$)
1.76
1.94
0.91
0.83
0.86
2.02
2.02
2.10
2.16
2.16
12.33
7.84
7.83
7.83
7.82
7.75
7.74
7.74
7.74
7.73
7.29
7.28
7.28
7.28
5.97
5.97
5.96
5.96
4.21
4.20
4.19
2.60
2.59
1.33
1.33
1.33
1.32
1.31
1.31
1.31
1.31
1.31
1.30
1.29
1.29
1.28
1.28
0.00
f1 (ppm)

S5: ^{13}C NMR (126 MHz, $CDCl_3$)



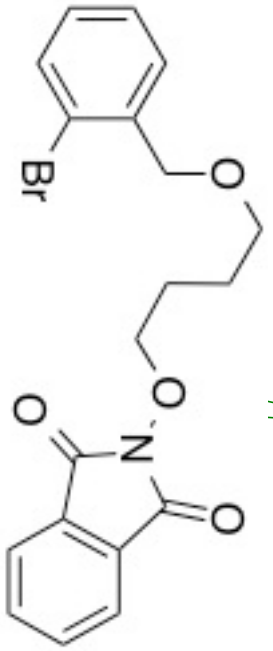
S6: ^{1}H NMR (500 MHz, $CDCl_3$)





S6: ^{13}C NMR (126 MHz, $CDCl_3$)

S7: ^{1}H NMR (500 MHz, $CDCl_3$)

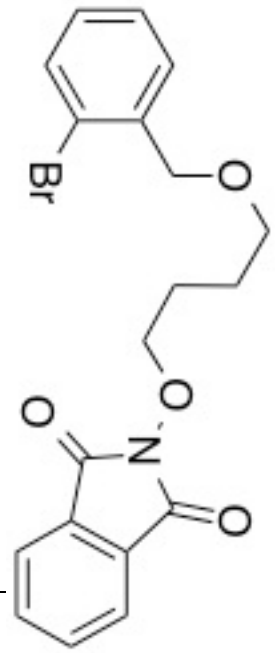


1.83
1.96
0.88
0.91
0.98
1.01
2.03
2.08
2.04
4.18

7.84
7.83
7.83
7.82
7.75
7.74
7.74
7.73
7.52
7.52
7.51
7.51
7.48
7.48
7.47
7.46
7.30
7.30
7.27
7.13
7.13
4.56
4.27
4.26
4.24
3.66
3.65
3.63
1.94
1.94
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.89
1.89

f1 (ppm)

S7: ^{13}C NMR (126 MHz, $CDCl_3$)



163.62

137.83
134.41
132.44
128.99
128.96
128.78
127.36
123.46
122.64

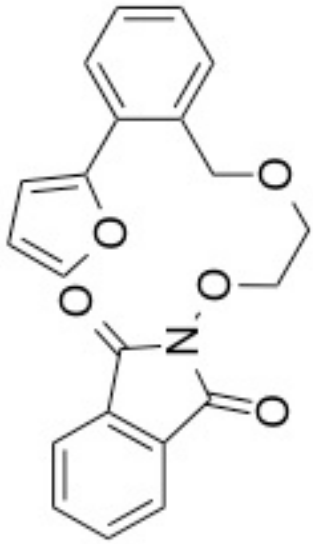
78.22
77.29
77.03
76.78
72.13
70.18

25.90
25.15

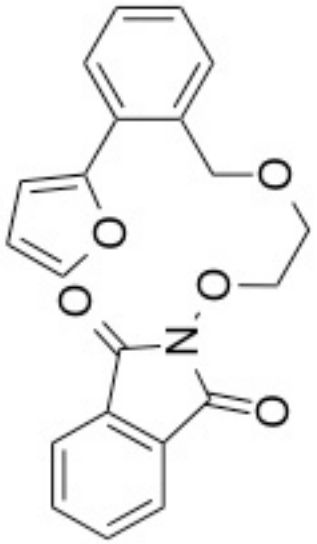
-0.00

f1 (ppm)

S8: ^{1}H NMR (500 MHz, $CDCl_3$)



S8: ^{13}C NMR (126 MHz, $CDCl_3$)



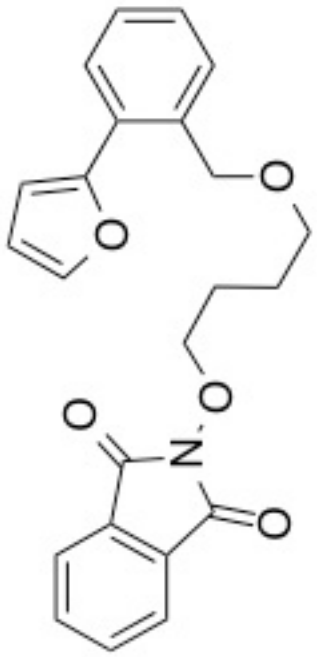
163.41
152.34
142.18
134.31
133.85
129.80
129.19
128.89
127.69
127.42
127.30
123.39
111.54
109.10

77.33
77.08
77.05
76.82
71.64
68.43

0.00

f1 (ppm)

S9: ^{1}H NMR (500 MHz, $CDCl_3$)

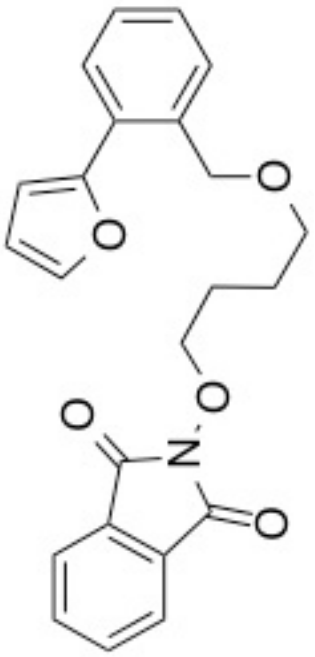


1.97
2.21
0.95
1.92
1.08
1.02
0.99
0.94
2.15
2.19
2.05
4.36

7.84
7.83
7.82
7.82
7.75
7.74
7.74
7.73
7.51
7.51
7.51
7.51
7.34
7.33
7.30
7.30
7.26
6.63
6.63
6.62
6.62
6.50
6.50
6.49
6.49
4.65
4.23
4.22
4.21
3.62
3.61
3.60
1.89
1.89
1.88
1.88
1.87
1.87
-0.00

f1 (ppm)

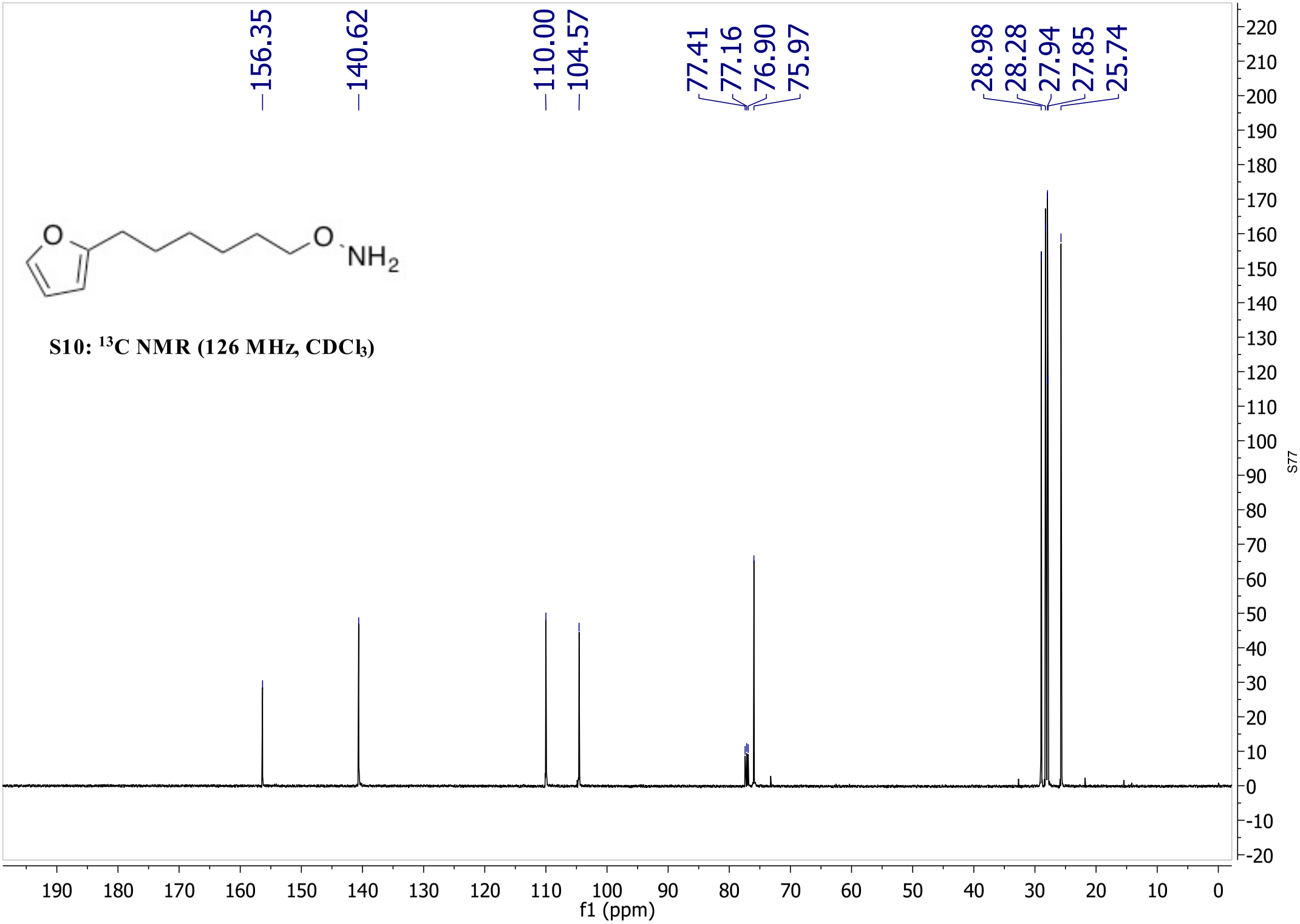
S9: ^{13}C NMR (126 MHz, $CDCl_3$)



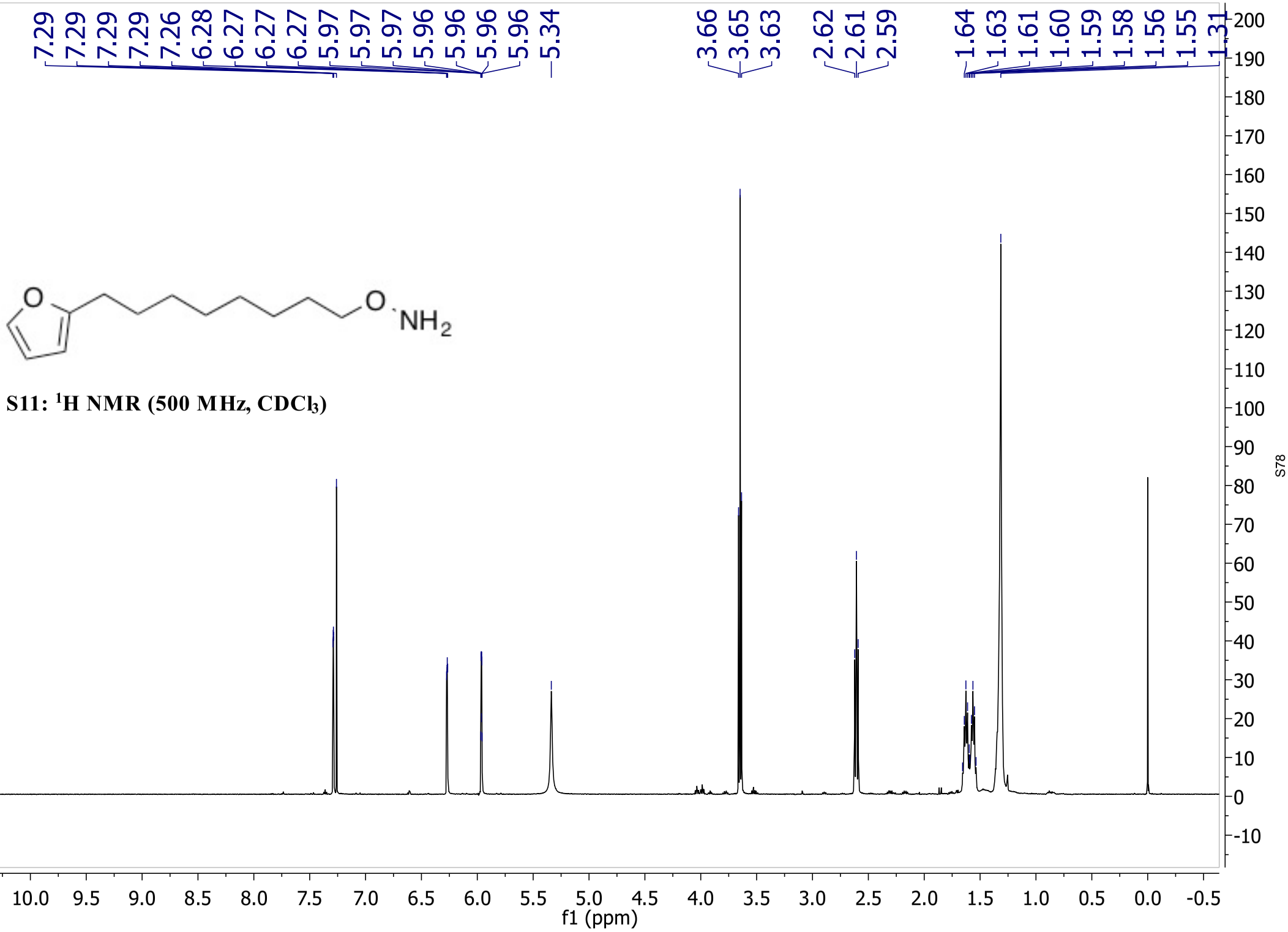
163.59
152.57
142.19
134.41
129.90
129.33
128.93
128.34
127.71
127.56
127.41
123.42
111.56
109.01
78.23
77.42
77.16
76.91
71.31
69.69
25.98
25.20

f1 (ppm)

S10: ^{1}H NMR (500 MHz, CDCl$_3$)

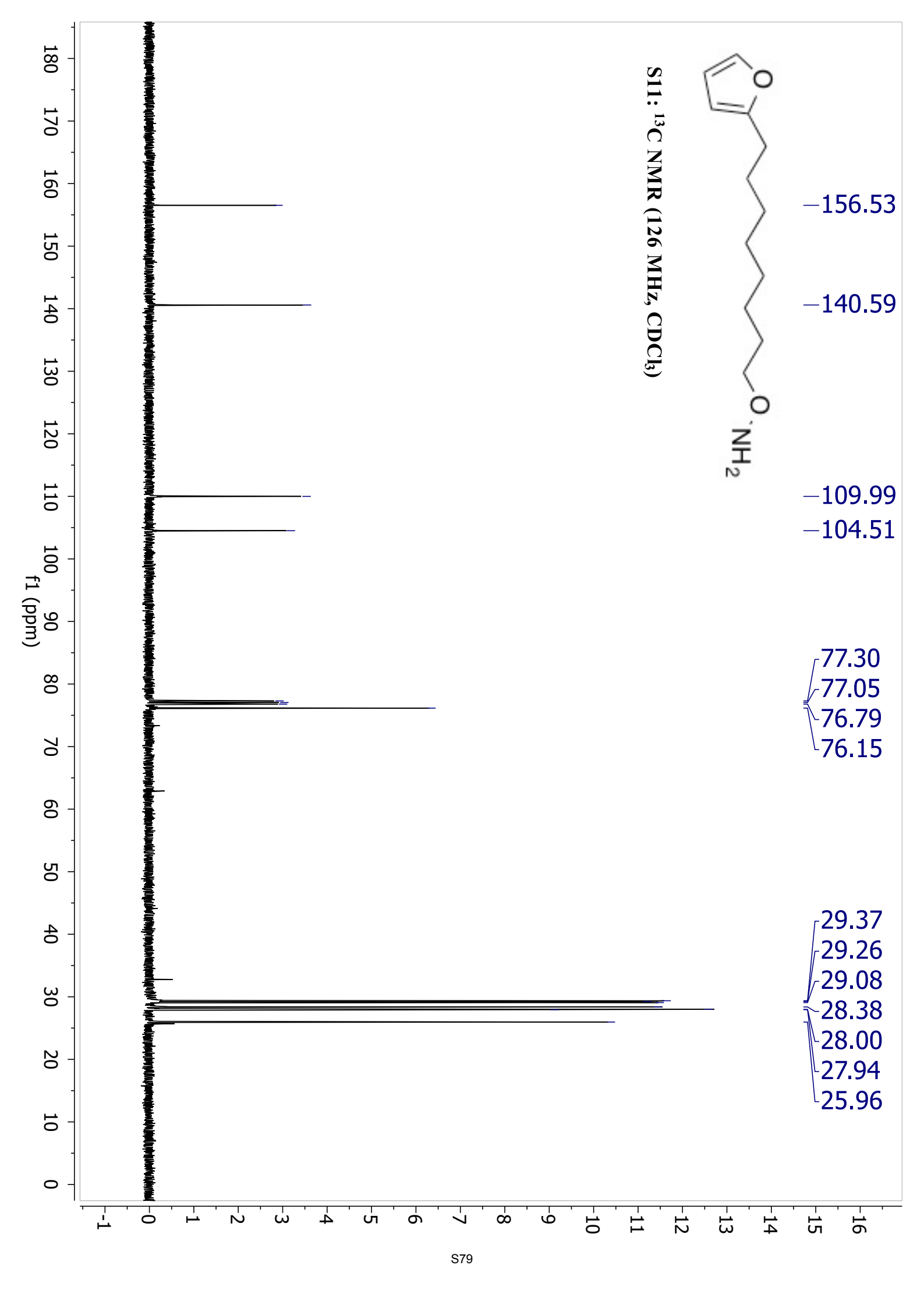


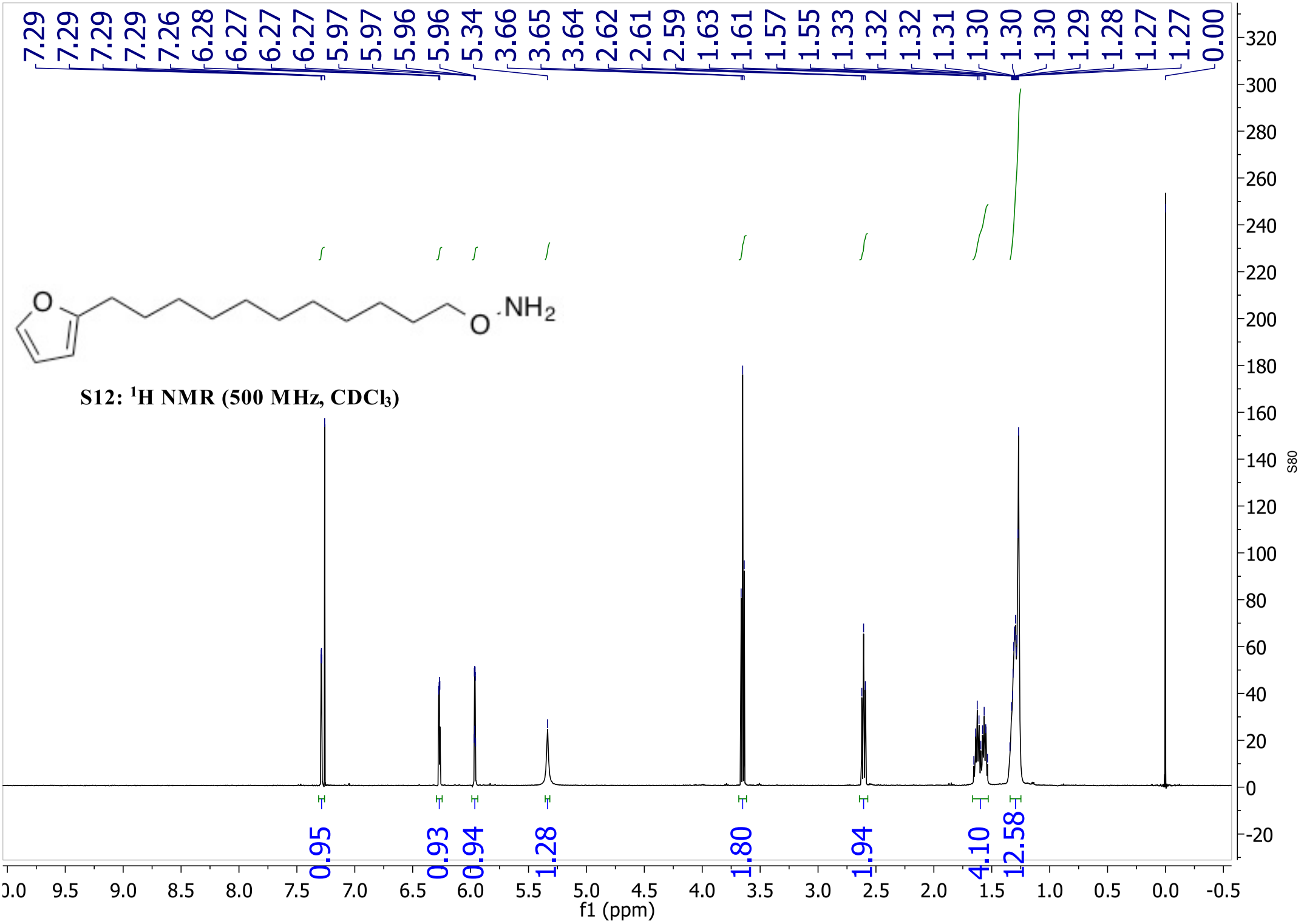
S10: ^{13}C NMR (126 MHz, $CDCl_3$)



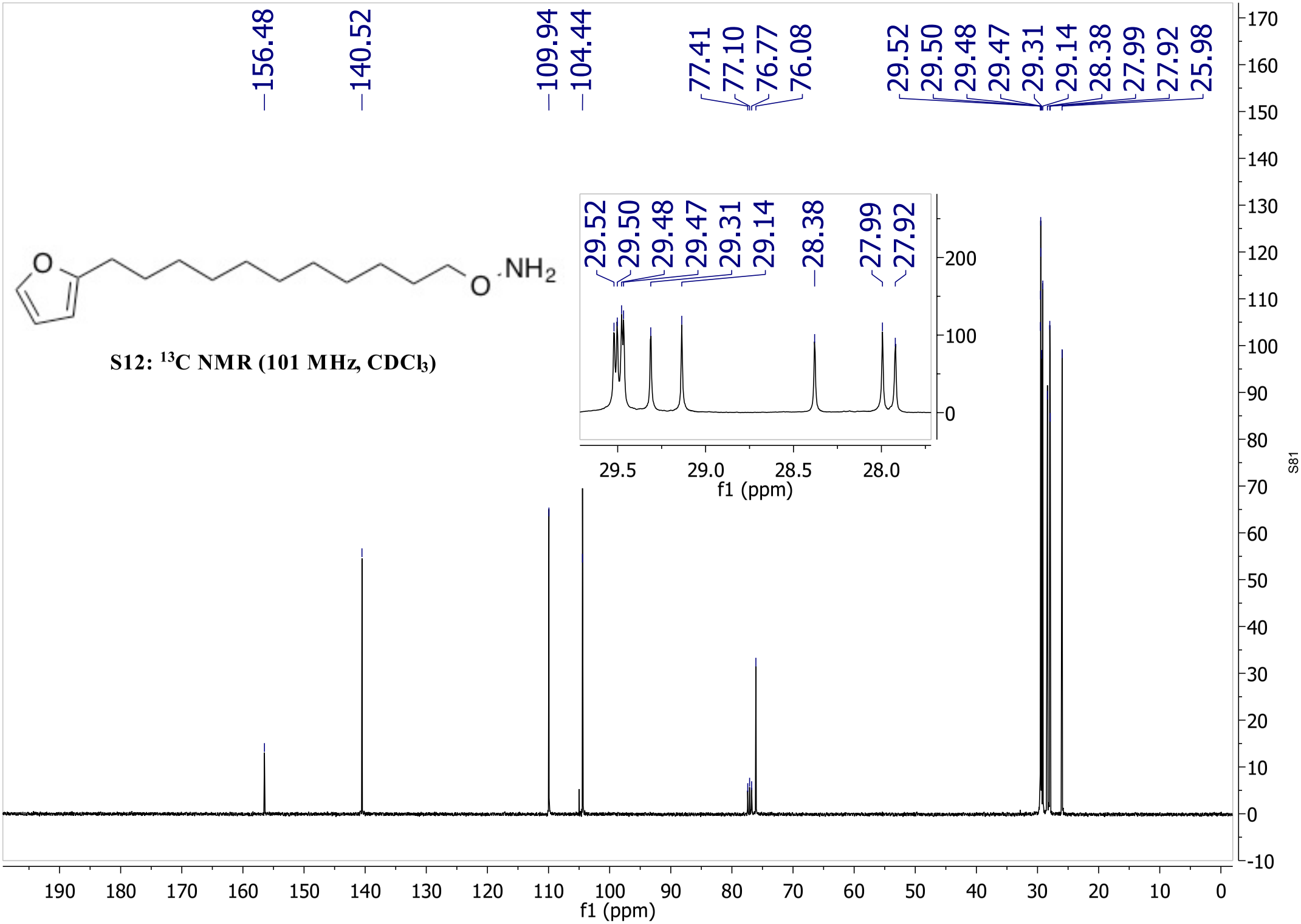
S11: ^{1}H NMR (500 MHz, $CDCl_3$)

S11: ^{13}C NMR (126 MHz, $CDCl_3$)

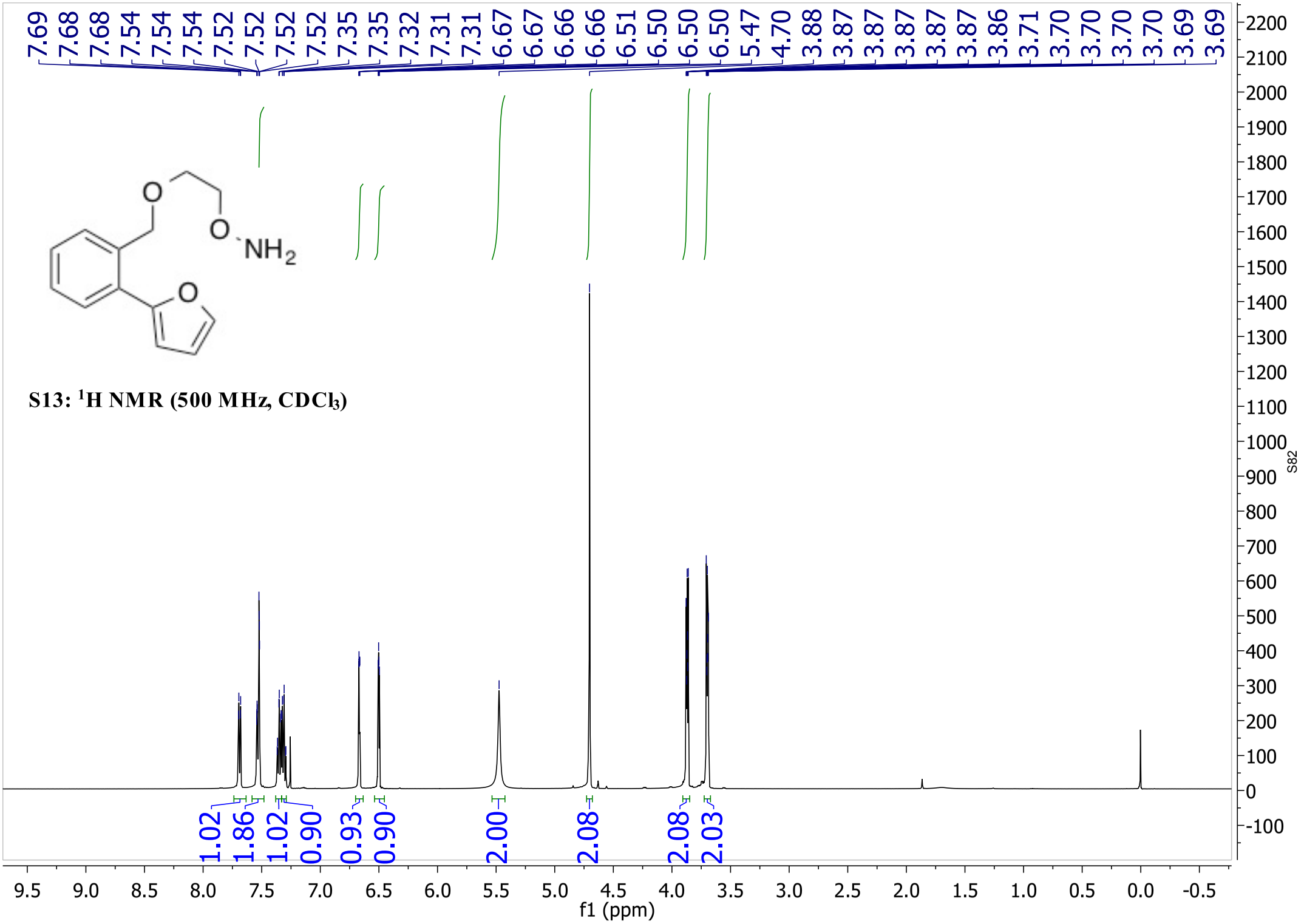




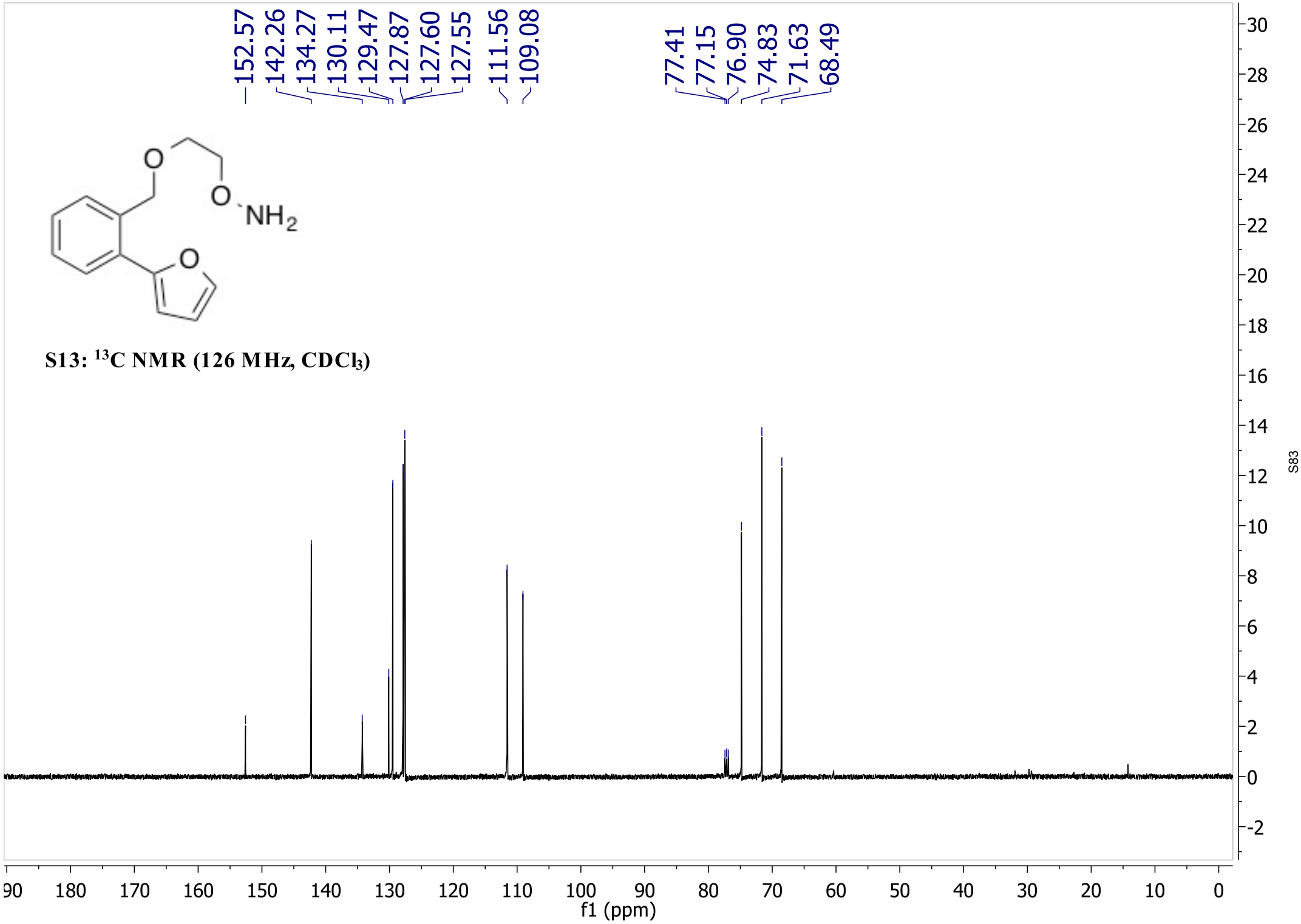
S12: ^{1}H NMR (500 MHz, $CDCl_3$)



S12: ^{13}C NMR (101 MHz, $CDCl_3$)

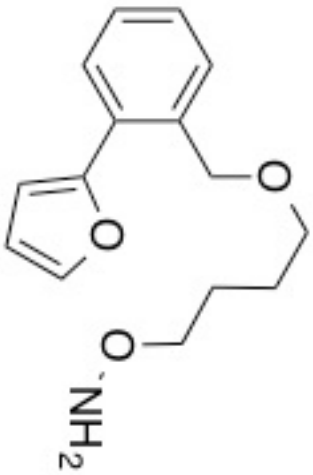


S13: ^{1}H NMR (500 MHz, $CDCl_3$)

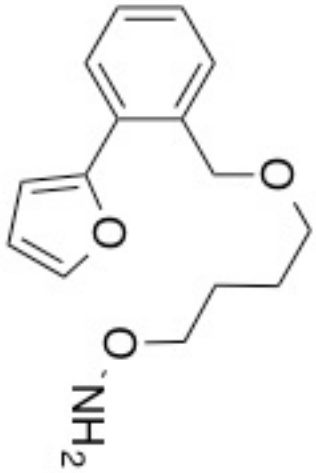


S13: ^{13}C NMR (126 MHz, $CDCl_3$)

S14: ^{1}H NMR (500 MHz, CDCl$_3$)



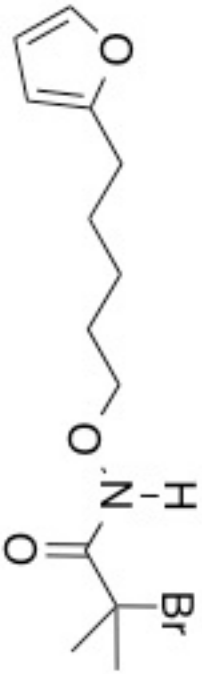
S14: ^{13}C NMR (101 MHz, $CDCl_3$)



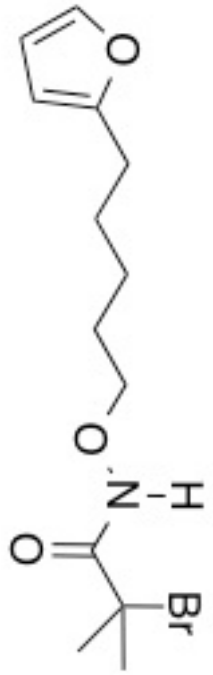
152.60
142.16
134.70
129.89
129.23
127.67
127.54
127.42
111.49
108.95
77.40
77.08
76.76
75.76
71.25
70.10
26.37
25.20

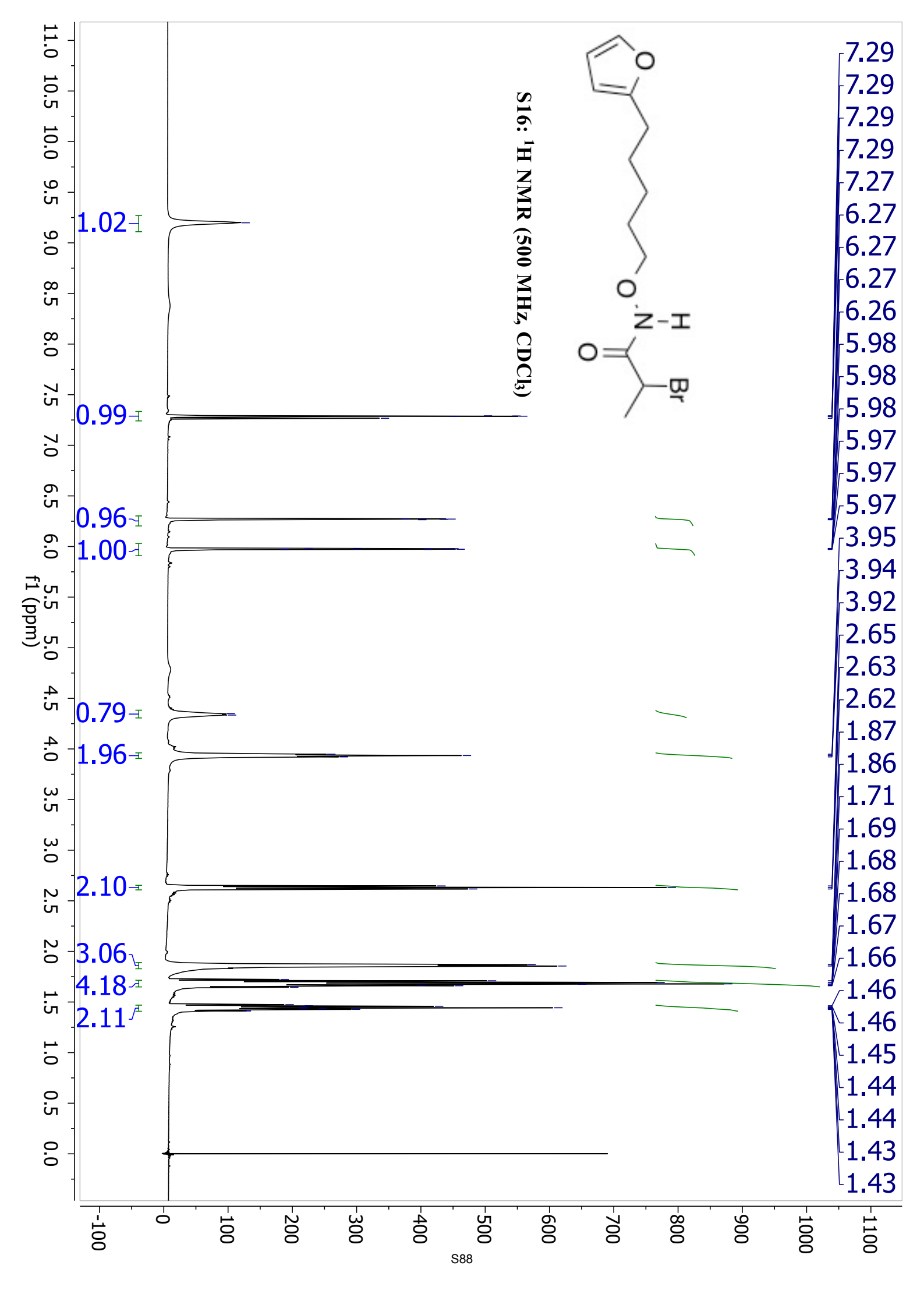
f1 (ppm)

S15: ^{1}H NMR (500 MHz, $CDCl_3$)

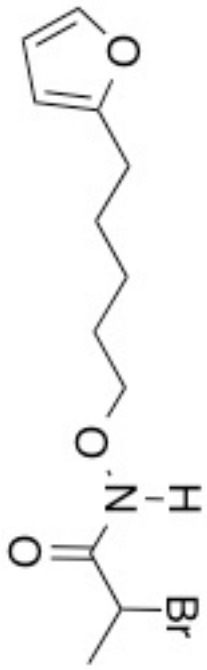


S15: ^{13}C NMR (126 MHz, $CDCl_3$)



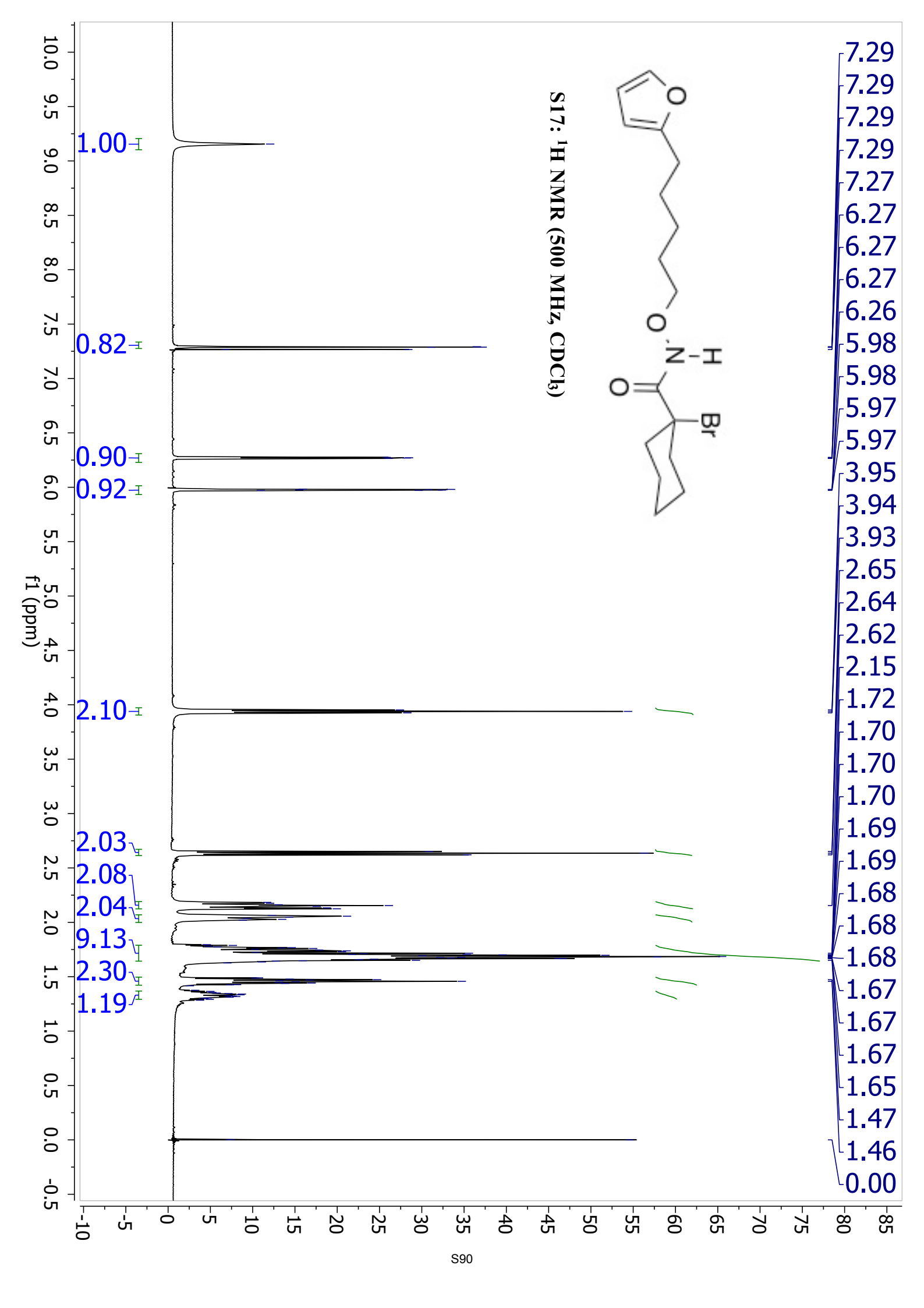

S16: ¹H NMR (500 MHz, CDCl₃)
O
O
N-H
O
Br
1.02
0.99
0.96
1.00
0.79
1.96
2.10
3.06
4.18
2.11
7.29
7.29
7.29
7.29
7.27
6.27
6.27
6.27
6.26
5.98
5.98
5.98
5.97
5.97
5.97
3.95
3.94
3.92
2.65
2.63
2.62
1.87
1.86
1.71
1.69
1.68
1.68
1.67
1.66
1.46
1.46
1.45
1.44
1.44
1.43
1.43
f1 (ppm)

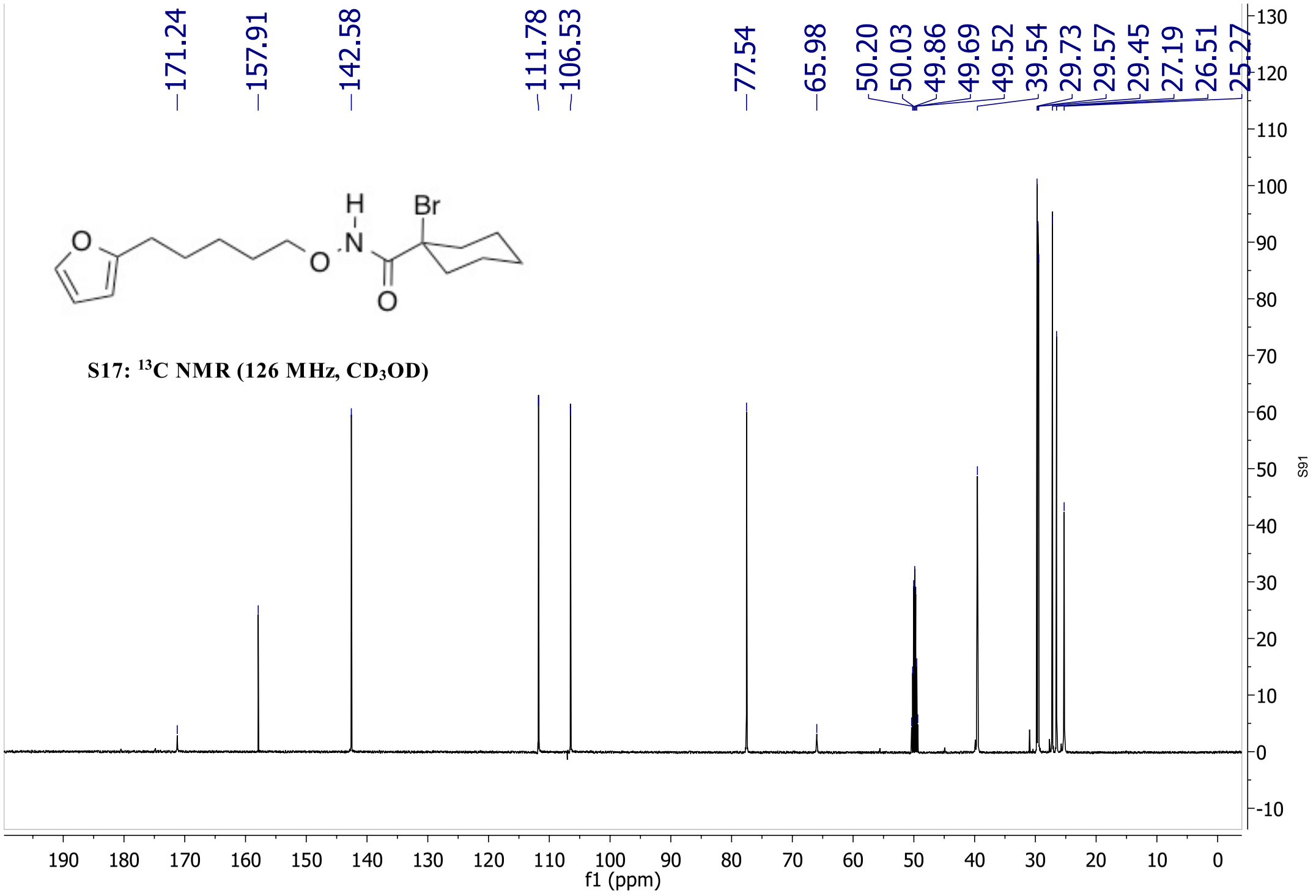
S16: ^{13}C NMR (126 MHz, $CDCl_3$)



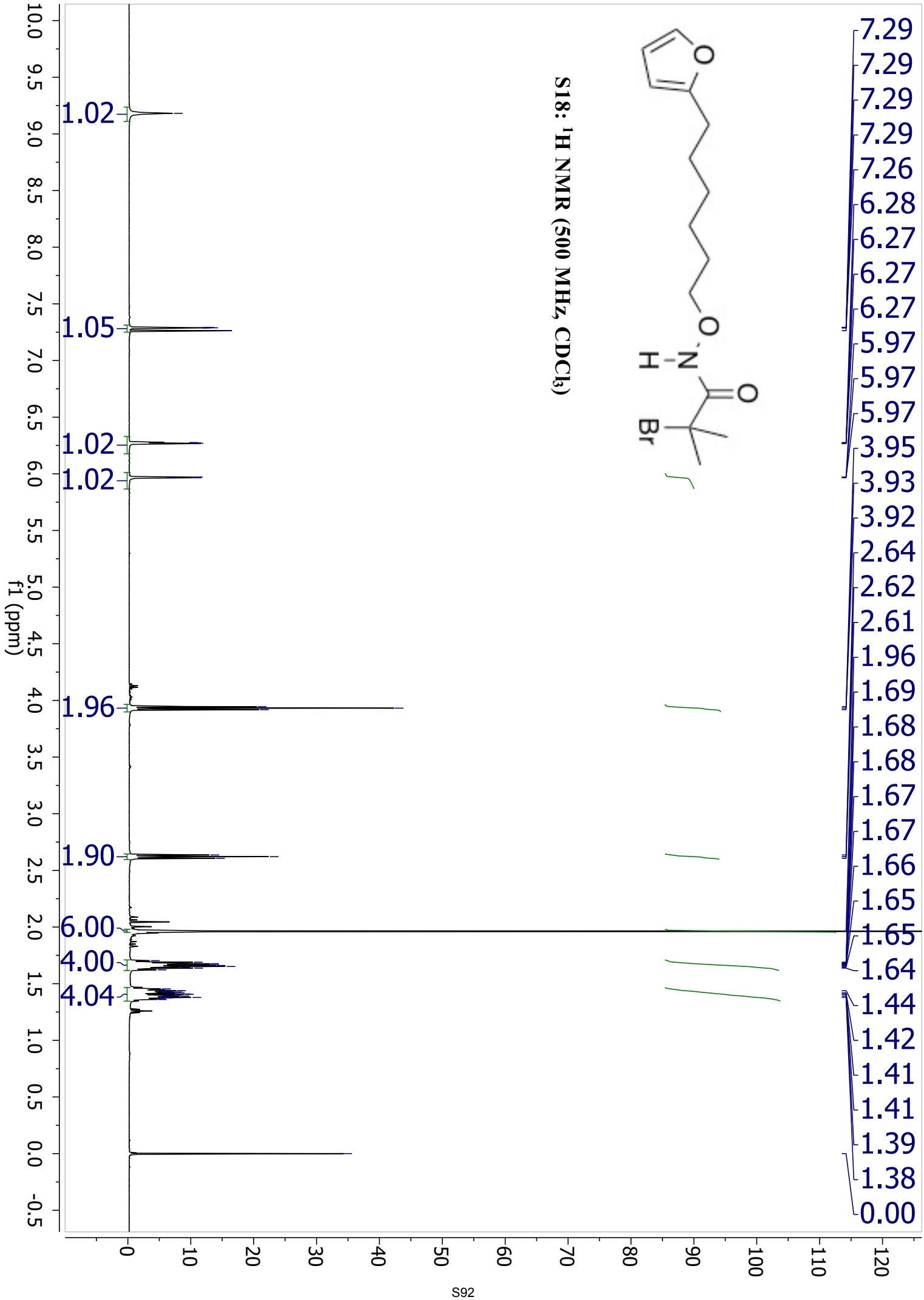
169.34
157.31
142.02
111.21
105.97
77.25
49.80
49.63
49.46
49.29
49.12
48.95
48.78
40.81
29.08
28.85
28.83
26.52
22.19

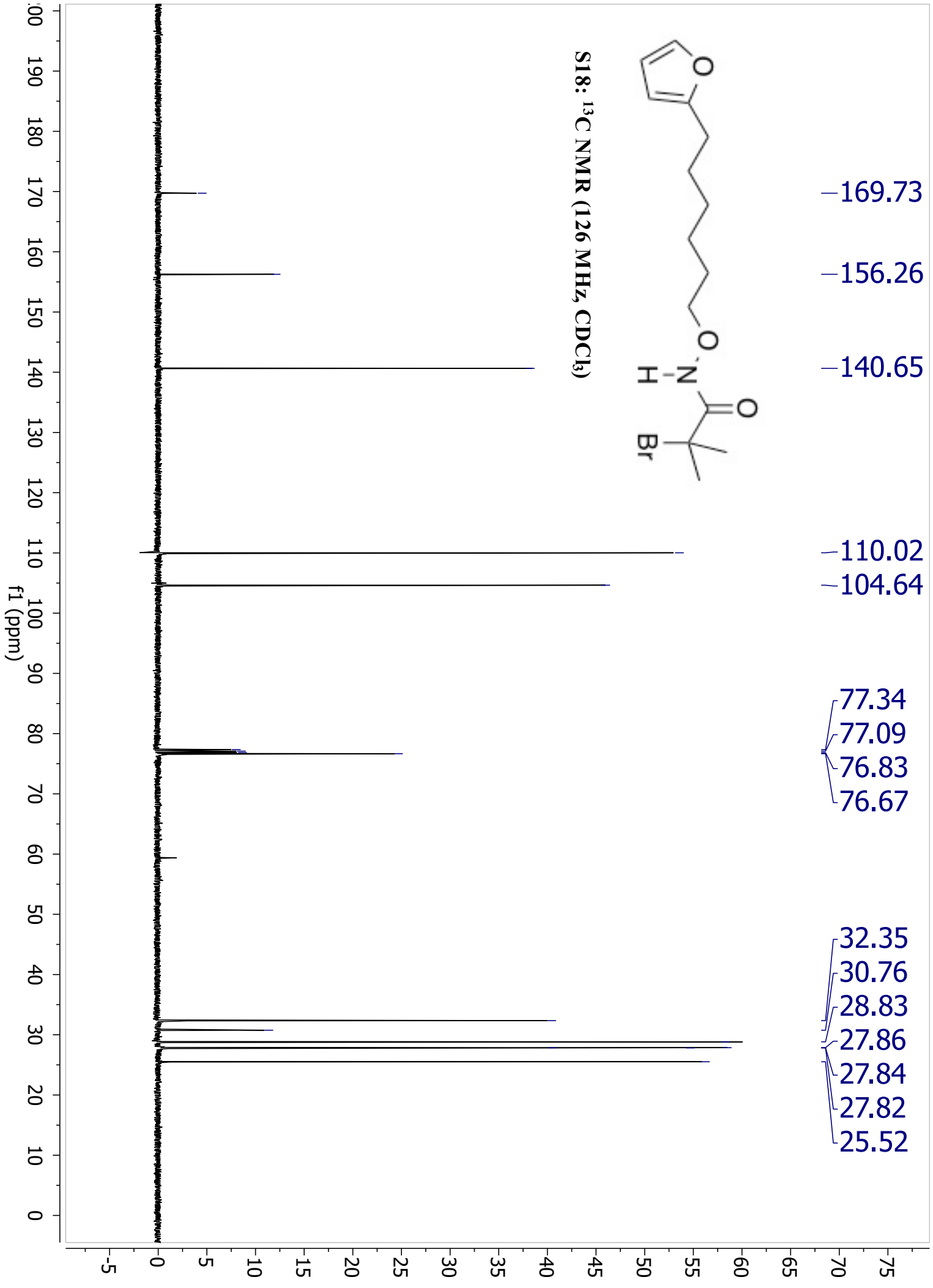
f1 (ppm)


S17: ^{1}H NMR (500 MHz, CDCl$_3$)
1.00
0.82
0.90
0.92
2.10
2.03
2.08
2.04
9.13
2.30
1.19
7.29
7.29
7.29
7.29
7.27
6.27
6.27
6.27
6.26
5.98
5.98
5.97
5.97
3.95
3.94
3.93
2.65
2.64
2.62
2.15
1.72
1.70
1.70
1.70
1.69
1.69
1.68
1.68
1.68
1.67
1.67
1.67
1.65
1.47
1.46
0.00
f1 (ppm)

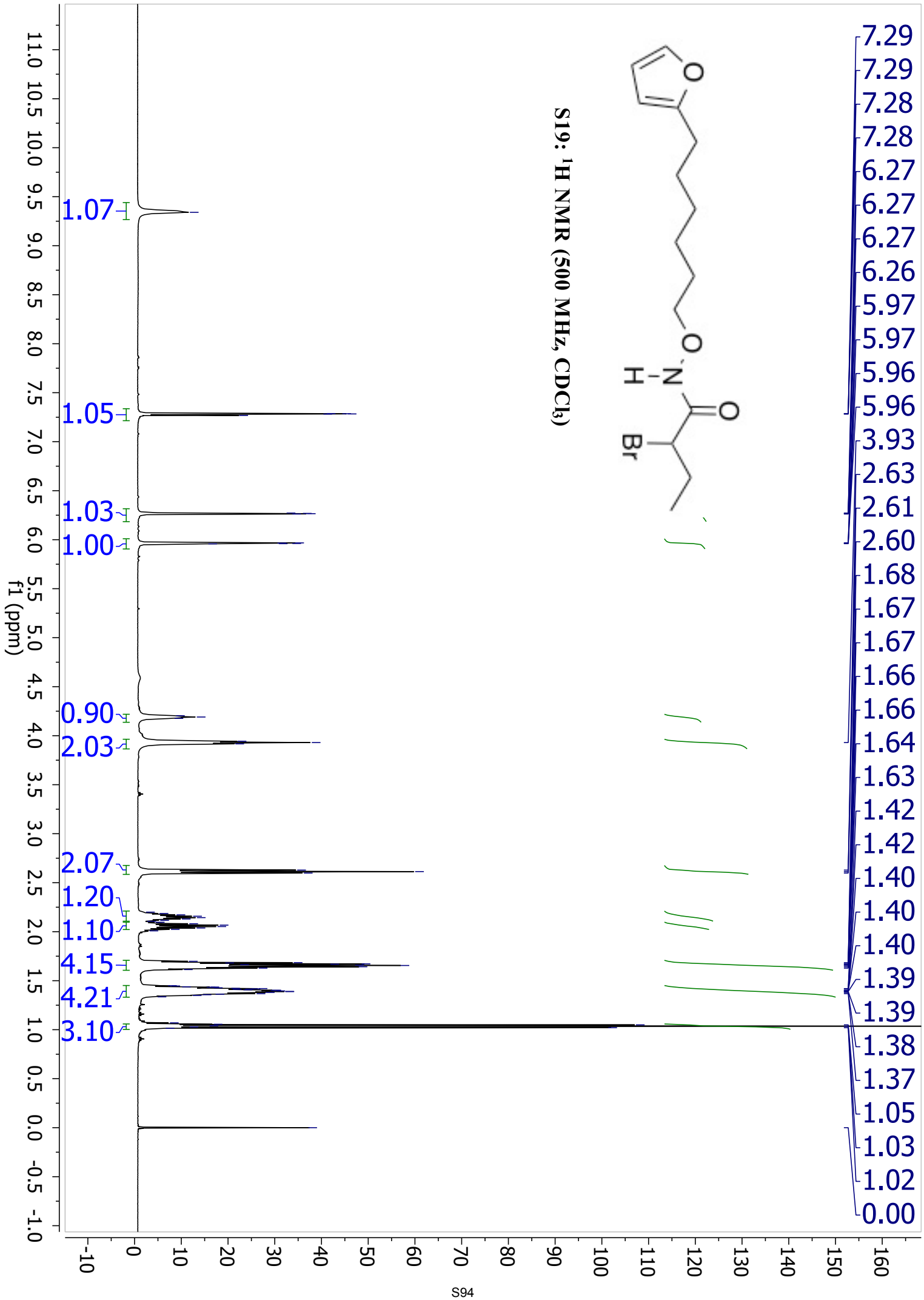


S17: ^{13}C NMR (126 MHz, CD_3OD)

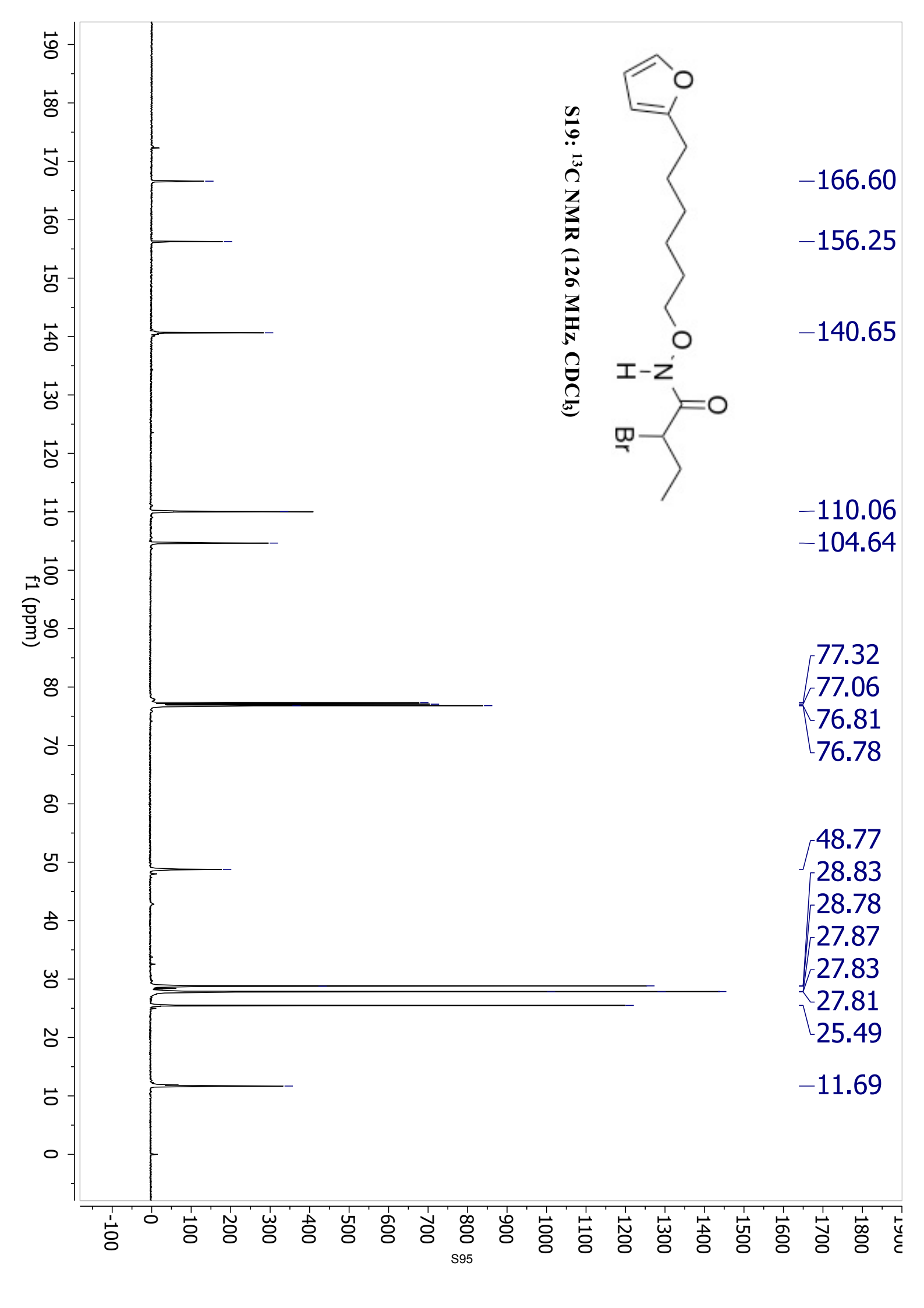

S18: ¹H NMR (500 MHz, CDCl₃)
1.02
1.05
1.02
1.02
1.96
1.90
6.00
4.00
4.04
7.29
7.29
7.29
7.29
7.26
6.28
6.27
6.27
6.27
5.97
5.97
5.97
3.95
3.93
3.92
2.64
2.62
2.61
1.96
1.69
1.68
1.68
1.67
1.67
1.66
1.65
1.65
1.64
1.44
1.42
1.41
1.41
1.39
1.38
0.00
f1 (ppm)



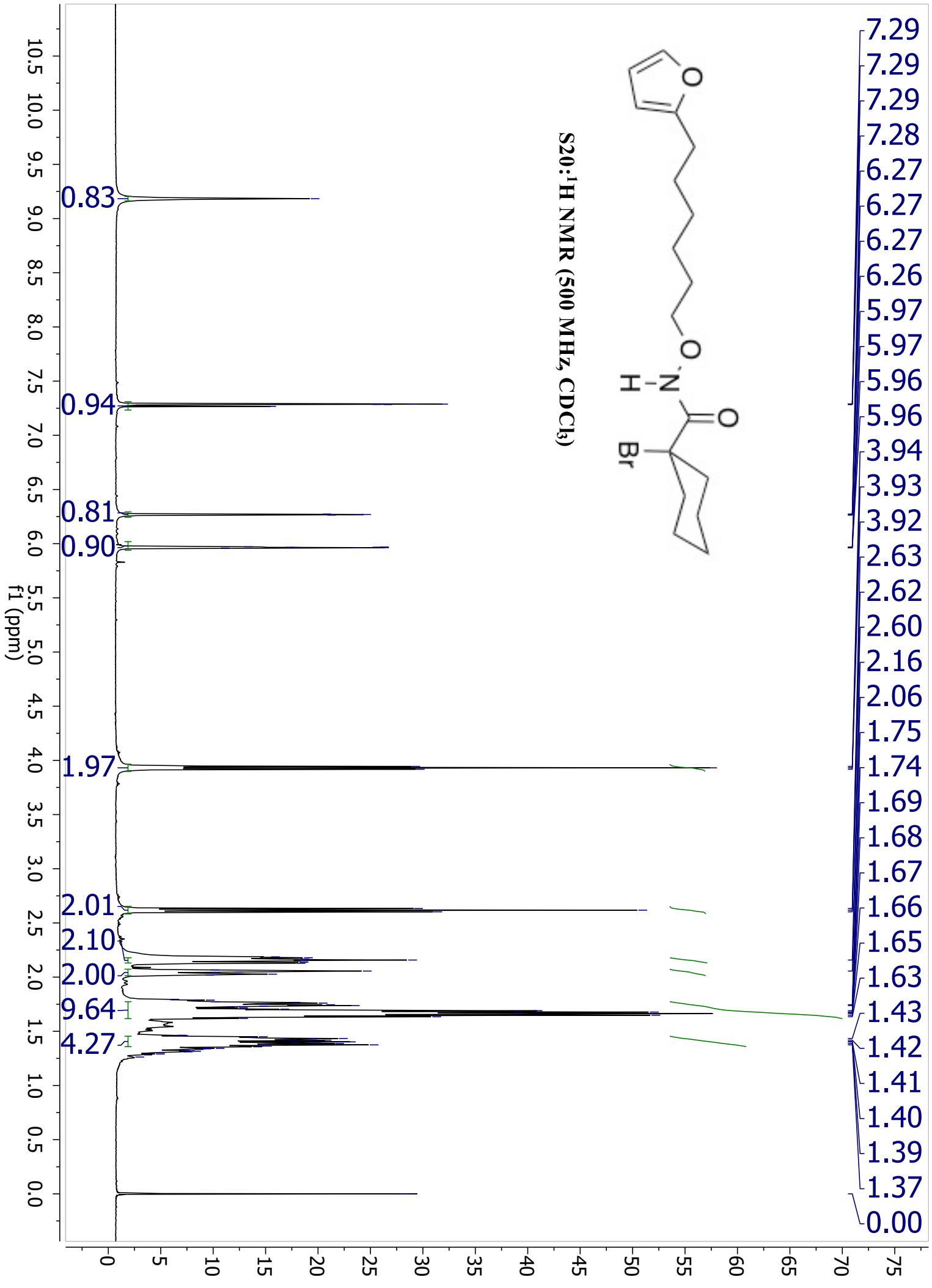
S18: ^{13}C NMR (126 MHz, $CDCl_3$)



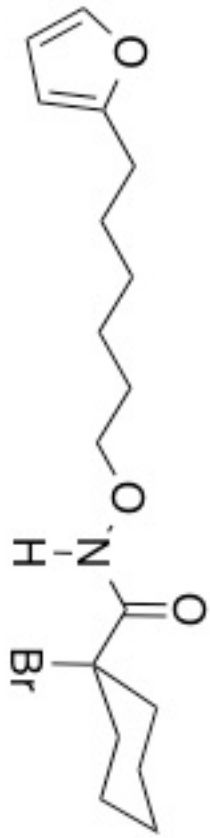
S19: ^{1}H NMR (500 MHz, $CDCl_3$)



S19: ^{13}C NMR (126 MHz, $CDCl_3$)

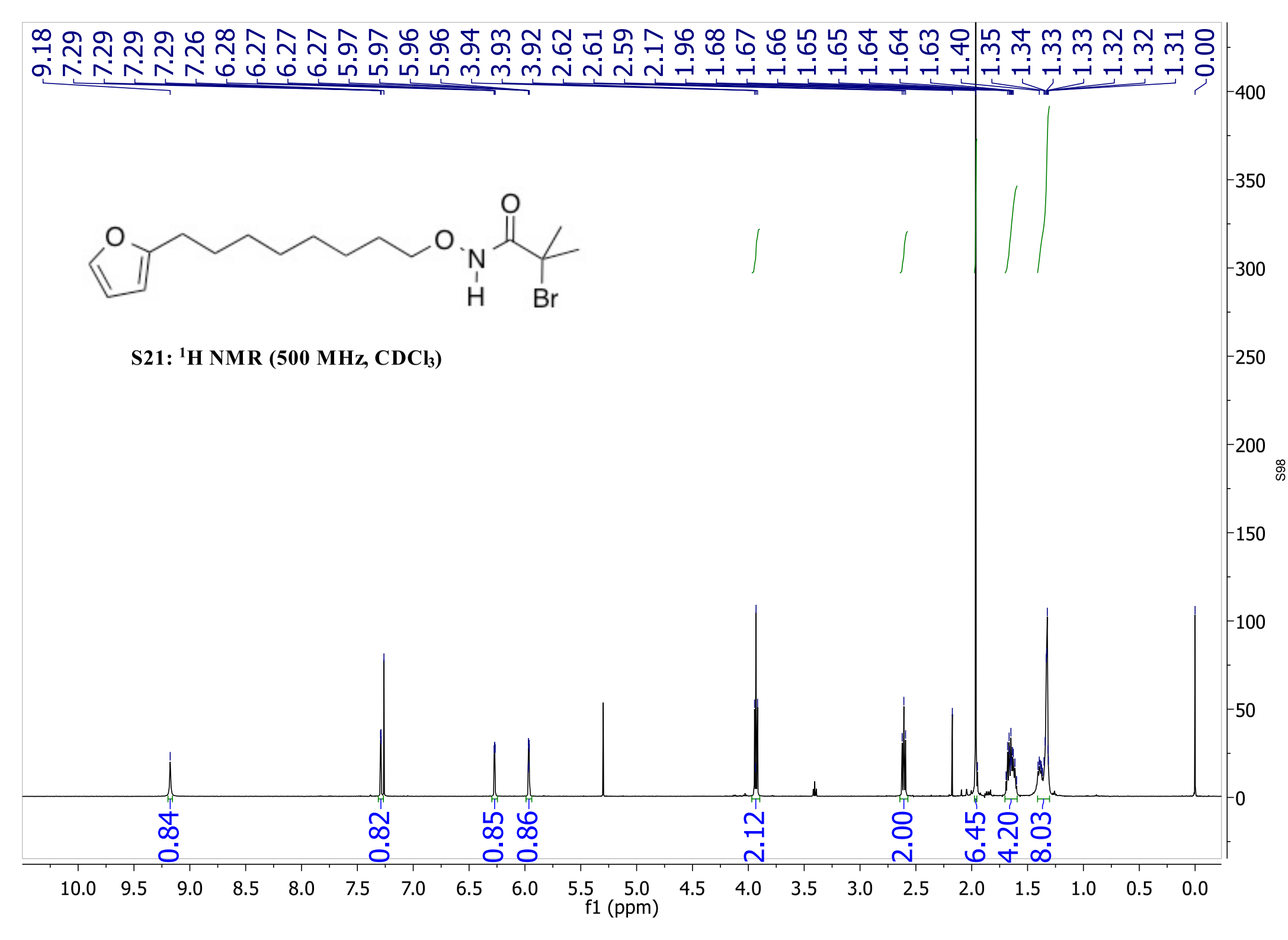

S20: ^{1}H NMR (500 MHz, $CDCl_3$)
O
O
H
N
O
Br
0.83
0.94
0.81
0.90
1.97
2.01
2.10
2.00
9.64
4.27
7.29
7.29
7.29
7.28
6.27
6.27
6.27
6.26
5.97
5.97
5.96
5.96
3.94
3.93
3.92
2.63
2.62
2.60
2.16
2.06
1.75
1.74
1.69
1.68
1.67
1.66
1.65
1.63
1.43
1.42
1.41
1.40
1.39
1.37
0.00
f1 (ppm)

S20: ^{13}C NMR (126 MHz, $CDCl_3$)



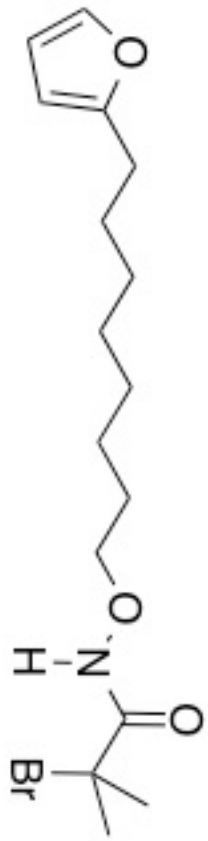
169.70
156.32
140.67
110.03
104.64
77.27
77.02
76.76
76.67
68.99
38.02
28.86
27.89
27.88
27.85
25.55
24.63
22.43
0.00

f1 (ppm)



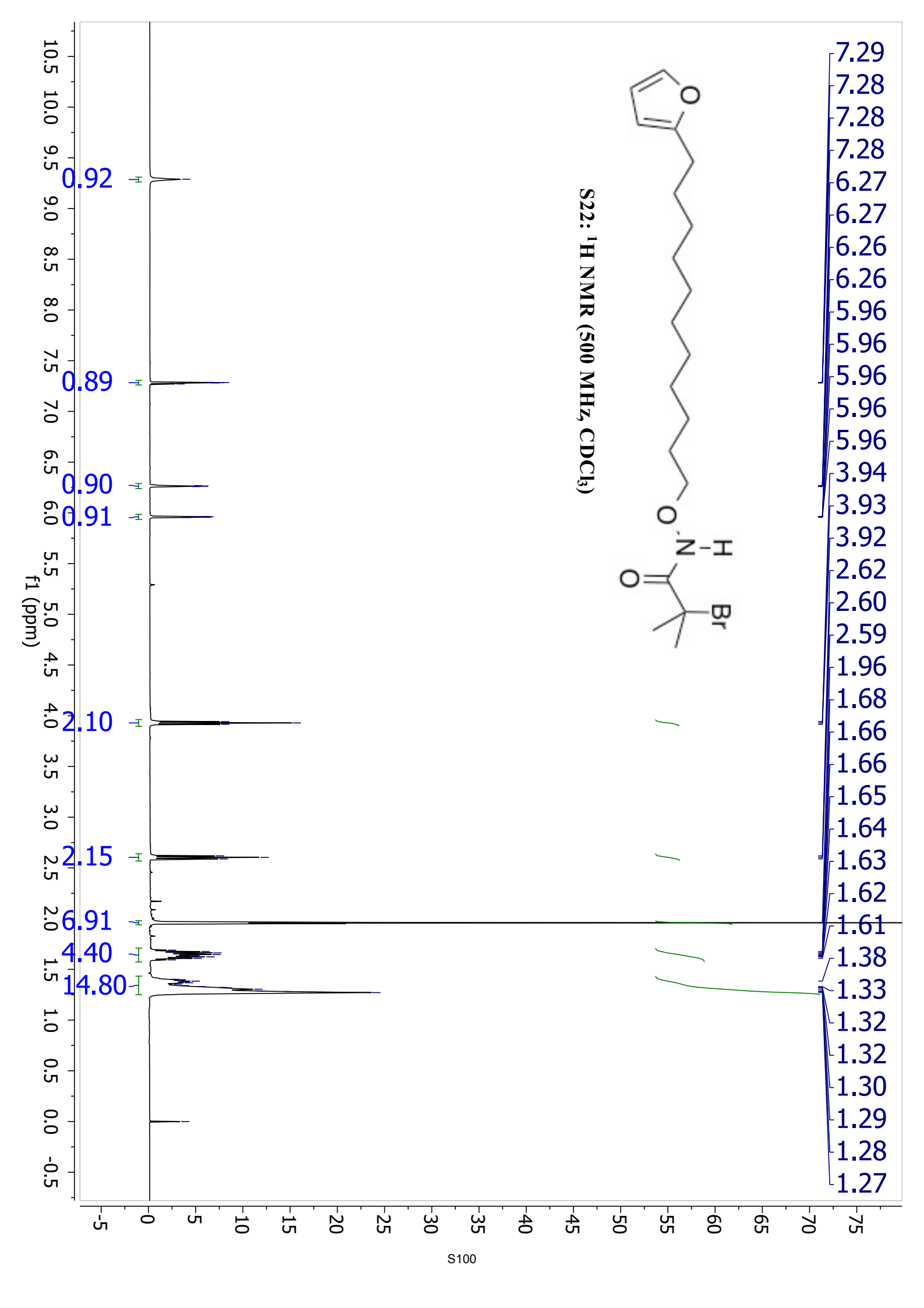
S21: ^{1}H NMR (500 MHz, $CDCl_3$)

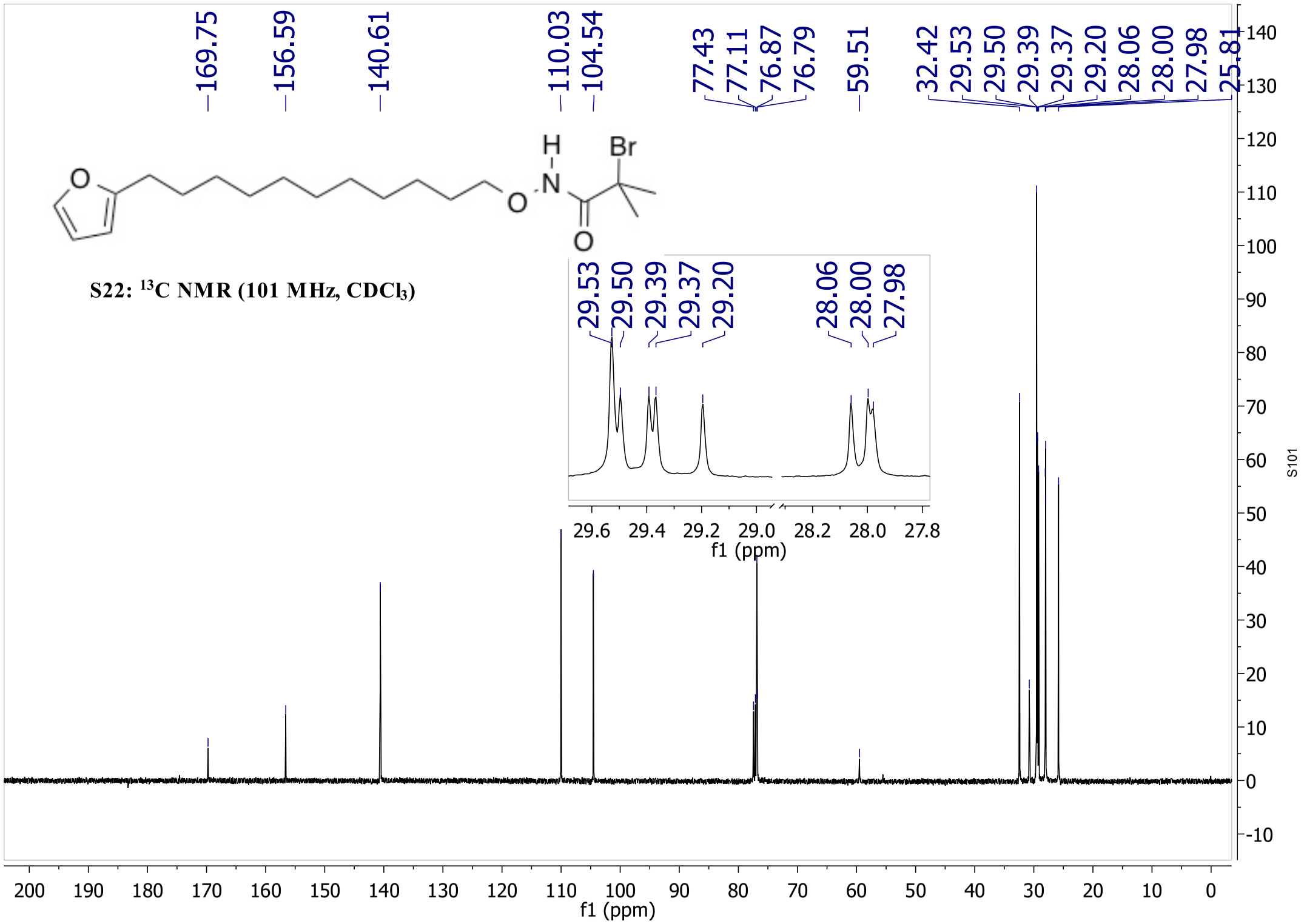
S21: ^{13}C NMR (126 MHz, CDCl$_3$)



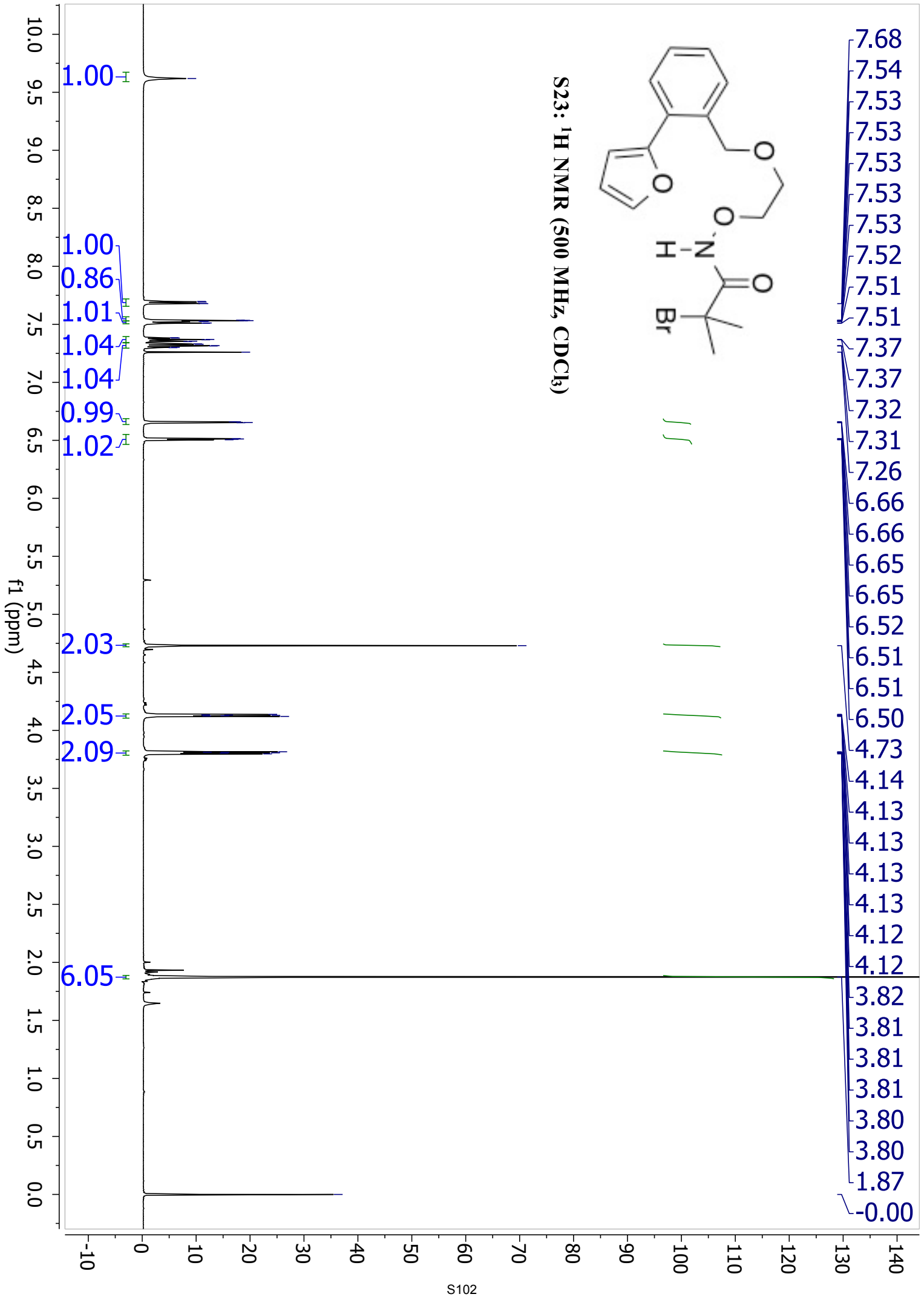
169.71
156.43
140.59
110.00
104.54
77.38
77.12
76.87
76.73
59.26
32.31
30.77
29.23
29.17
29.02
27.97
27.91
25.73

f1 (ppm)

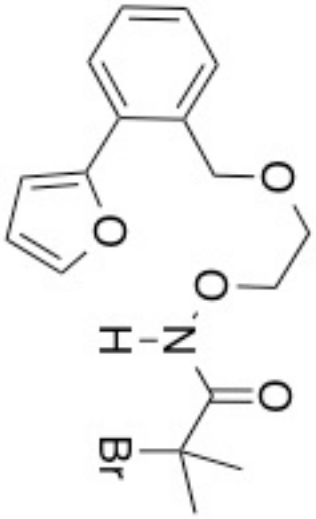

S22: ^{1}H NMR (500 MHz, CDCl$_3$)
O
O
N
H
O
Br
0.92
0.89
0.90
0.91
2.10
2.15
6.91
4.40
14.80
7.29
7.28
7.28
7.28
6.27
6.27
6.26
6.26
5.96
5.96
5.96
5.96
5.96
5.96
3.94
3.93
3.92
2.62
2.60
2.59
1.96
1.68
1.66
1.66
1.65
1.64
1.63
1.62
1.61
1.38
1.33
1.32
1.32
1.30
1.29
1.28
1.27
f1 (ppm)



S22: ^{13}C NMR (101 MHz, $CDCl_3$)

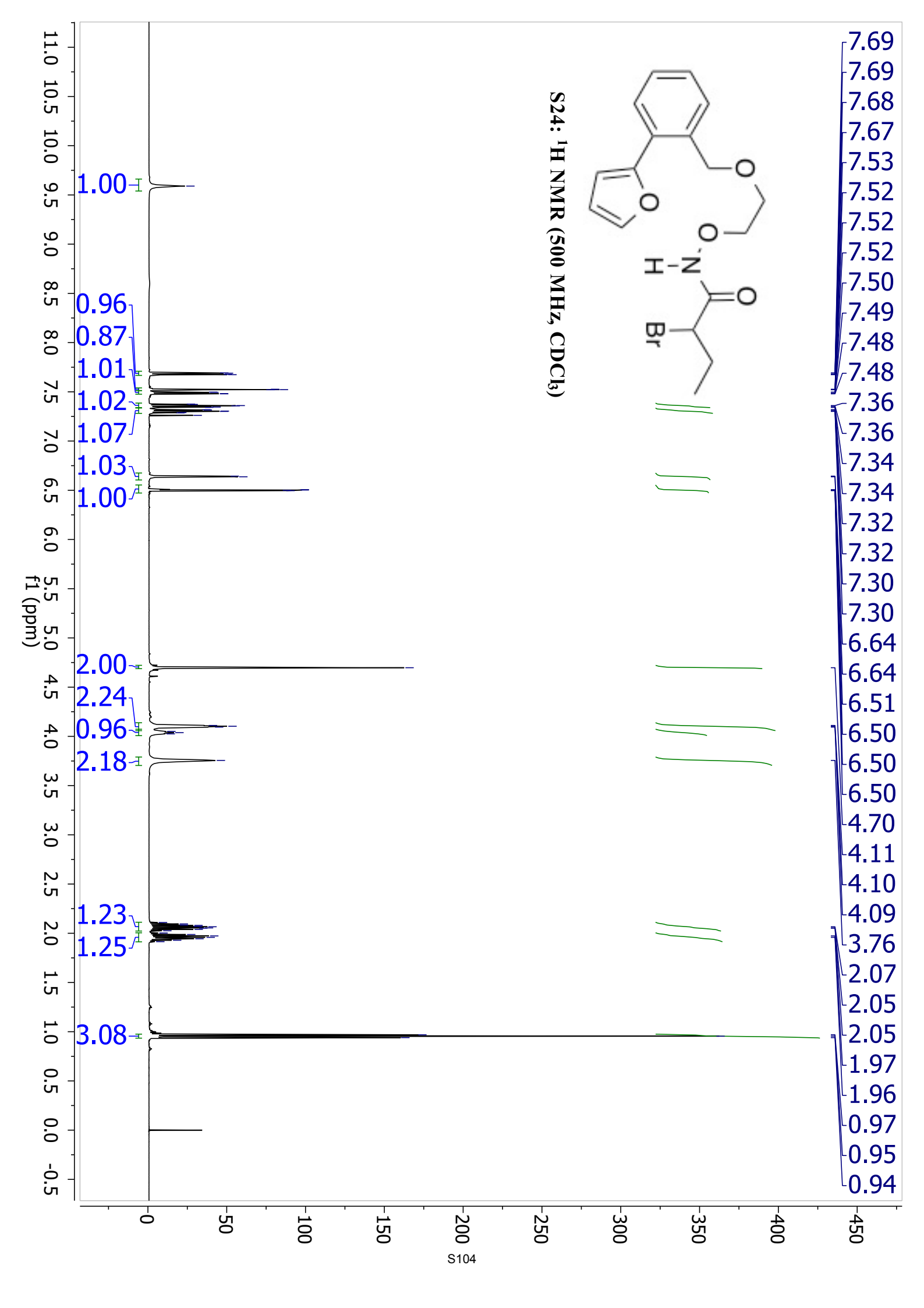

S23: ^{1}H NMR (500 MHz, CDCl$_3$)
1.00
1.00
0.86
1.01
1.04
1.04
0.99
1.02
2.03
2.05
2.09
6.05
7.68
7.54
7.53
7.53
7.53
7.53
7.53
7.52
7.51
7.51
7.37
7.37
7.32
7.31
7.26
6.66
6.66
6.65
6.65
6.52
6.51
6.51
6.50
4.73
4.14
4.13
4.13
4.13
4.13
4.12
4.12
3.82
3.81
3.81
3.81
3.80
3.80
1.87
-0.00
f1 (ppm)

S23: ^{13}C NMR (126 MHz, $CDCl_3$)

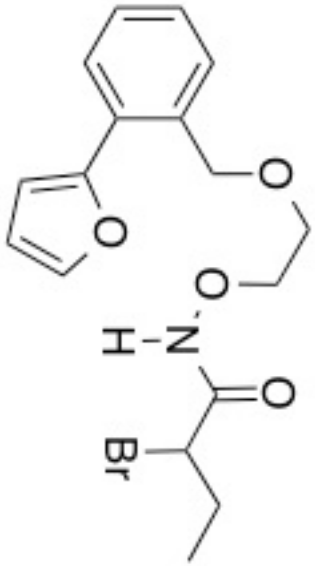


168.94
152.43
142.23
133.46
130.14
129.71
128.04
127.56
127.53
111.43
108.81
77.11
76.85
76.60
74.89
71.84
69.09
58.78
32.05

f1 (ppm)


S24: ¹H NMR (500 MHz, CDCl₃)
1.00
0.96
0.87
1.01
1.02
1.07
1.03
1.00
2.00
2.24
0.96
2.18
1.23
1.25
3.08
7.69
7.69
7.68
7.67
7.53
7.52
7.52
7.52
7.50
7.49
7.48
7.48
7.36
7.36
7.34
7.34
7.32
7.32
7.30
7.30
6.64
6.64
6.51
6.50
6.50
6.50
4.70
4.11
4.10
4.09
3.76
2.07
2.05
2.05
1.97
1.96
0.97
0.95
0.94
f1 (ppm)

S24: ^{13}C NMR (126 MHz, $CDCl_3$)

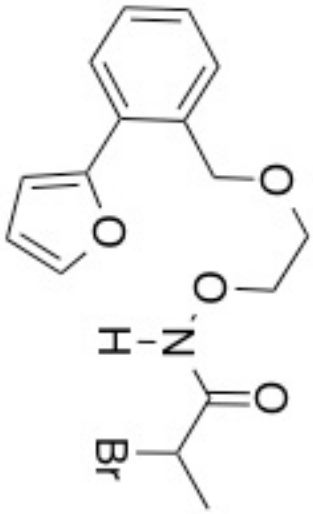


166.18
152.55
142.41
133.71
130.17
129.84
128.18
127.70
127.66
111.65
109.00
77.38
77.13
76.87
75.16
71.90
68.94
48.62
28.66
11.65

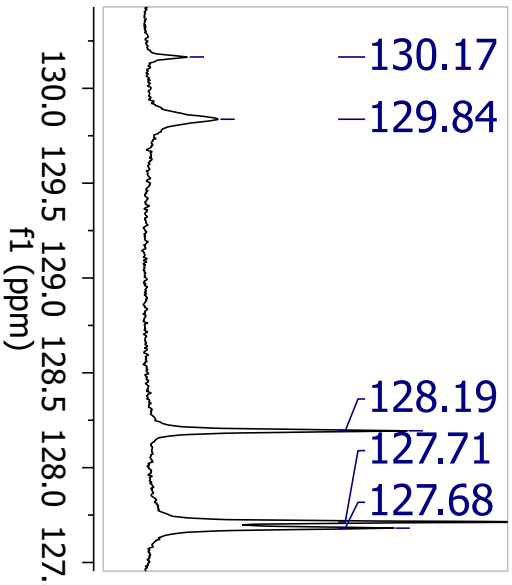
f1 (ppm)

S25: ^{1}H NMR (500 MHz, $CDCl_3$)

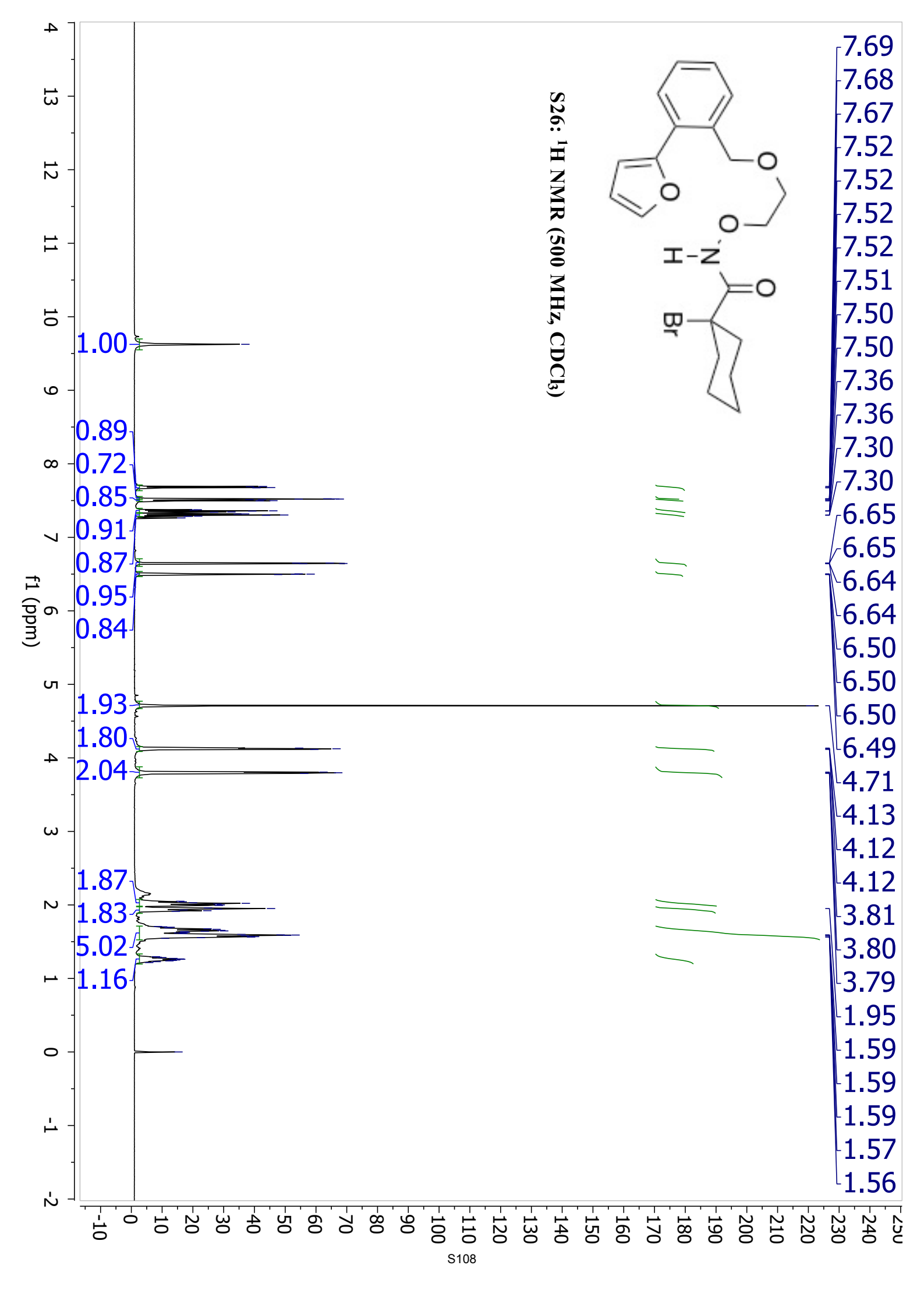
S25: ^{13}C NMR (126 MHz, $CDCl_3$)



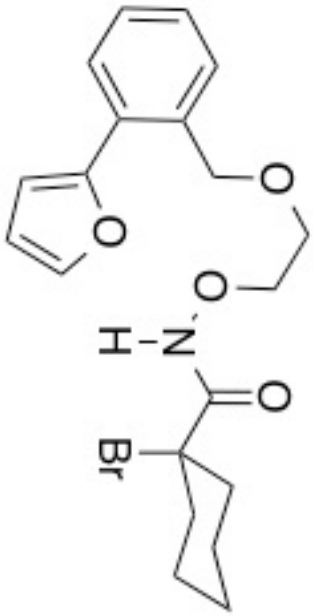
166.89
152.55
142.42
133.69
130.17
129.84
128.19
127.71
127.68
111.65
109.00
77.39
77.14
76.88
75.12
71.90
68.92
40.59
22.19



f1 (ppm)


S26: ^{1}H NMR (500 MHz, CDCl$_3$)
1.00
0.89
0.72
0.85
0.91
0.87
0.95
0.84
1.93
1.80
2.04
1.87
1.83
5.02
1.16
7.69
7.68
7.67
7.52
7.52
7.52
7.52
7.51
7.50
7.50
7.36
7.36
7.30
7.30
6.65
6.65
6.64
6.64
6.50
6.50
6.50
6.49
4.71
4.13
4.12
4.12
3.81
3.80
3.79
1.95
1.59
1.59
1.59
1.57
1.56
f1 (ppm)

S26: ^{13}C NMR (126 MHz, $CDCl_3$)



169.07

152.54
142.40
133.63
130.27
129.92
128.20
127.68
127.67

111.63
109.01

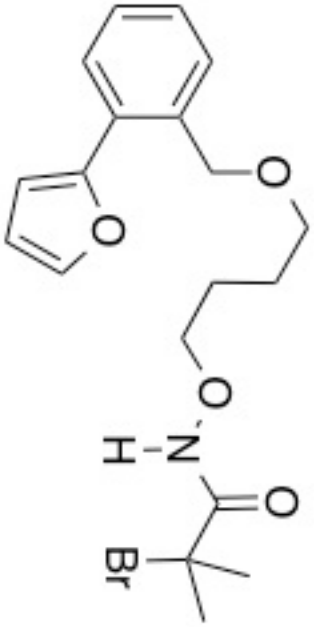
77.36
77.11
76.85
74.91
71.96
69.27
67.64

37.69

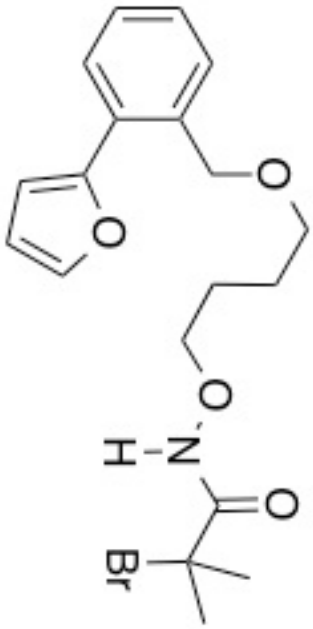
24.60
22.48

f1 (ppm)

S27: ^{1}H NMR (500 MHz, $CDCl_3$)

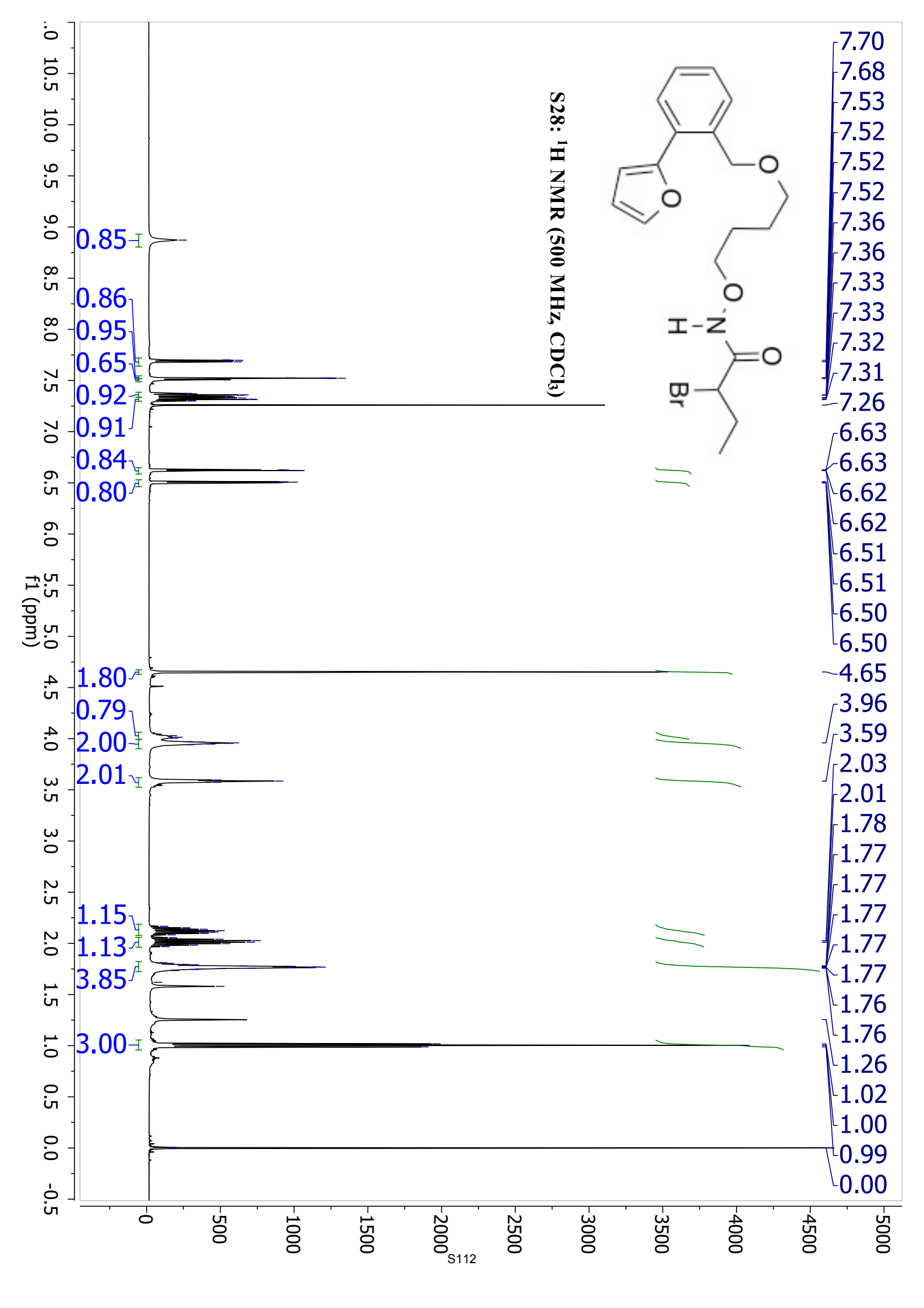


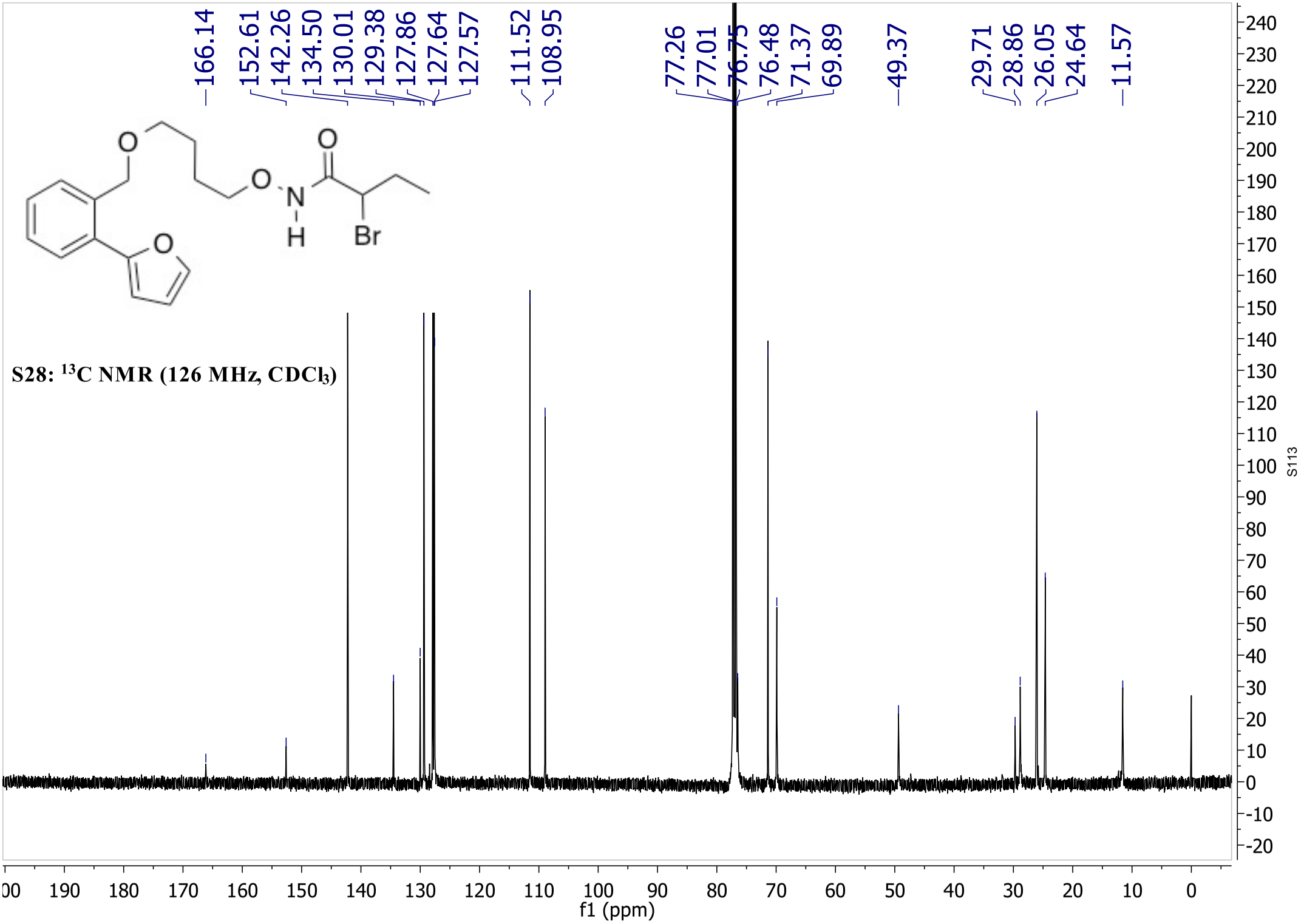
S27: ^{13}C NMR (101 MHz, $CDCl_3$)



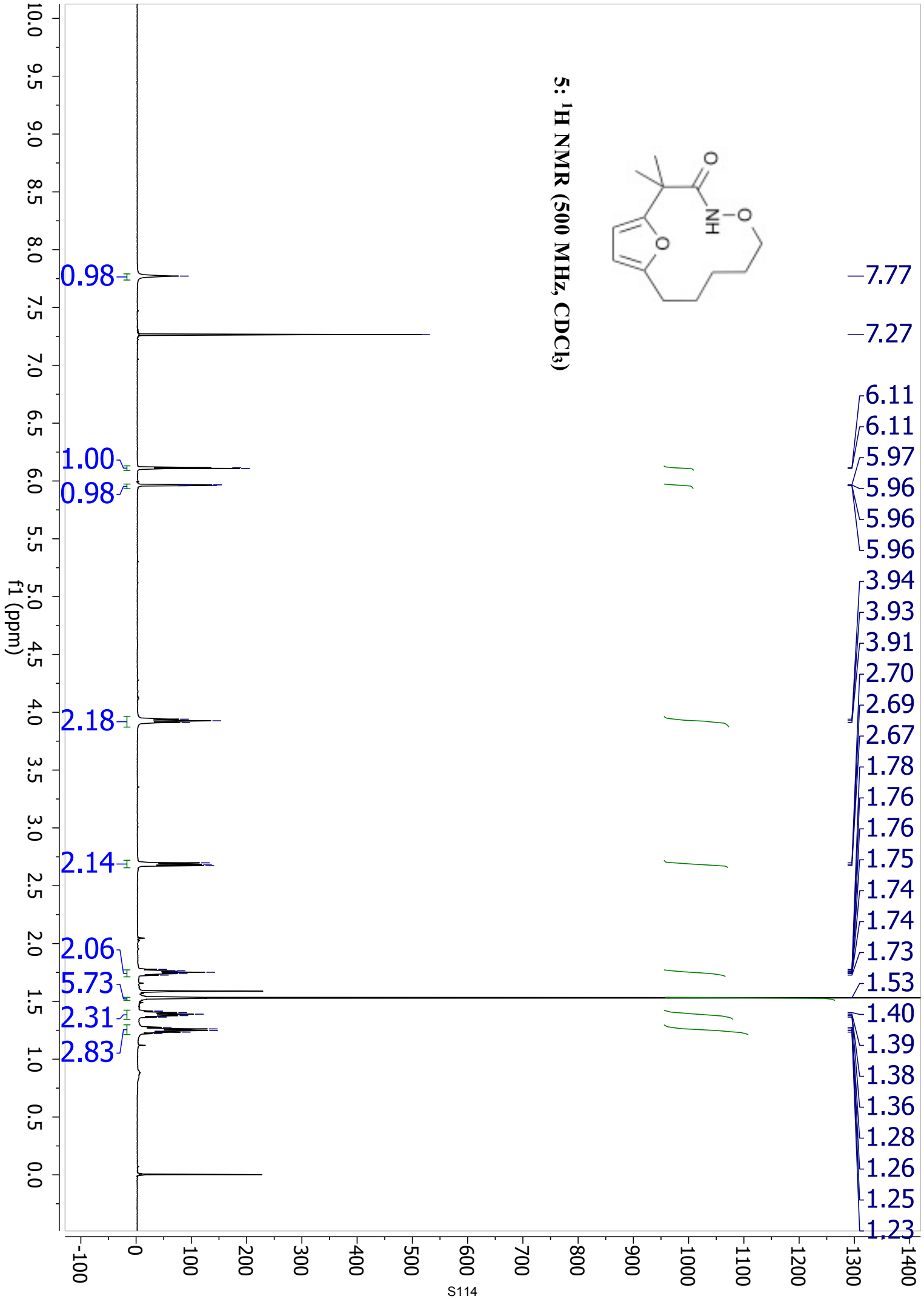
169.67
152.63
142.20
134.60
129.93
129.27
127.75
127.59
127.49
111.50
108.94
77.33
77.01
76.69
76.43
71.29
69.79
59.50
32.40
26.15
24.80
-0.00

f1 (ppm)

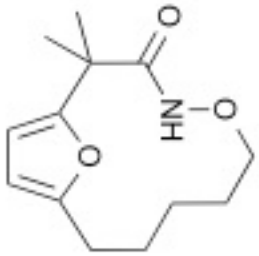

S28: ^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
0.85
0.86
0.95
0.65
0.92
0.91
0.84
0.80
1.80
0.79
2.00
2.01
1.15
1.13
3.85
3.00
7.70
7.68
7.53
7.52
7.52
7.52
7.36
7.36
7.33
7.33
7.32
7.31
7.26
6.63
6.63
6.62
6.62
6.51
6.51
6.50
6.50
4.65
3.96
3.59
2.03
2.01
1.78
1.77
1.77
1.77
1.77
1.77
1.76
1.76
1.26
1.02
1.00
0.99
0.00
O
O
O
N
H
O
Br



S28: ^{13}C NMR (126 MHz, $CDCl_3$)

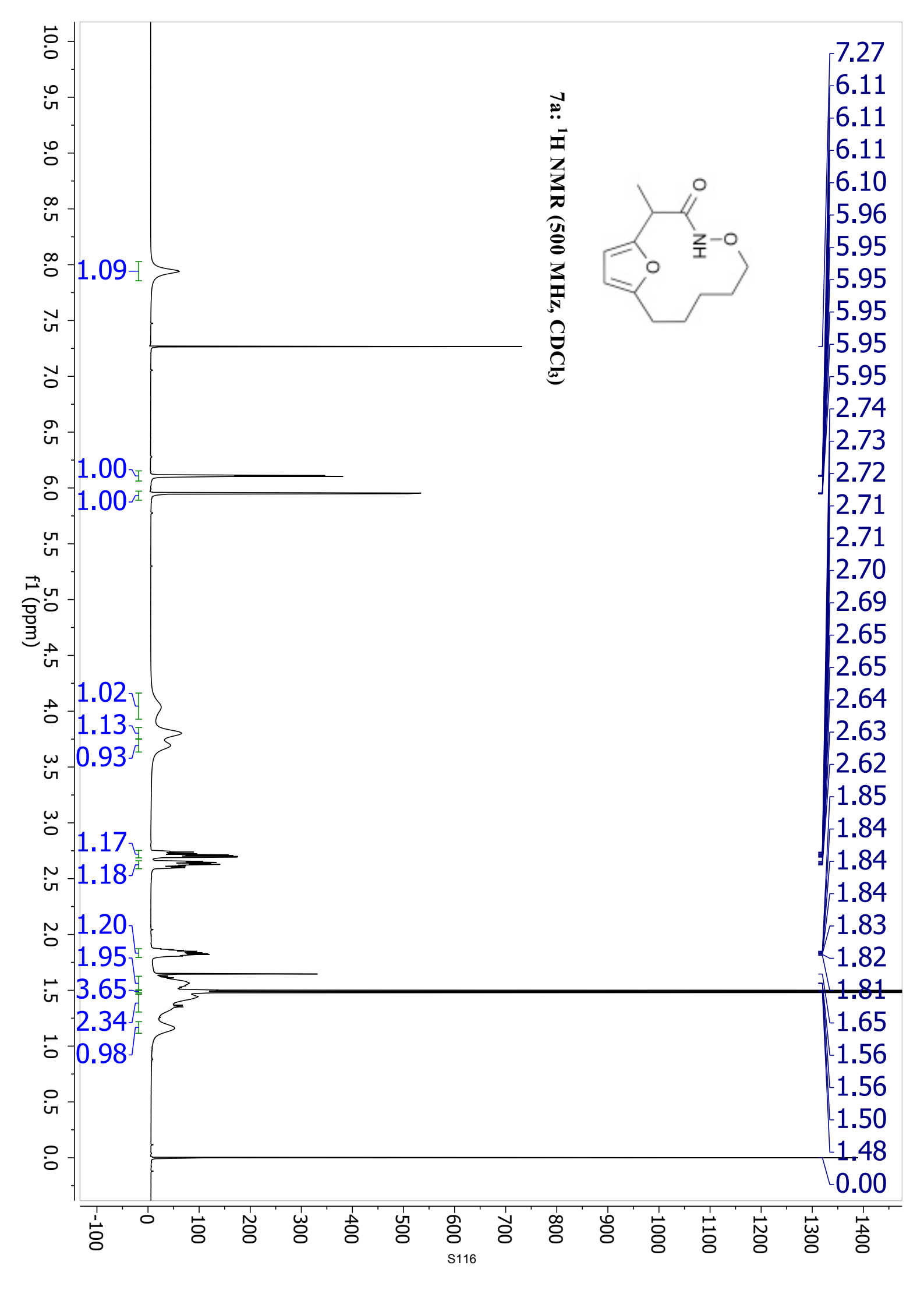

5: ^{1}H NMR (500 MHz, CDCl$_3$)
0.98
1.00
0.98
2.18
2.14
2.06
5.73
2.31
2.83
7.77
7.27
6.11
6.11
5.97
5.96
5.96
5.96
3.94
3.93
3.91
2.70
2.69
2.67
1.78
1.76
1.76
1.75
1.74
1.74
1.73
1.53
1.40
1.39
1.38
1.36
1.28
1.26
1.25
1.23
f1 (ppm)

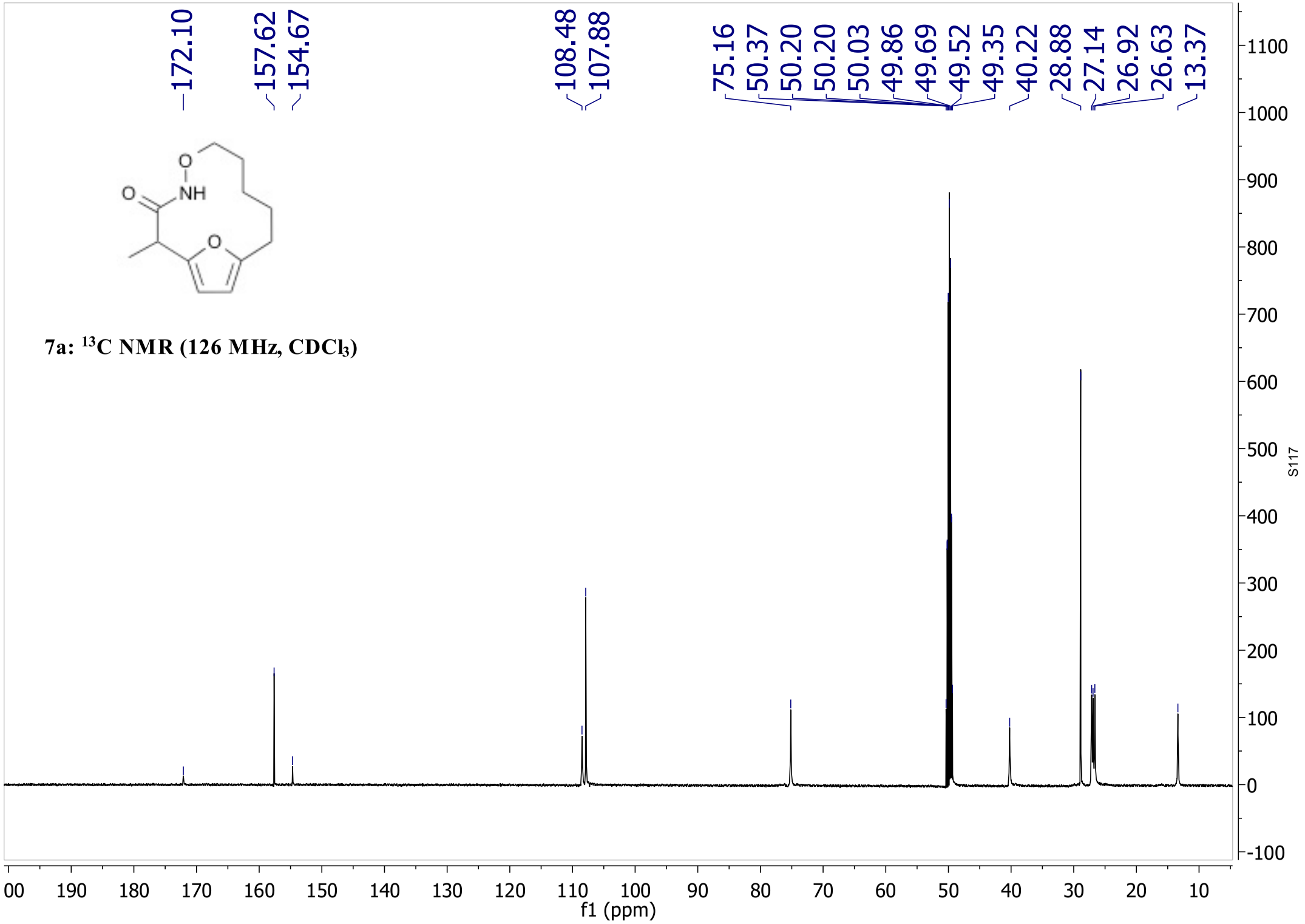
5: ^{13}C NMR (126 MHz, $CDCl_3$)

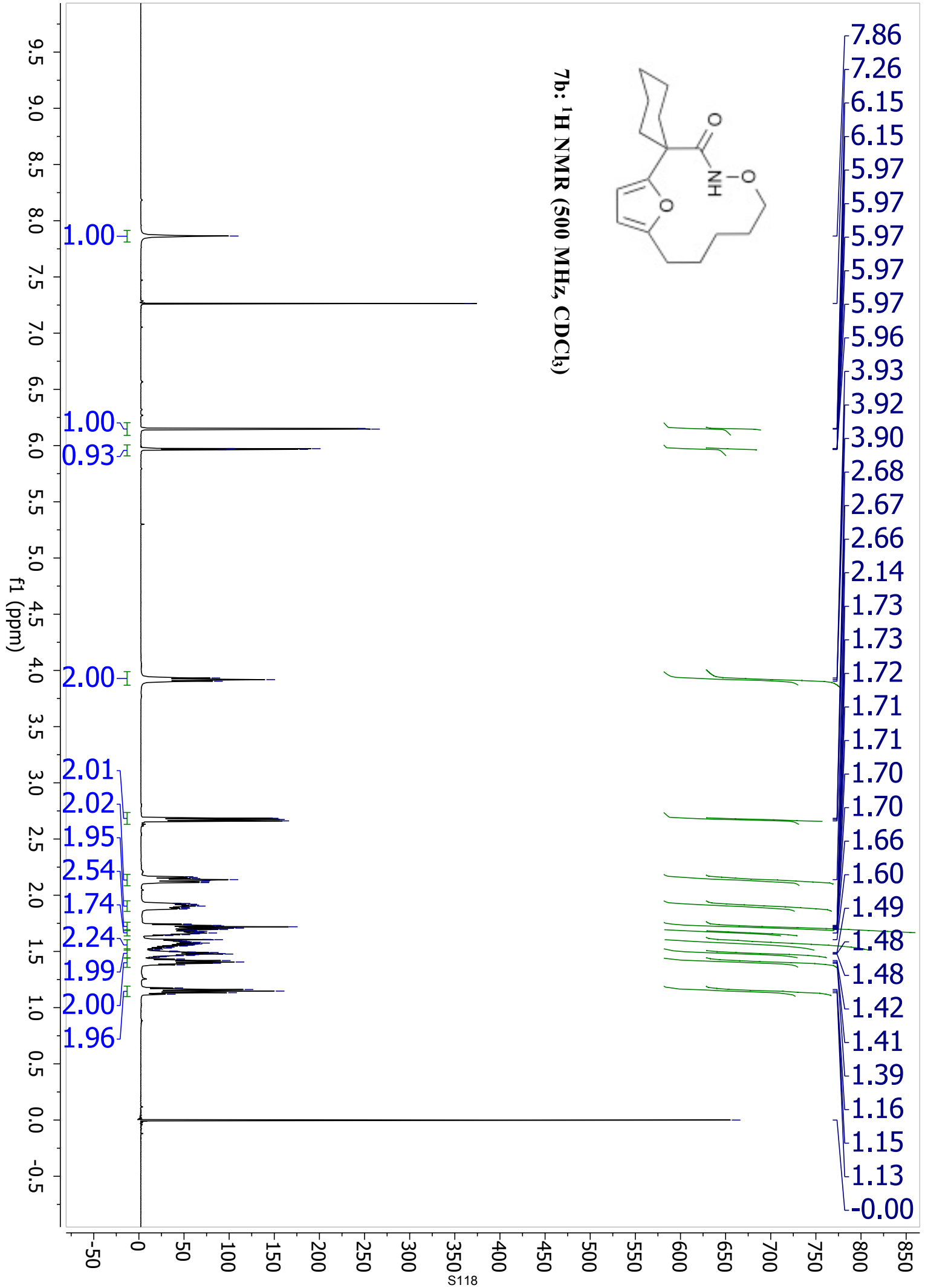


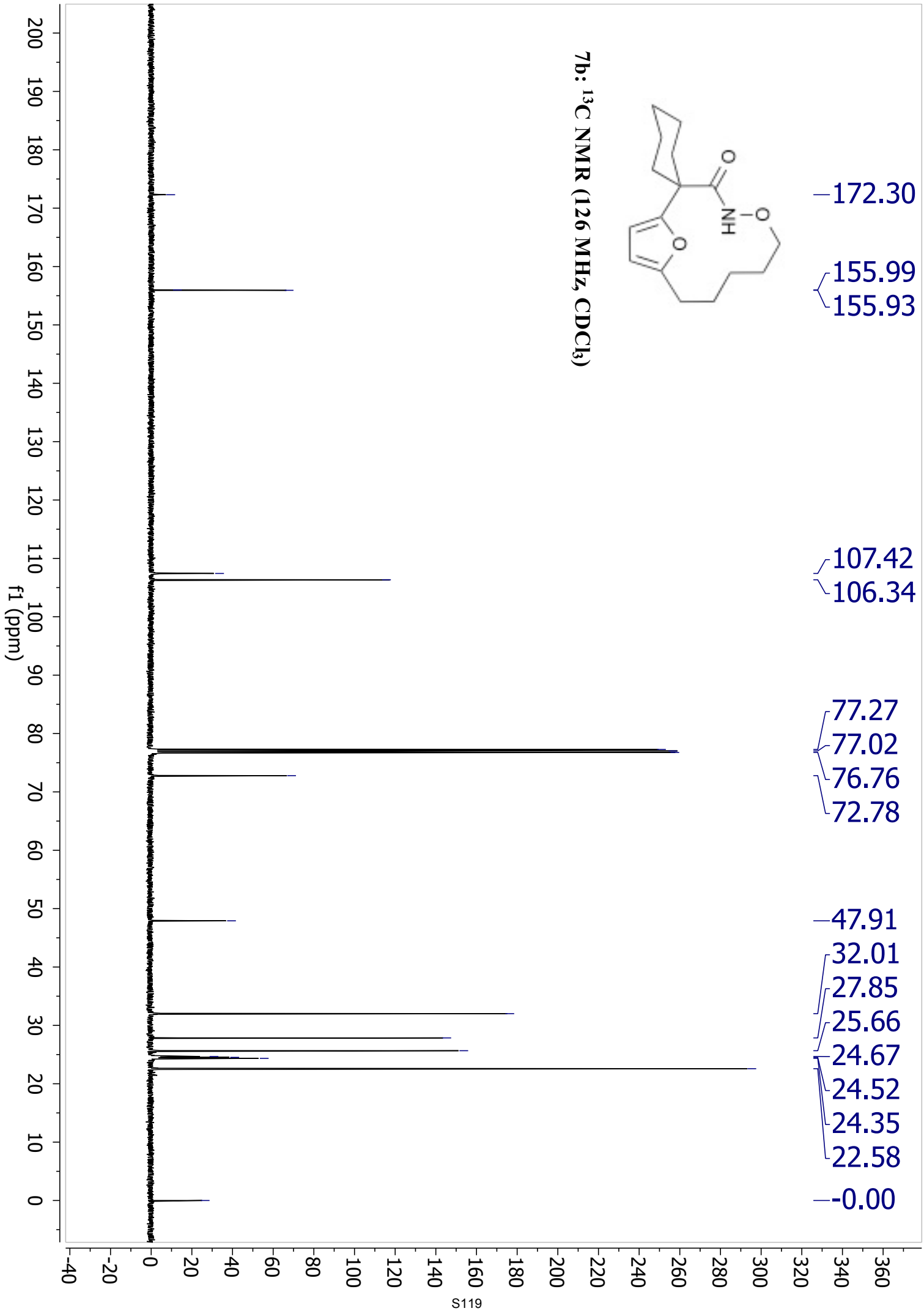
172.95
157.23
156.12
106.34
106.03
77.30
77.05
76.80
73.36
43.15
27.79
25.03
24.21
24.04
23.47
0.00

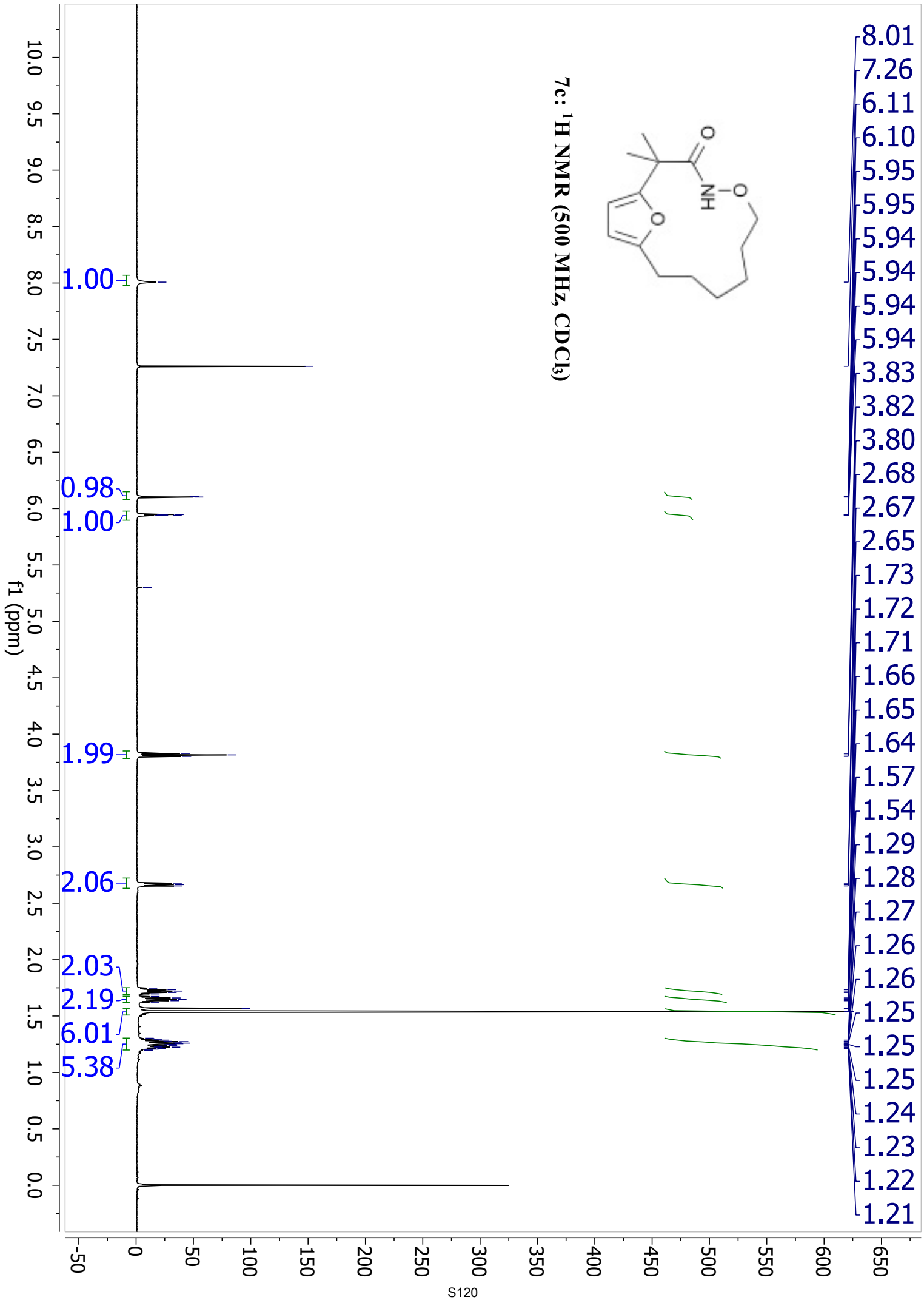
f1 (ppm)

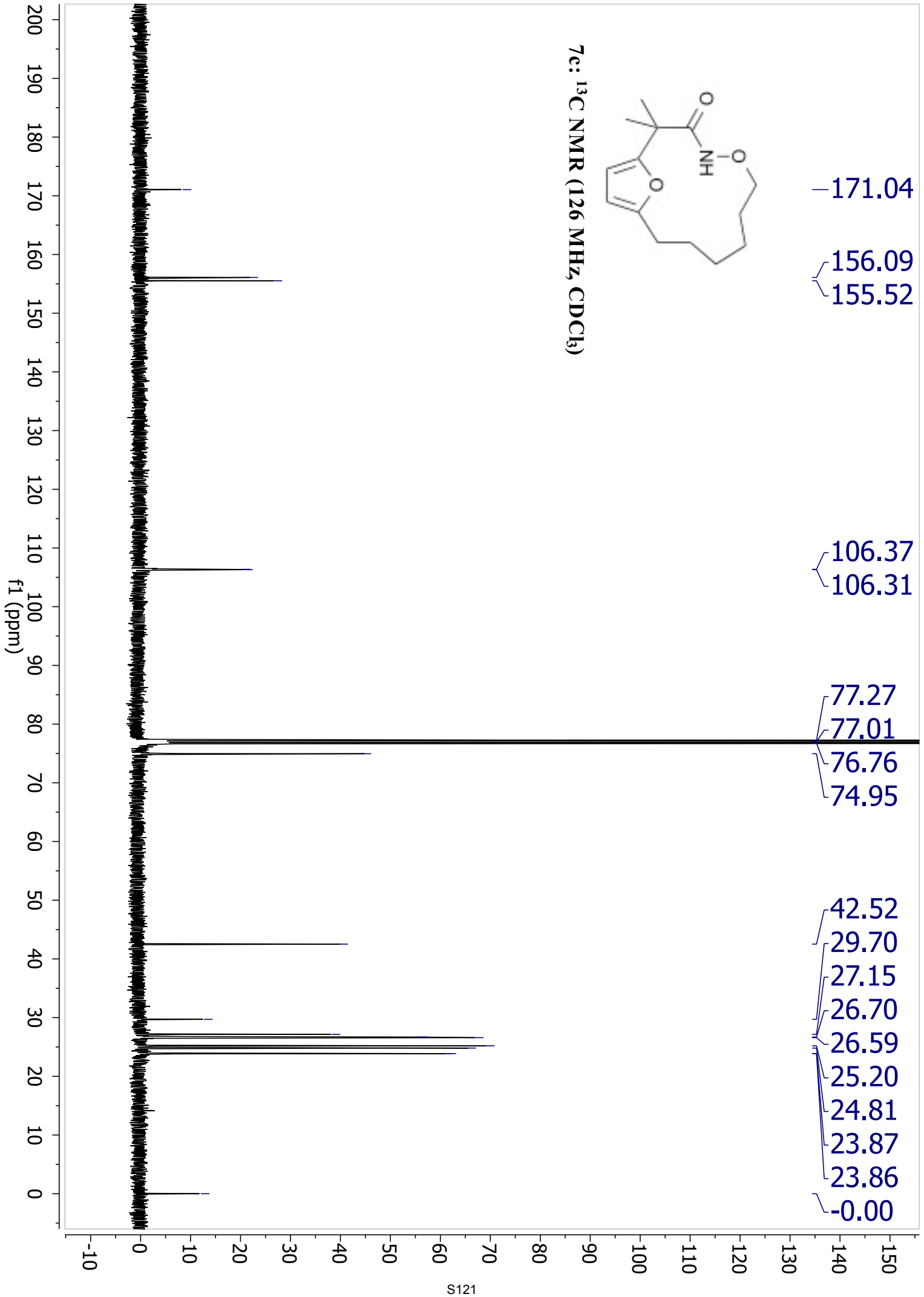

7a: ^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
1.09
1.00
1.00
1.02
1.13
0.93
1.17
1.18
1.20
1.95
3.65
2.34
0.98
7.27
6.11
6.11
6.11
6.10
5.96
5.95
5.95
5.95
5.95
5.95
2.74
2.73
2.72
2.71
2.71
2.70
2.69
2.65
2.65
2.64
2.63
2.62
1.85
1.84
1.84
1.84
1.83
1.82
1.81
1.65
1.56
1.56
1.50
1.48
0.00

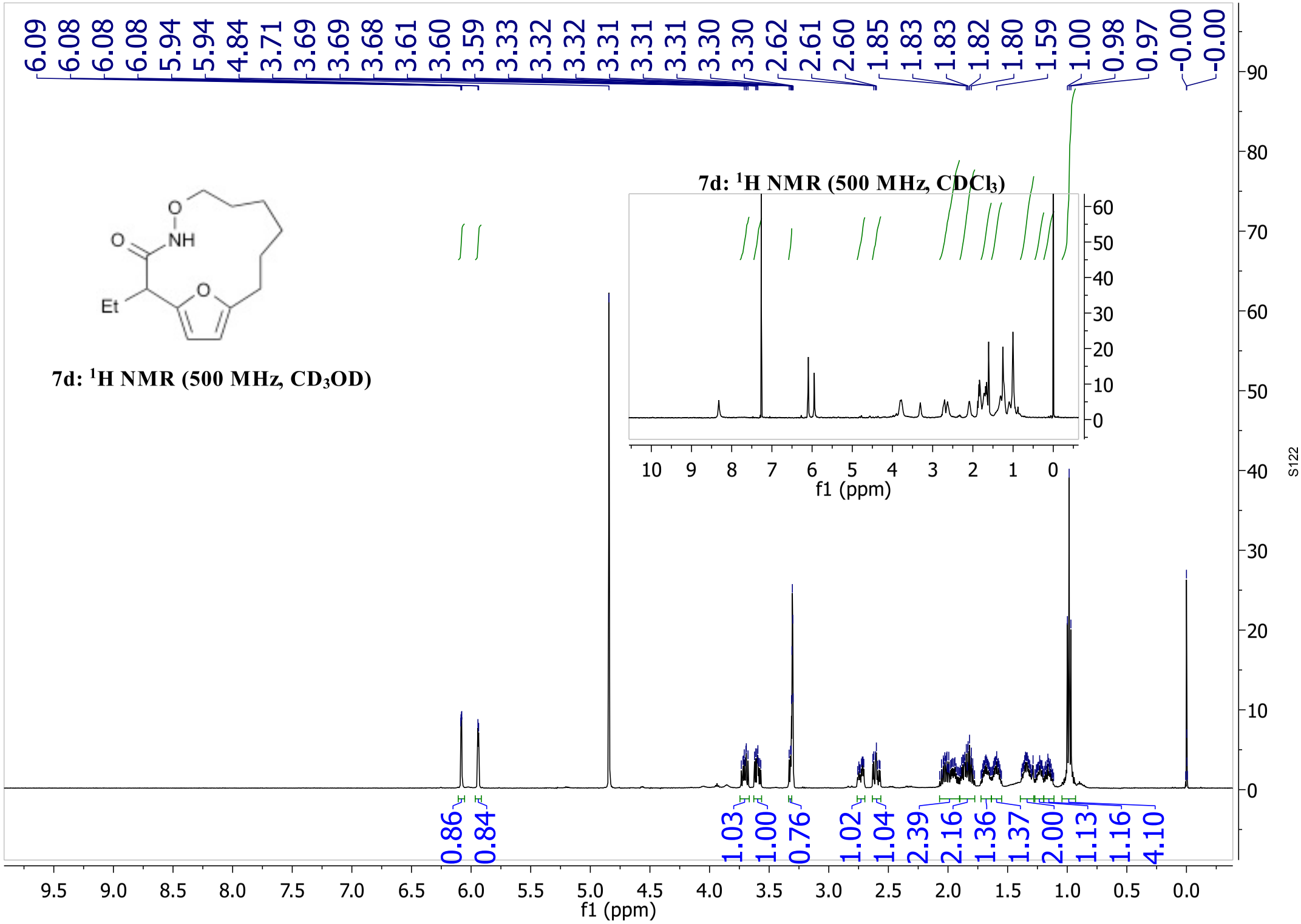

172.10
157.62
154.67
108.48
107.88
75.16
50.37
50.20
50.20
50.03
49.86
49.69
49.52
49.35
40.22
28.88
27.14
26.92
26.63
13.37
O
NH
O
O
7a: ^{13}C NMR (126 MHz, CDCl$_3$)
S117
f1 (ppm)

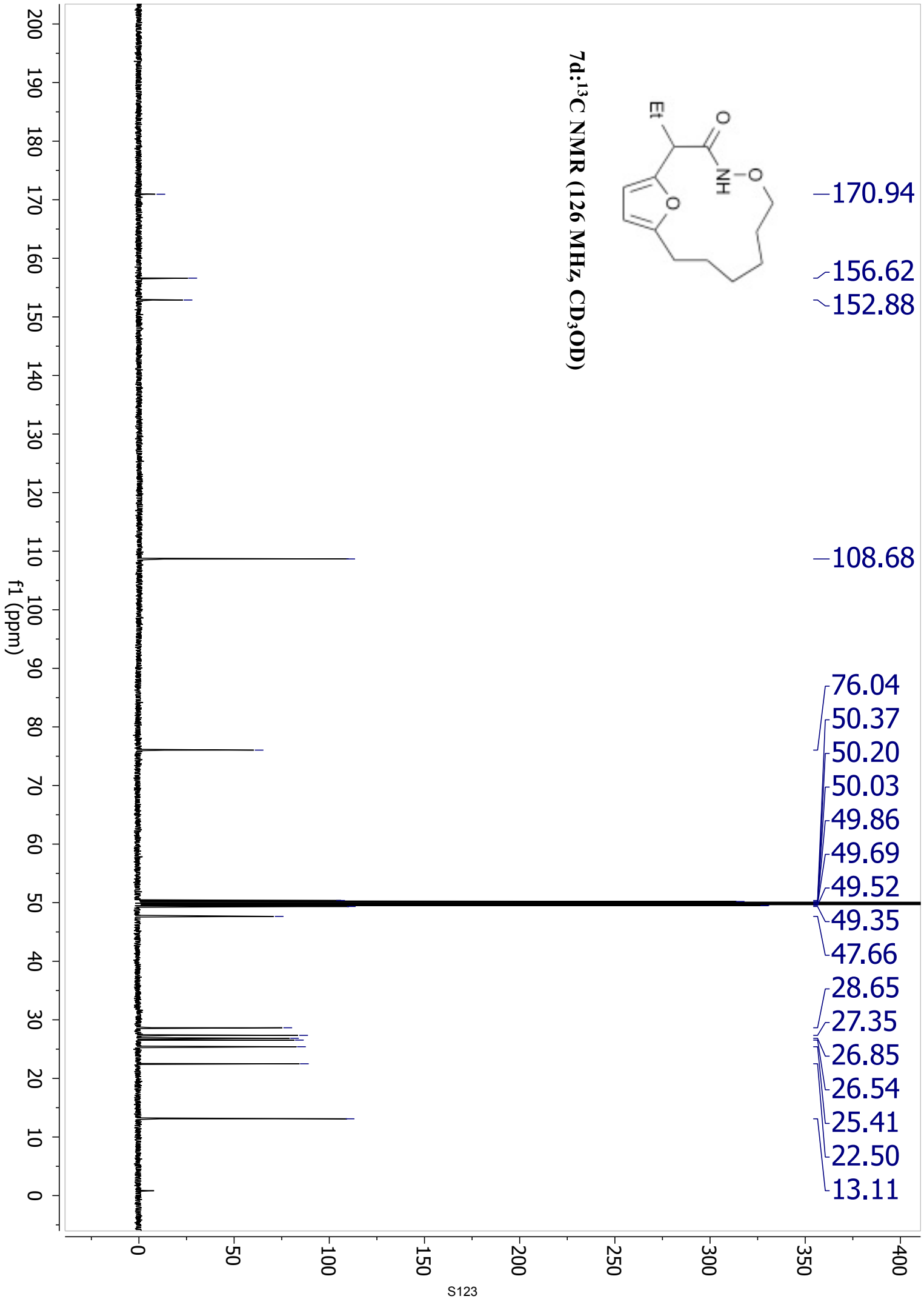

7b: ^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
1.00
1.00
0.93
2.00
2.01
2.02
1.95
2.54
1.74
2.24
1.99
2.00
1.96
7.86
7.26
6.15
6.15
5.97
5.97
5.97
5.97
5.97
5.96
3.93
3.92
3.90
2.68
2.67
2.66
2.14
1.73
1.73
1.72
1.71
1.71
1.70
1.70
1.66
1.60
1.49
1.48
1.48
1.42
1.41
1.39
1.16
1.15
1.13
-0.00
O
NH
O
O

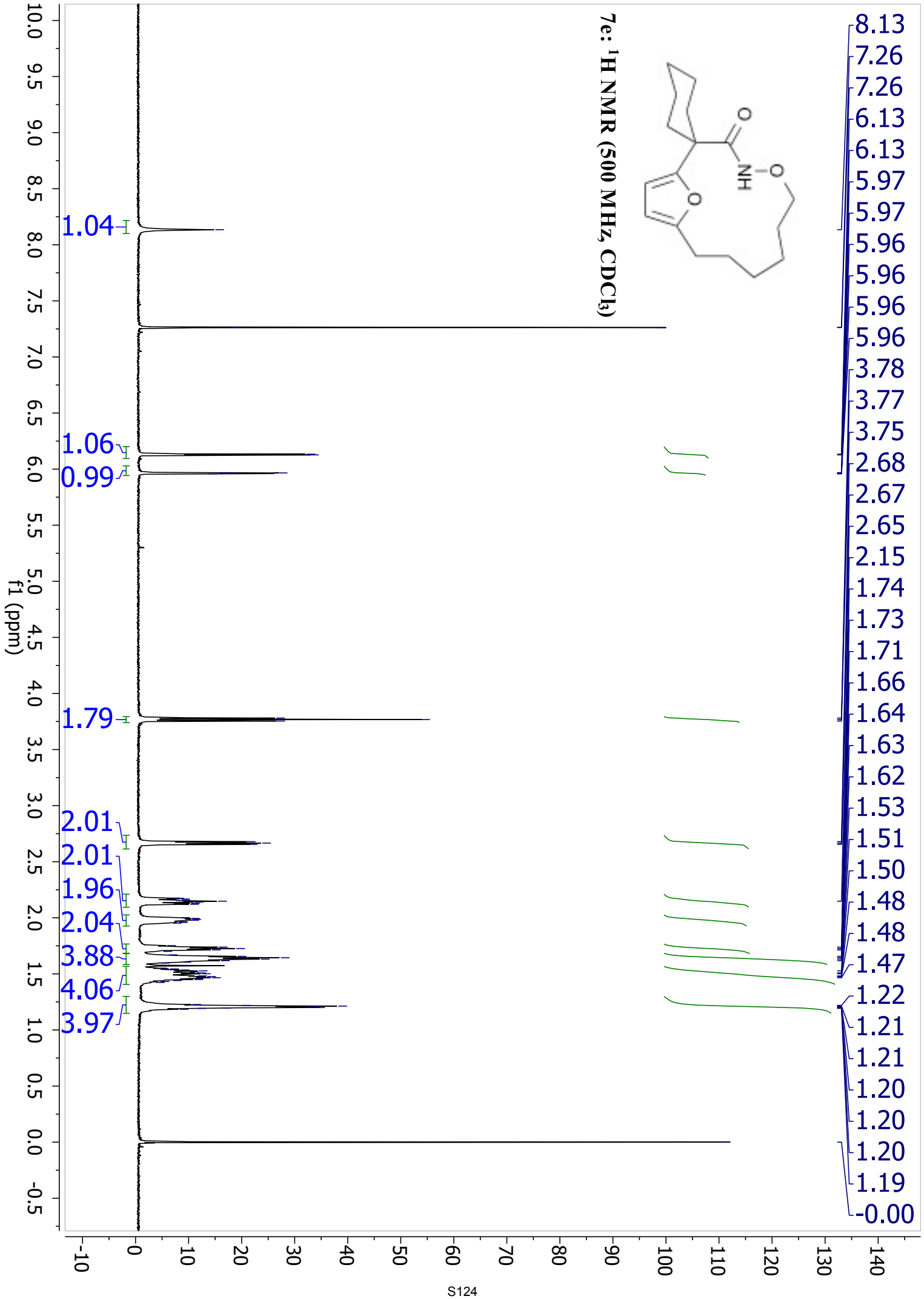

7b: ^{13}C NMR (126 MHz, CDCl$_3$)
O
NH
O
O
172.30
155.99
155.93
107.42
106.34
77.27
77.02
76.76
72.78
47.91
32.01
27.85
25.66
24.67
24.52
24.35
22.58
-0.00
f1 (ppm)

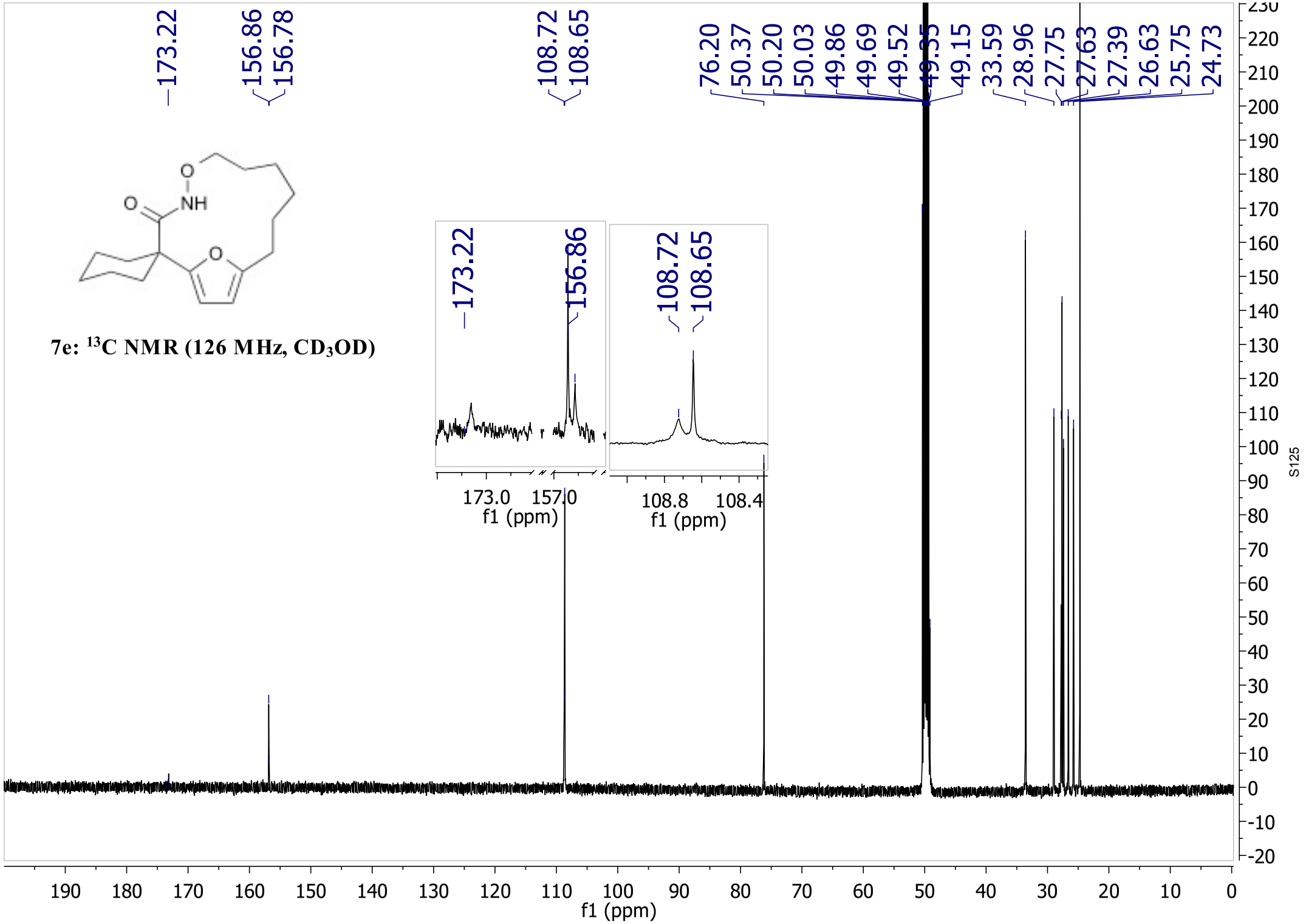

7c: ¹H NMR (500 MHz, CDCl₃)
NH
O
O
O
1.00
0.98
1.00
1.99
2.06
2.03
2.19
6.01
5.38
8.01
7.26
6.11
6.10
5.95
5.95
5.94
5.94
5.94
5.94
3.83
3.82
3.80
2.68
2.67
2.65
1.73
1.72
1.71
1.66
1.65
1.64
1.57
1.54
1.29
1.28
1.27
1.26
1.26
1.25
1.25
1.25
1.24
1.23
1.22
1.21
f1 (ppm)


7c: ^{13}C NMR (126 MHz, $CDCl_3$)
171.04
156.09
155.52
106.37
106.31
77.27
77.01
76.76
74.95
42.52
29.70
27.15
26.70
26.59
25.20
24.81
23.87
23.86
-0.00
f1 (ppm)

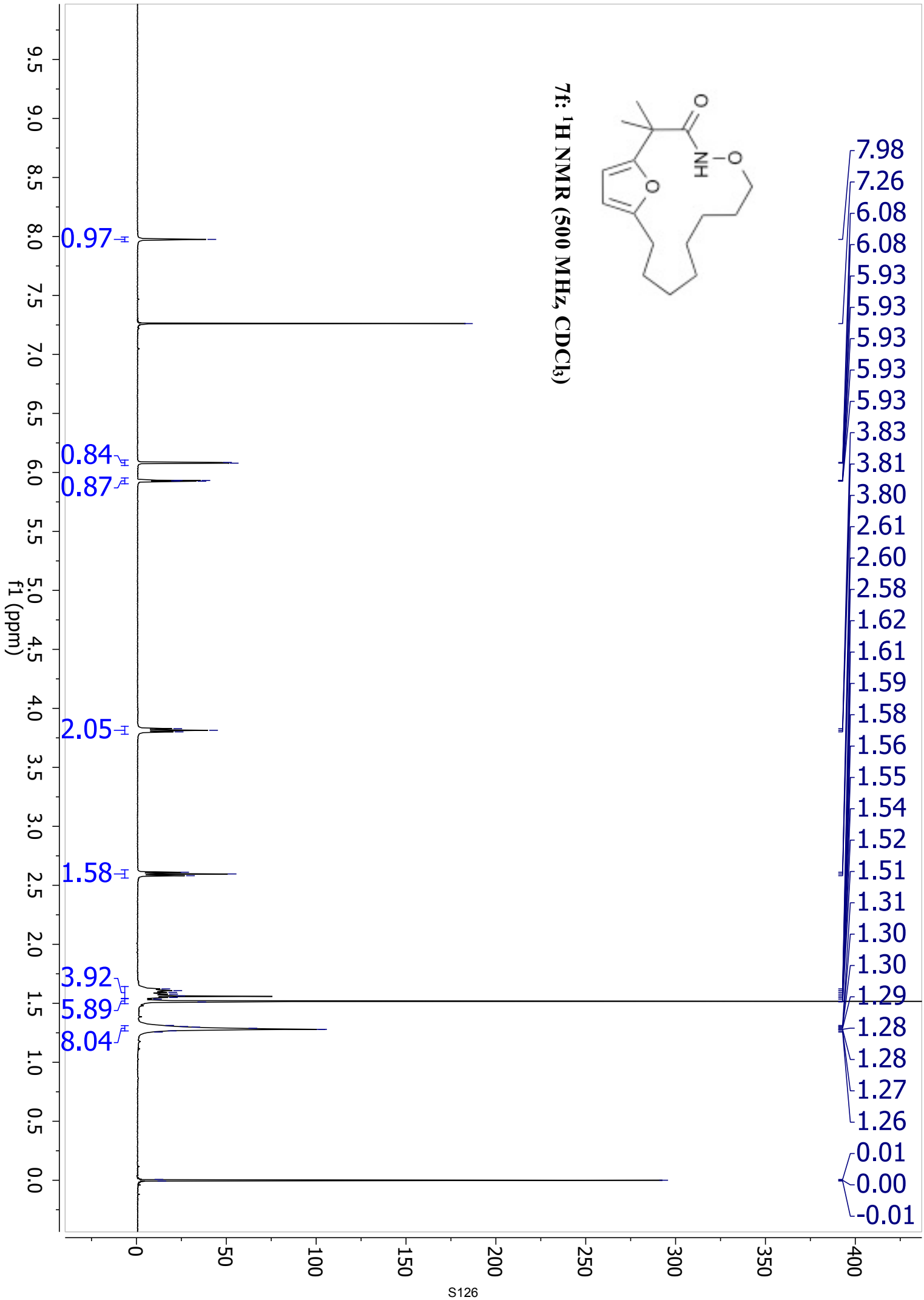

6.09 6.08 6.08 6.08 5.94 5.94 4.84 3.71 3.69 3.69 3.68 3.61 3.60 3.59 3.33 3.32 3.32 3.31 3.31 3.31 3.30 3.30 2.62 2.61 2.60 1.85 1.83 1.83 1.82 1.80 1.59 1.00 0.98 0.97 -0.00 -0.00
O
NH
O
O
Et
7d: ^{1}H NMR (500 MHz, CD$_3$OD)
7d: ^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
0.86 0.84 1.03 1.00 0.76 1.02 1.04 2.39 2.16 1.36 1.37 2.00 1.13 1.16 4.10
f1 (ppm)
S122

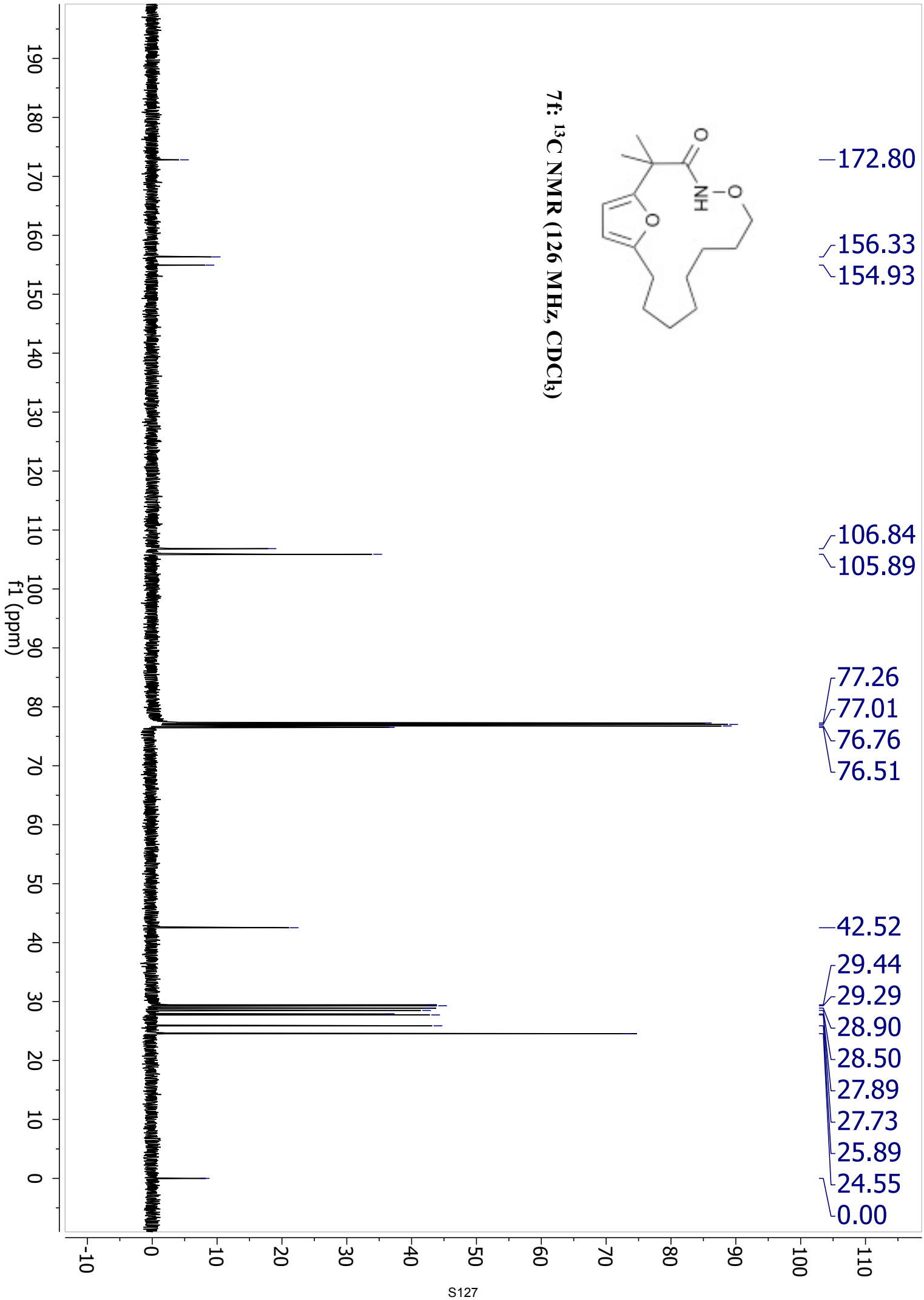

7d: ^{13}C NMR (126 MHz, CD_3OD)
Et
O
NH
O
O
170.94
156.62
152.88
108.68
76.04
50.37
50.20
50.03
49.86
49.69
49.52
49.35
47.66
28.65
27.35
26.85
26.54
25.41
22.50
13.11
f1 (ppm)

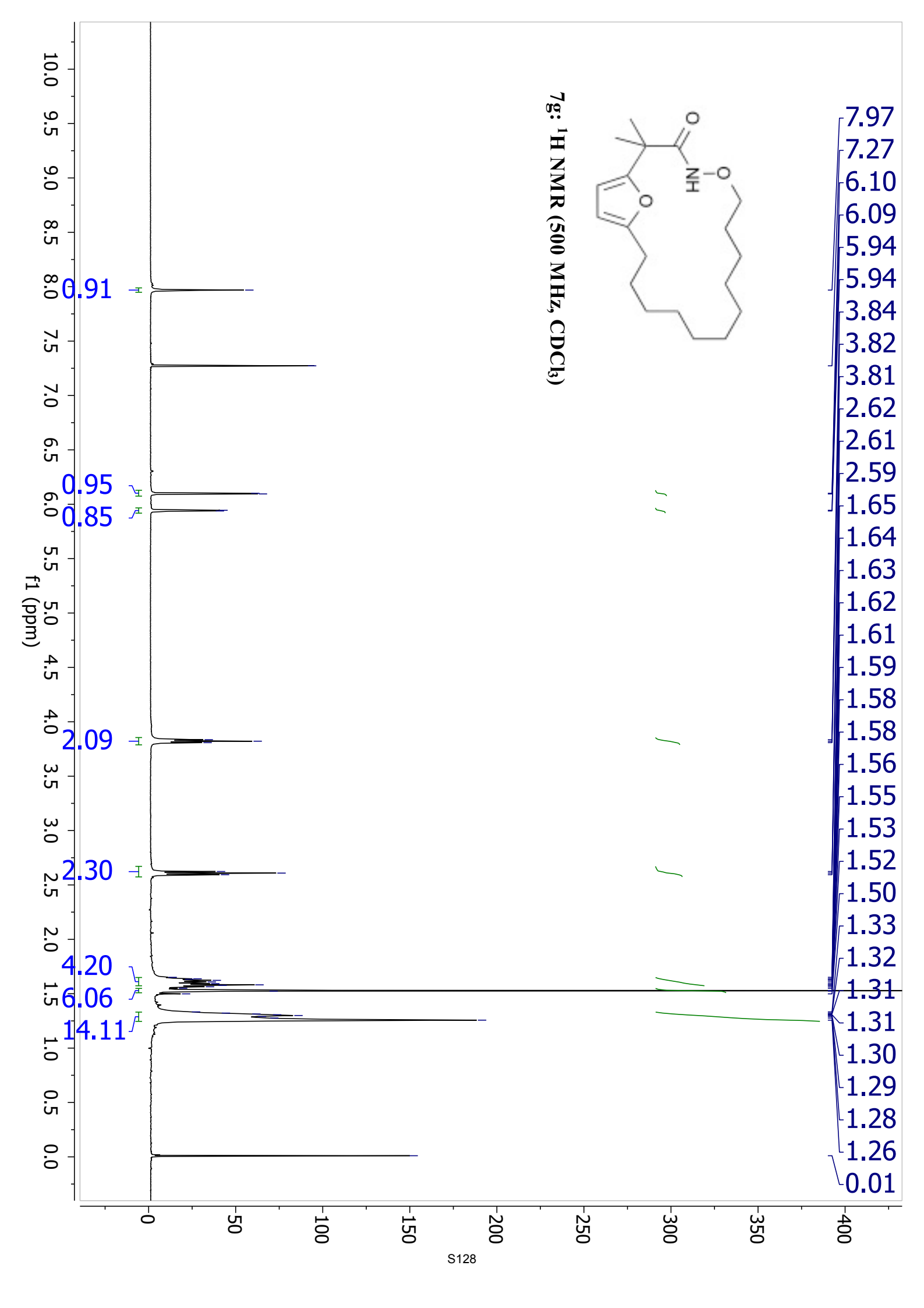

7e: ¹H NMR (500 MHz, CDCl₃)
O
NH
O
O
1.04
1.06
0.99
1.79
2.01
2.01
1.96
2.04
3.88
4.06
3.97
8.13
7.26
7.26
6.13
6.13
5.97
5.97
5.96
5.96
5.96
5.96
3.78
3.77
3.75
2.68
2.67
2.65
2.15
1.74
1.73
1.71
1.66
1.64
1.63
1.62
1.53
1.51
1.50
1.48
1.48
1.47
1.22
1.21
1.21
1.20
1.20
1.20
1.19
-0.00
f1 (ppm)

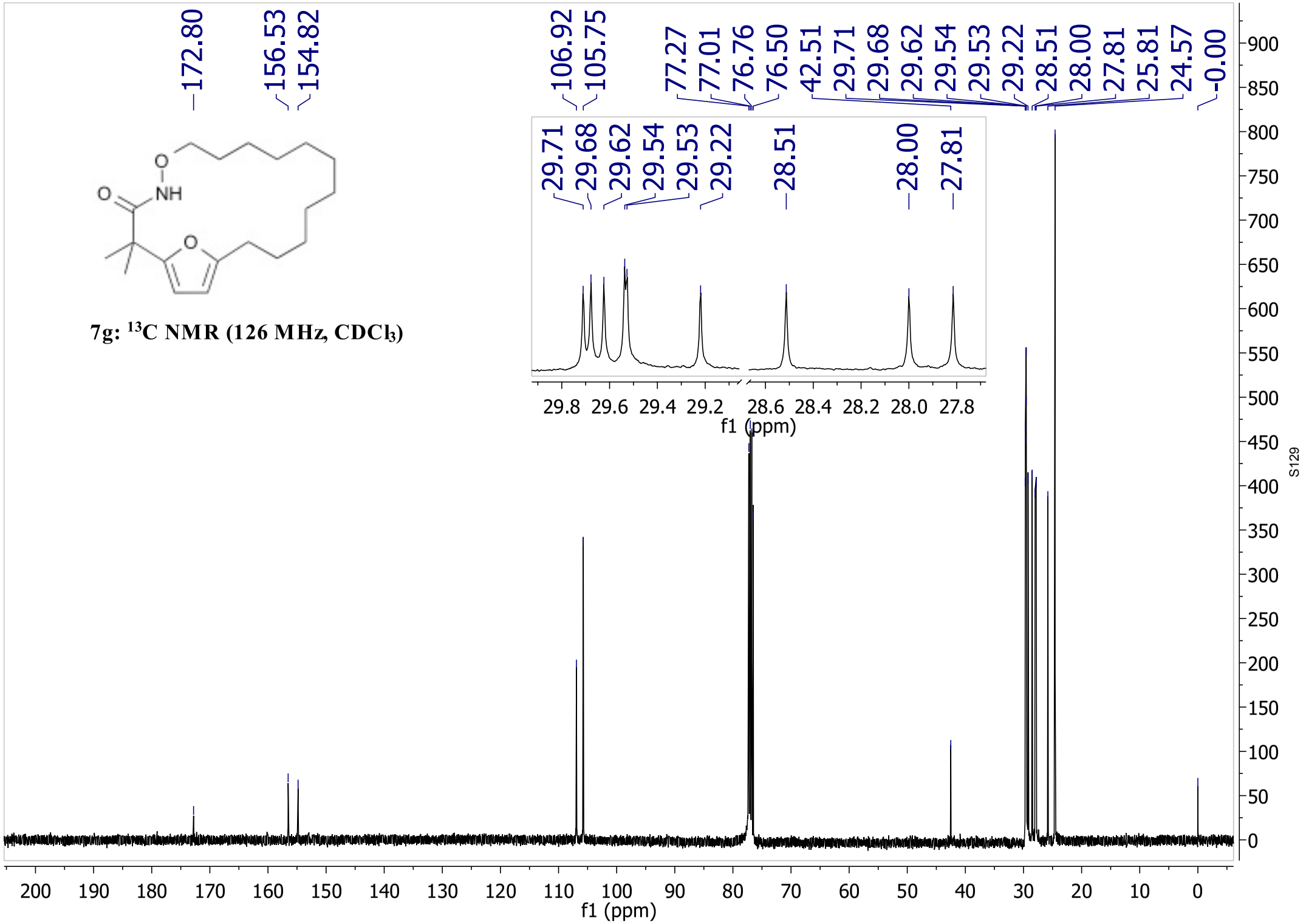


7e: ^{13}C NMR (126 MHz, CD_3OD)

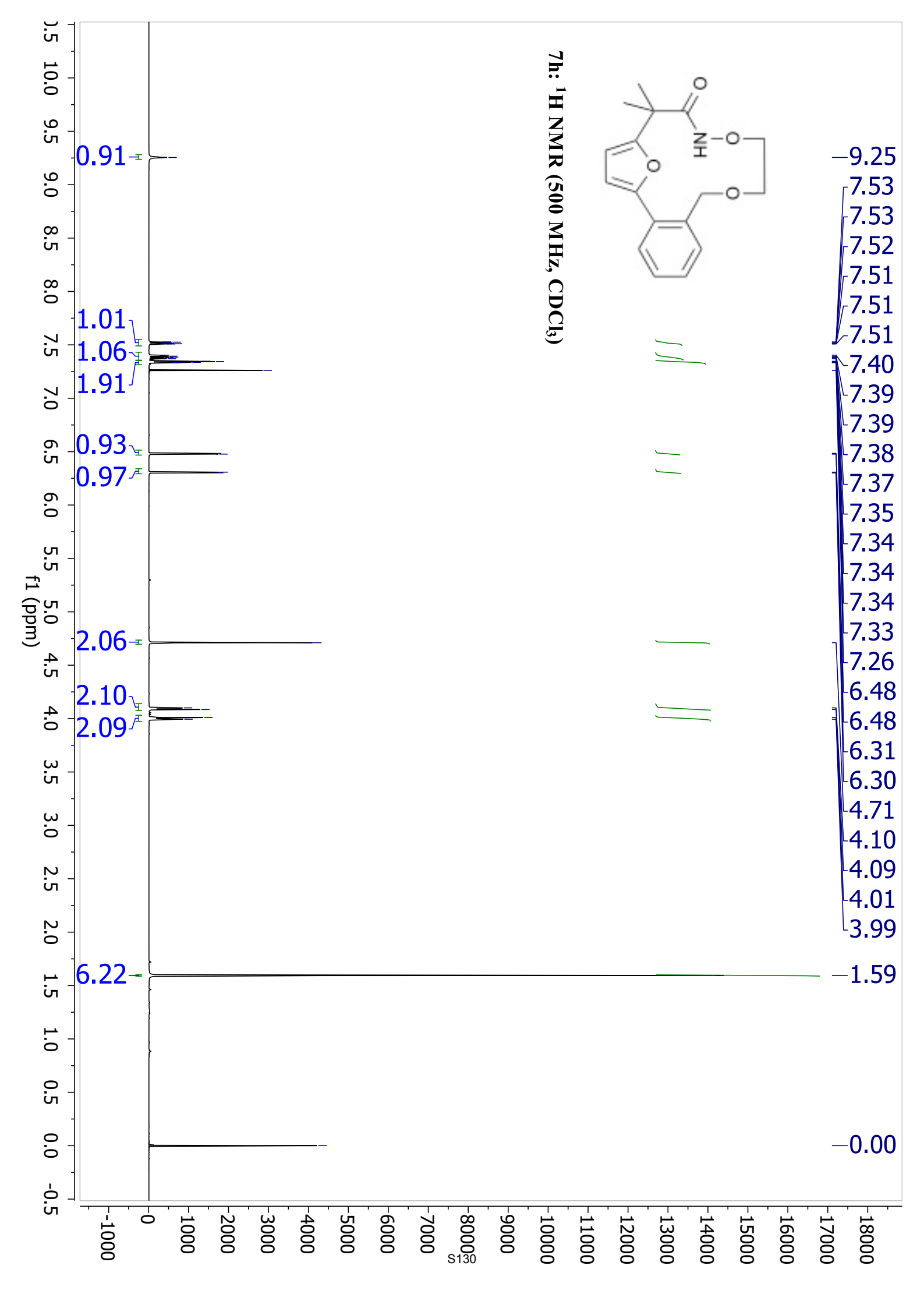

7f: ^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
0.97
0.84
0.87
2.05
1.58
3.92
5.89
8.04
7.98
7.26
6.08
6.08
5.93
5.93
5.93
5.93
5.93
5.93
3.83
3.81
3.80
2.61
2.60
2.58
1.62
1.61
1.59
1.58
1.56
1.55
1.54
1.52
1.51
1.31
1.30
1.30
1.29
1.28
1.28
1.27
1.26
0.01
0.00
-0.01

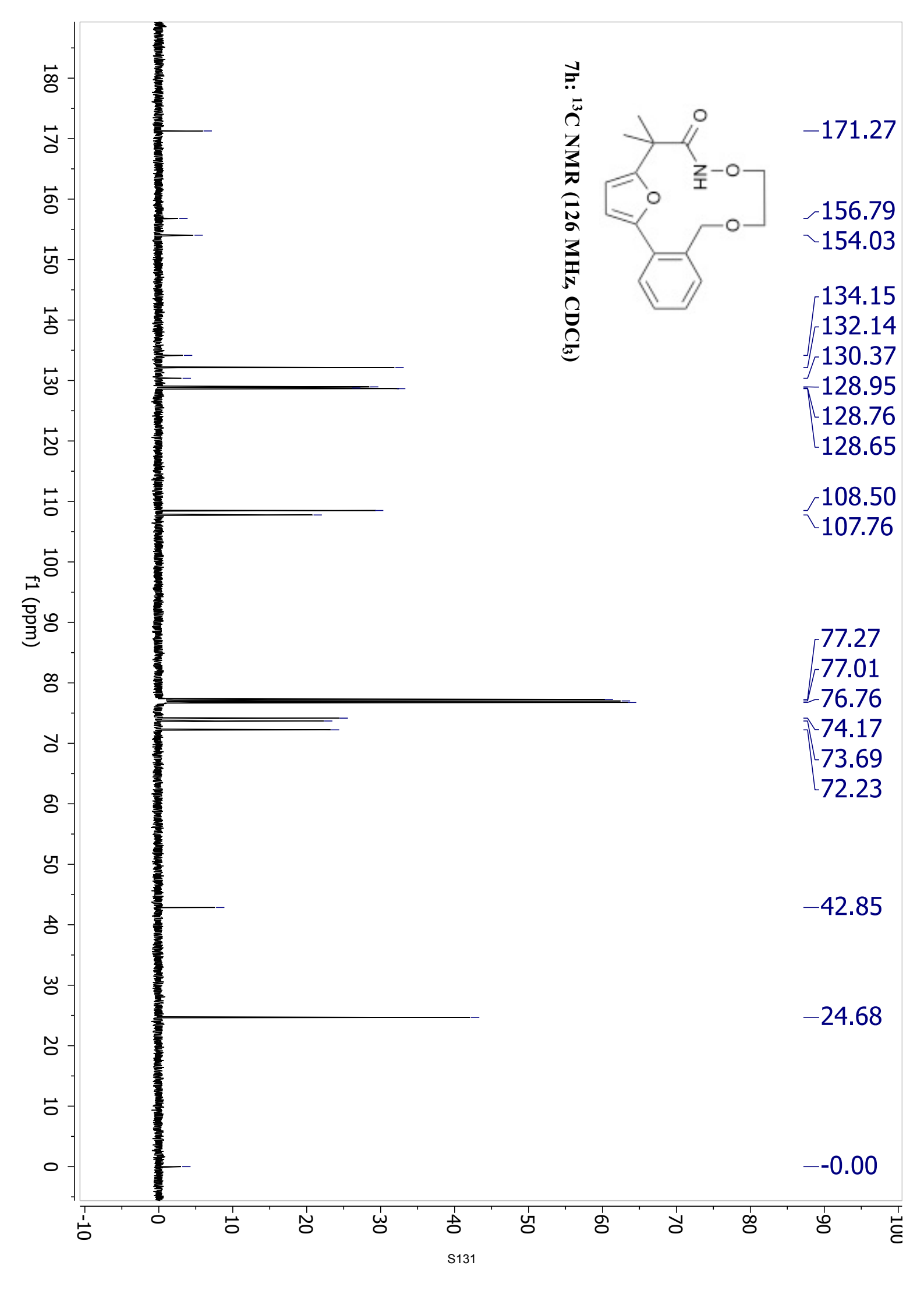

7f: ^{13}C NMR (126 MHz, CDCl$_3$)
O
NH
O
O
172.80
156.33
154.93
106.84
105.89
77.26
77.01
76.76
76.51
42.52
29.44
29.29
28.90
28.50
27.89
27.73
25.89
24.55
0.00
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-10 0 10 20 30 40 50 60 70 80 90 100 110

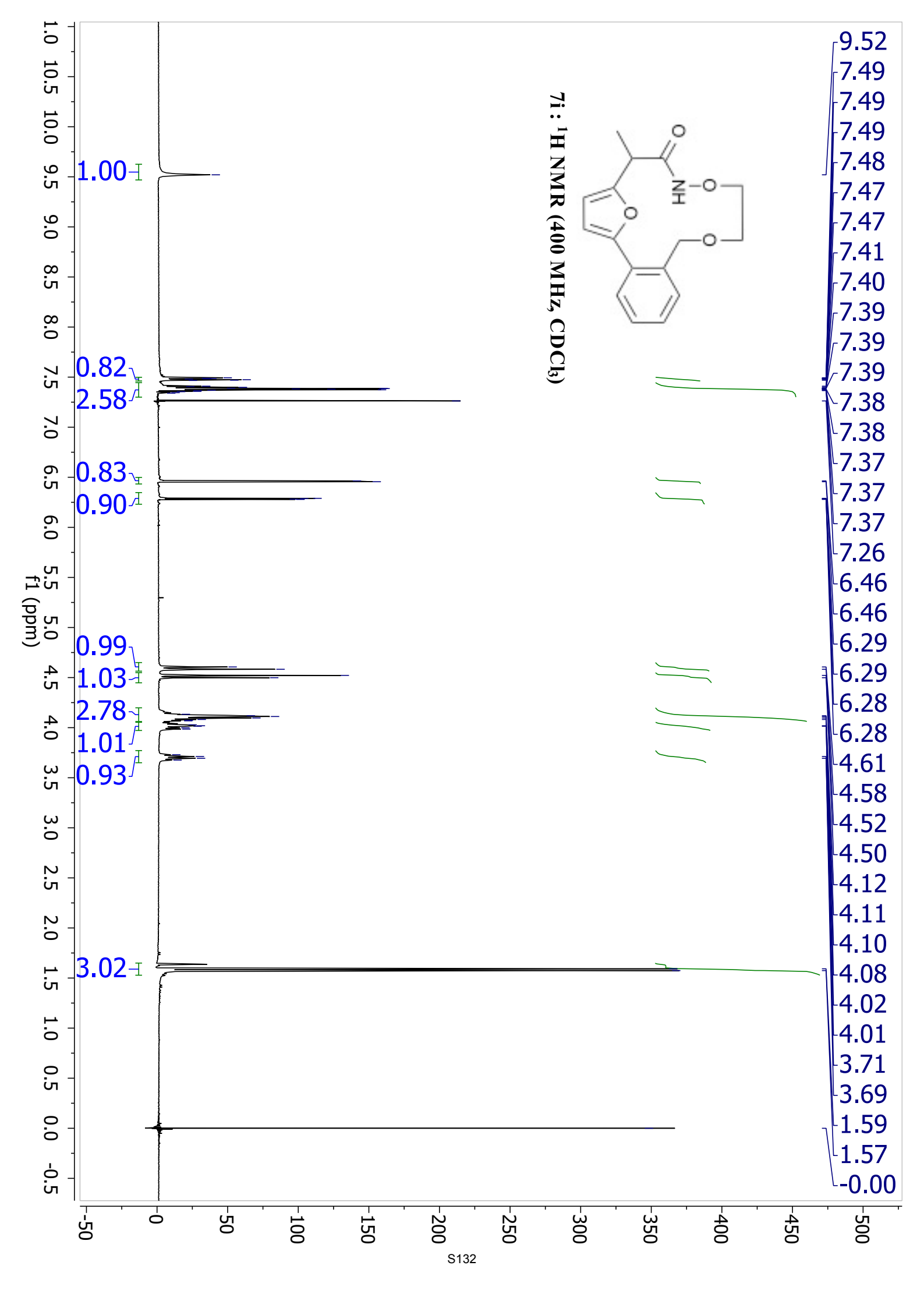

7g: ^{1}H NMR (500 MHz, CDCl$_3$)
O
NH
O
O
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.91
0.95
0.85
2.09
2.30
4.20
6.06
14.11
7.97
7.27
6.10
6.09
5.94
5.94
3.84
3.82
3.81
2.62
2.61
2.59
1.65
1.64
1.63
1.62
1.61
1.59
1.58
1.58
1.56
1.55
1.53
1.52
1.50
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.26
0.01
0
50
100
150
200
250
300
350
400

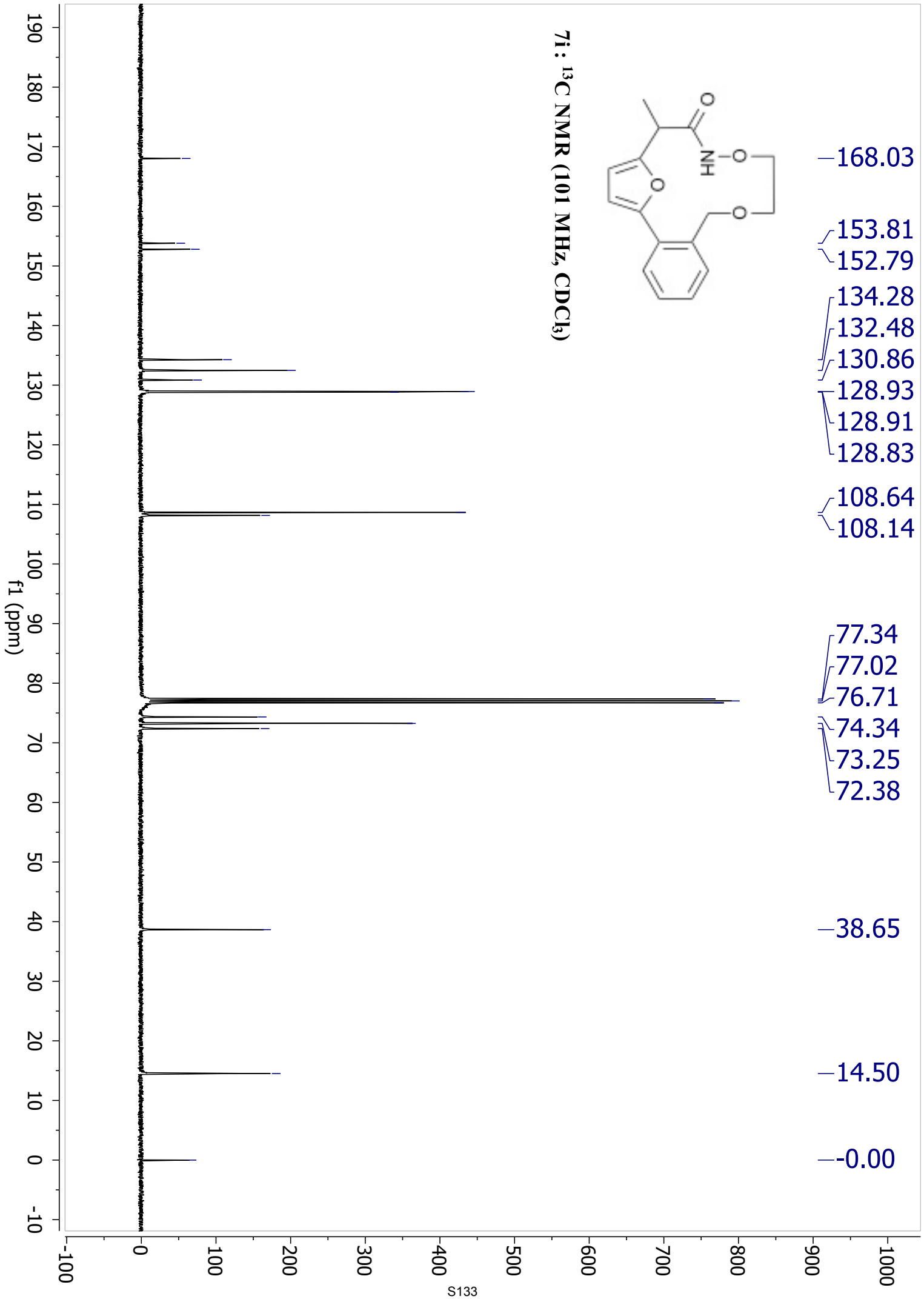


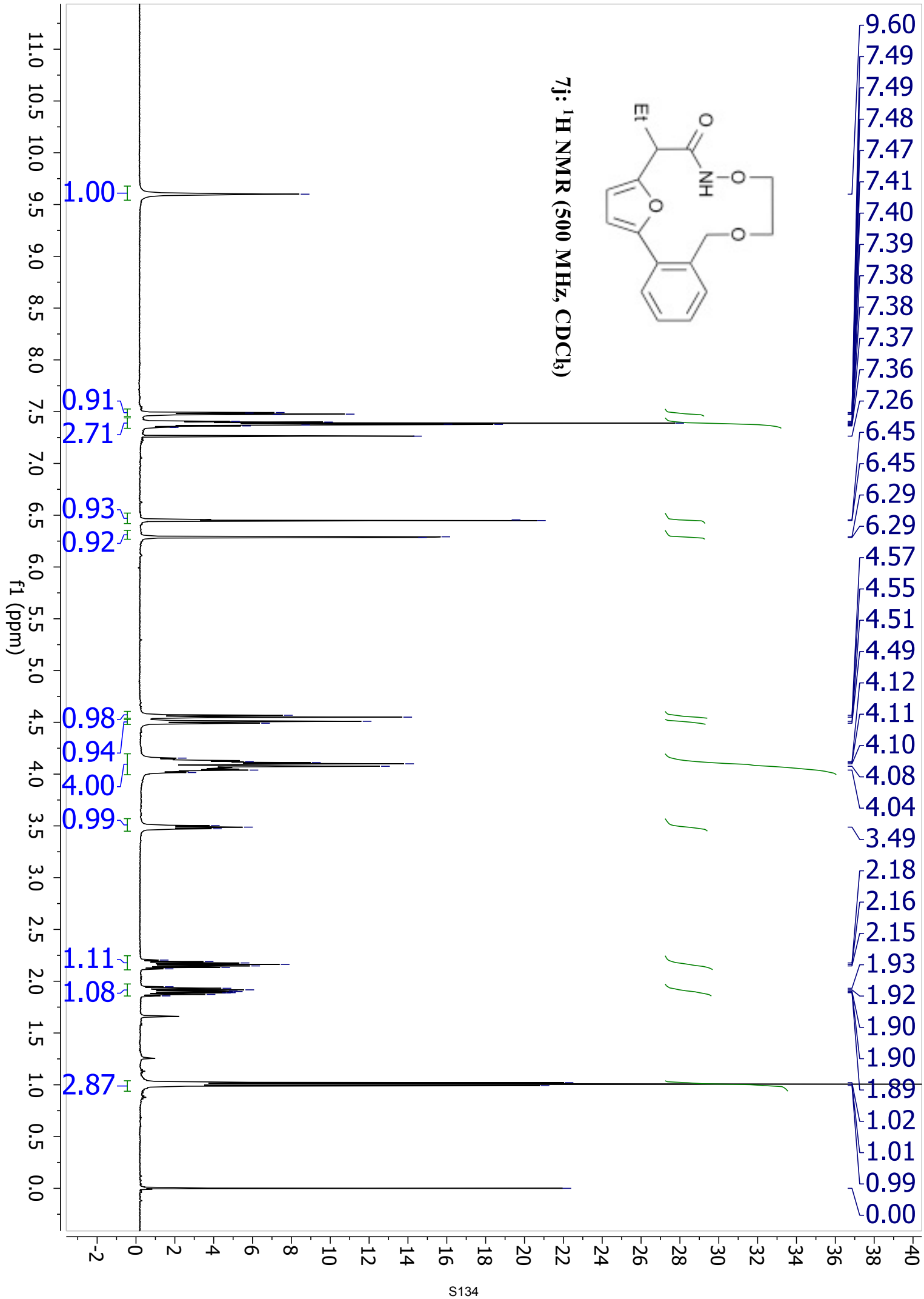
7g: ^{13}C NMR (126 MHz, $CDCl_3$)

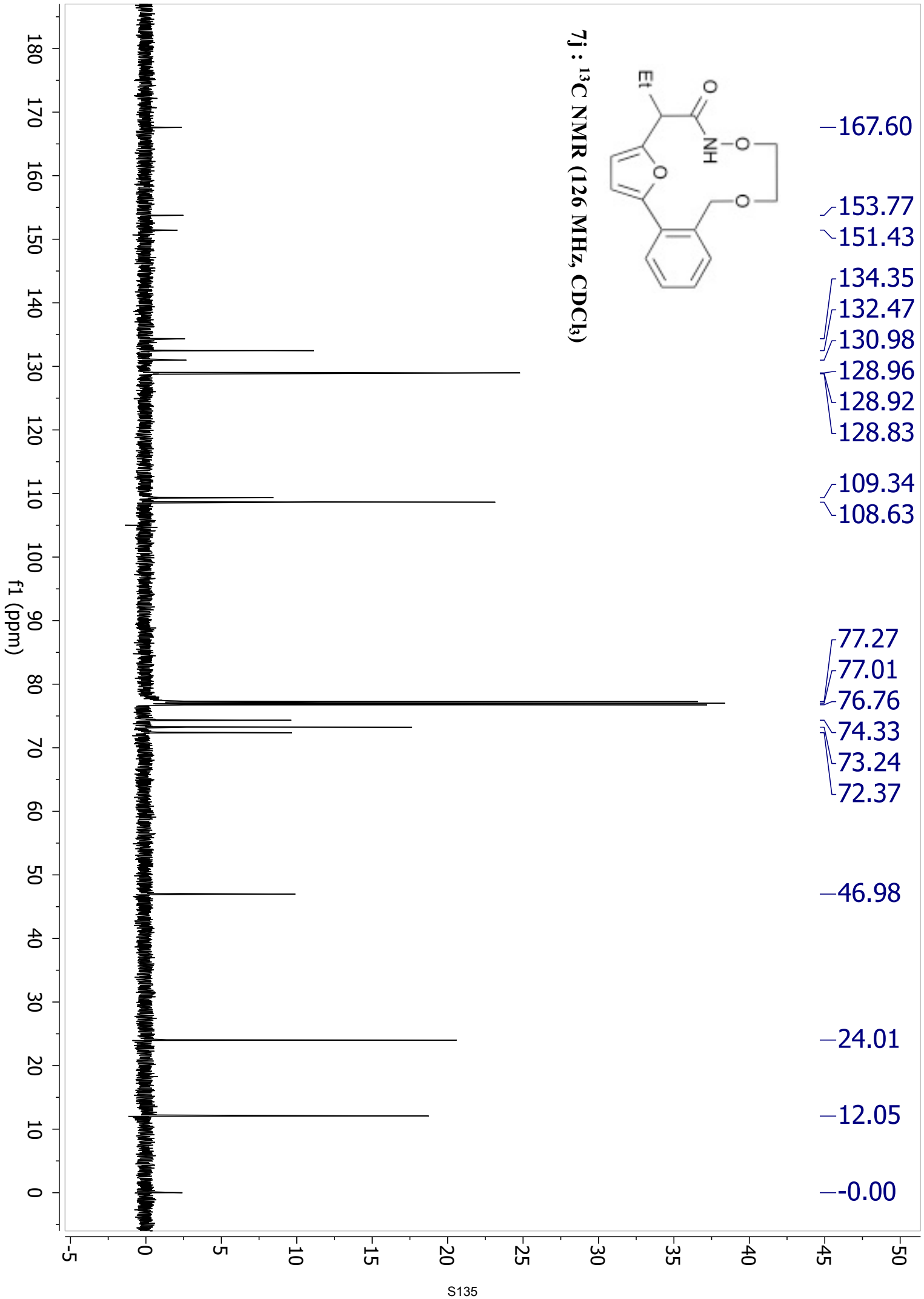

7h: ^{1}H NMR (500 MHz, CDCl$_3$)
NH
O
O
O
O
0.91
1.01
1.06
1.91
0.93
0.97
2.06
2.10
2.09
6.22
9.25
7.53
7.53
7.52
7.51
7.51
7.51
7.40
7.39
7.39
7.38
7.37
7.35
7.34
7.34
7.34
7.33
7.26
6.48
6.48
6.31
6.30
4.71
4.10
4.09
4.01
3.99
1.59
0.00
f1 (ppm)
S130

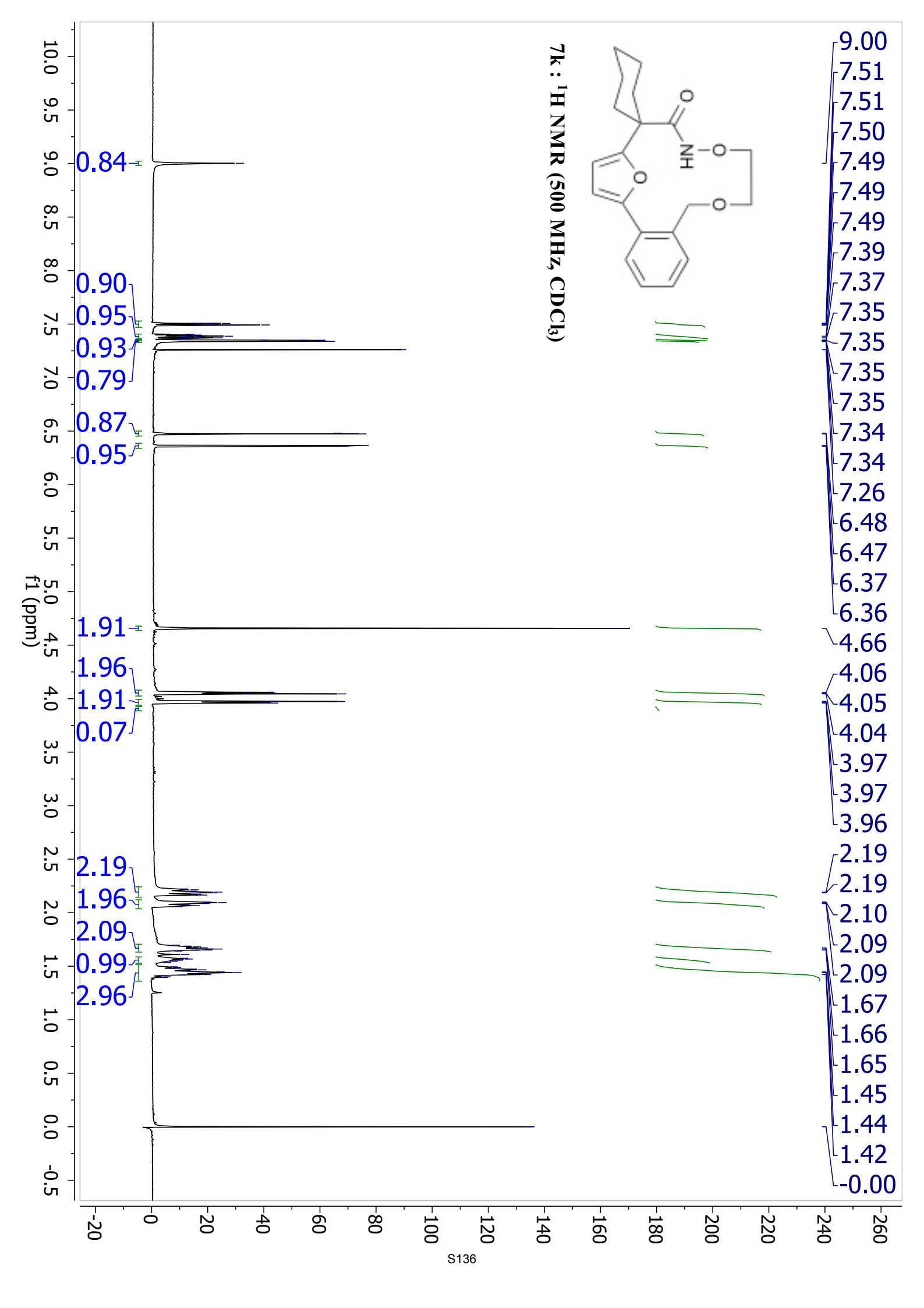

7h: ^{13}C NMR (126 MHz, CDCl$_3$)
171.27
156.79
154.03
134.15
132.14
130.37
128.95
128.76
128.65
108.50
107.76
77.27
77.01
76.76
74.17
73.69
72.23
42.85
24.68
-0.00
f1 (ppm)

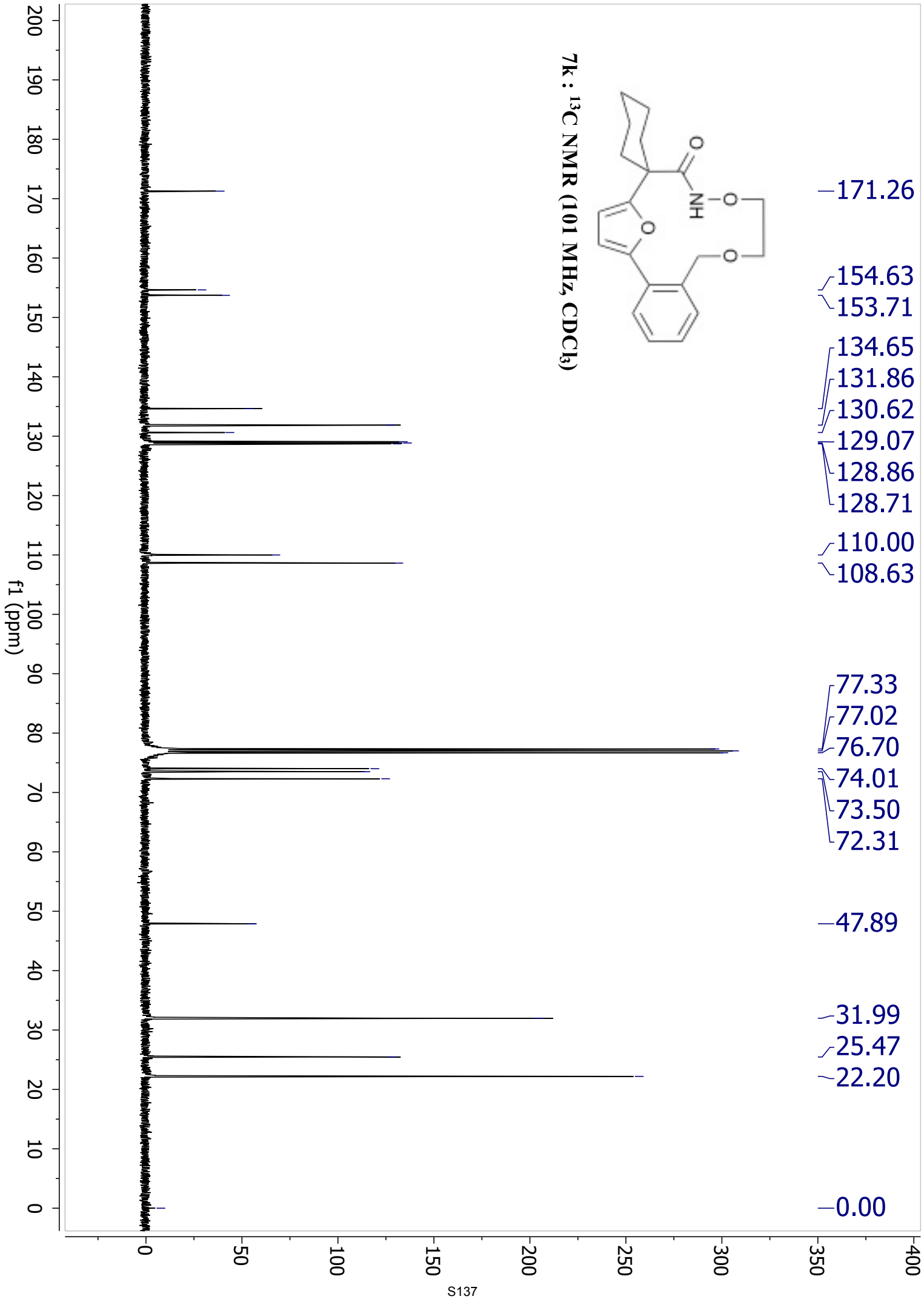

7i : ¹H NMR (400 MHz, CDCl₃)
NH
O
O
O
O
1.00
0.82
2.58
0.83
0.90
0.99
1.03
2.78
1.01
0.93
3.02
f1 (ppm)
9.52
7.49
7.49
7.49
7.48
7.47
7.47
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.26
6.46
6.46
6.29
6.29
6.28
6.28
4.61
4.58
4.52
4.50
4.12
4.11
4.10
4.08
4.02
4.01
3.71
3.69
1.59
1.57
-0.00

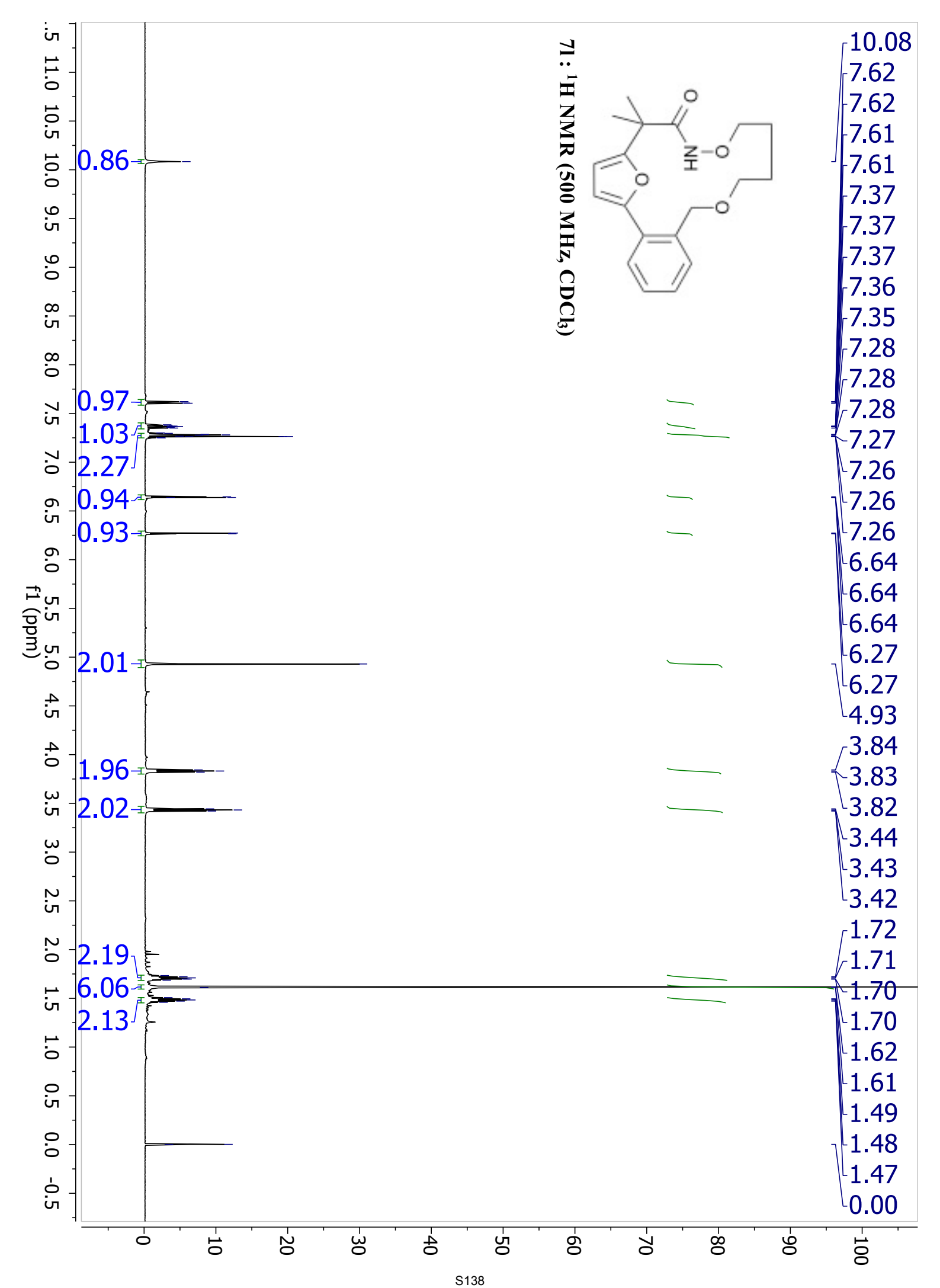

7i : ^{13}C NMR (101 MHz, CDCl$_3$)
168.03
153.81
152.79
134.28
132.48
130.86
128.93
128.91
128.83
108.64
108.14
77.34
77.02
76.71
74.34
73.25
72.38
38.65
14.50
-0.00
f1 (ppm)


7j: ¹H NMR (500 MHz, CDCl₃)
Et
O
NH
O
O
O
1.00
0.91
2.71
0.93
0.92
0.98
0.94
4.00
0.99
1.11
1.08
2.87
9.60
7.49
7.49
7.48
7.47
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.26
6.45
6.45
6.29
6.29
4.57
4.55
4.51
4.49
4.12
4.11
4.10
4.08
4.04
3.49
2.18
2.16
2.15
1.93
1.92
1.90
1.90
1.89
1.02
1.01
0.99
0.00
f1 (ppm)

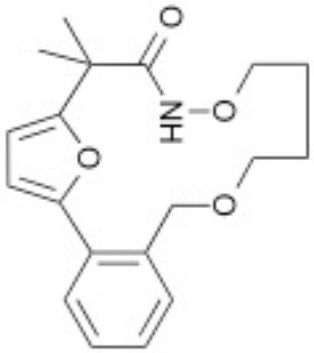

7j : ^{13}C NMR (126 MHz, CDCl$_3$)
Et
O
NH
O
O
O
167.60
153.77
151.43
134.35
132.47
130.98
128.96
128.92
128.83
109.34
108.63
77.27
77.01
76.76
74.33
73.24
72.37
46.98
24.01
12.05
-0.00
f1 (ppm)


7k : ¹H NMR (500 MHz, CDCl₃)
f1 (ppm)
0.84
0.90
0.95
0.93
0.79
0.87
0.95
1.91
1.96
1.91
0.07
2.19
1.96
2.09
0.99
2.96
9.00
7.51
7.51
7.50
7.49
7.49
7.49
7.39
7.37
7.35
7.35
7.35
7.35
7.34
7.34
7.26
6.48
6.47
6.37
6.36
4.66
4.06
4.05
4.04
3.97
3.97
3.96
2.19
2.19
2.10
2.09
2.09
1.67
1.66
1.65
1.45
1.44
1.42
-0.00


7k : ^{13}C NMR (101 MHz, $CDCl_3$)
171.26
154.63
153.71
134.65
131.86
130.62
129.07
128.86
128.71
110.00
108.63
77.33
77.02
76.70
74.01
73.50
72.31
47.89
31.99
25.47
22.20
0.00
f1 (ppm)

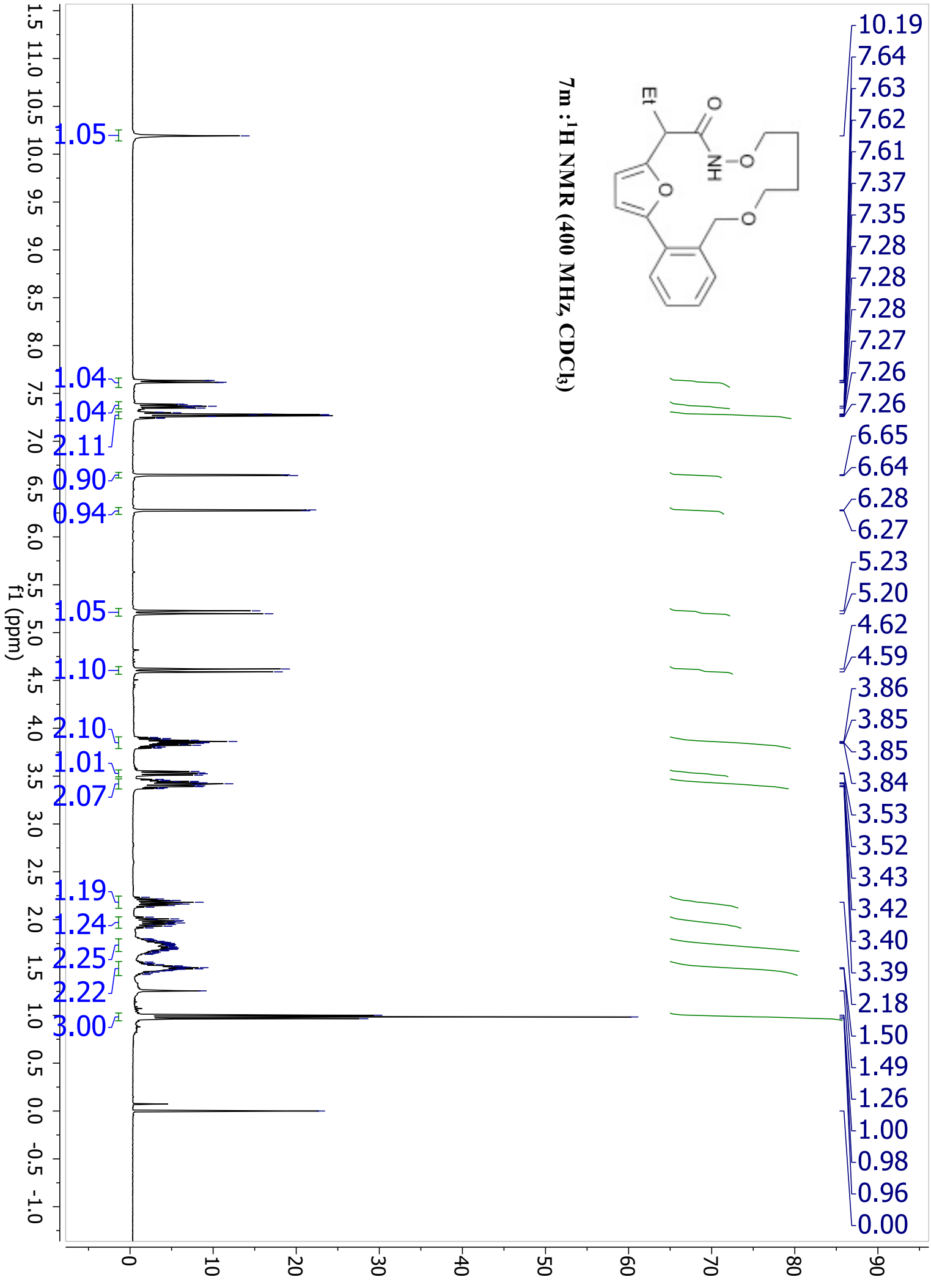

7l : ¹H NMR (500 MHz, CDCl₃)
f1 (ppm)
0.86
0.97
1.03
2.27
0.94
0.93
2.01
1.96
2.02
2.19
6.06
2.13
10.08
7.62
7.62
7.61
7.61
7.37
7.37
7.37
7.36
7.35
7.28
7.28
7.28
7.27
7.26
7.26
7.26
6.64
6.64
6.64
6.27
6.27
4.93
3.84
3.83
3.82
3.44
3.43
3.42
1.72
1.71
1.70
1.70
1.62
1.61
1.49
1.48
1.47
0.00

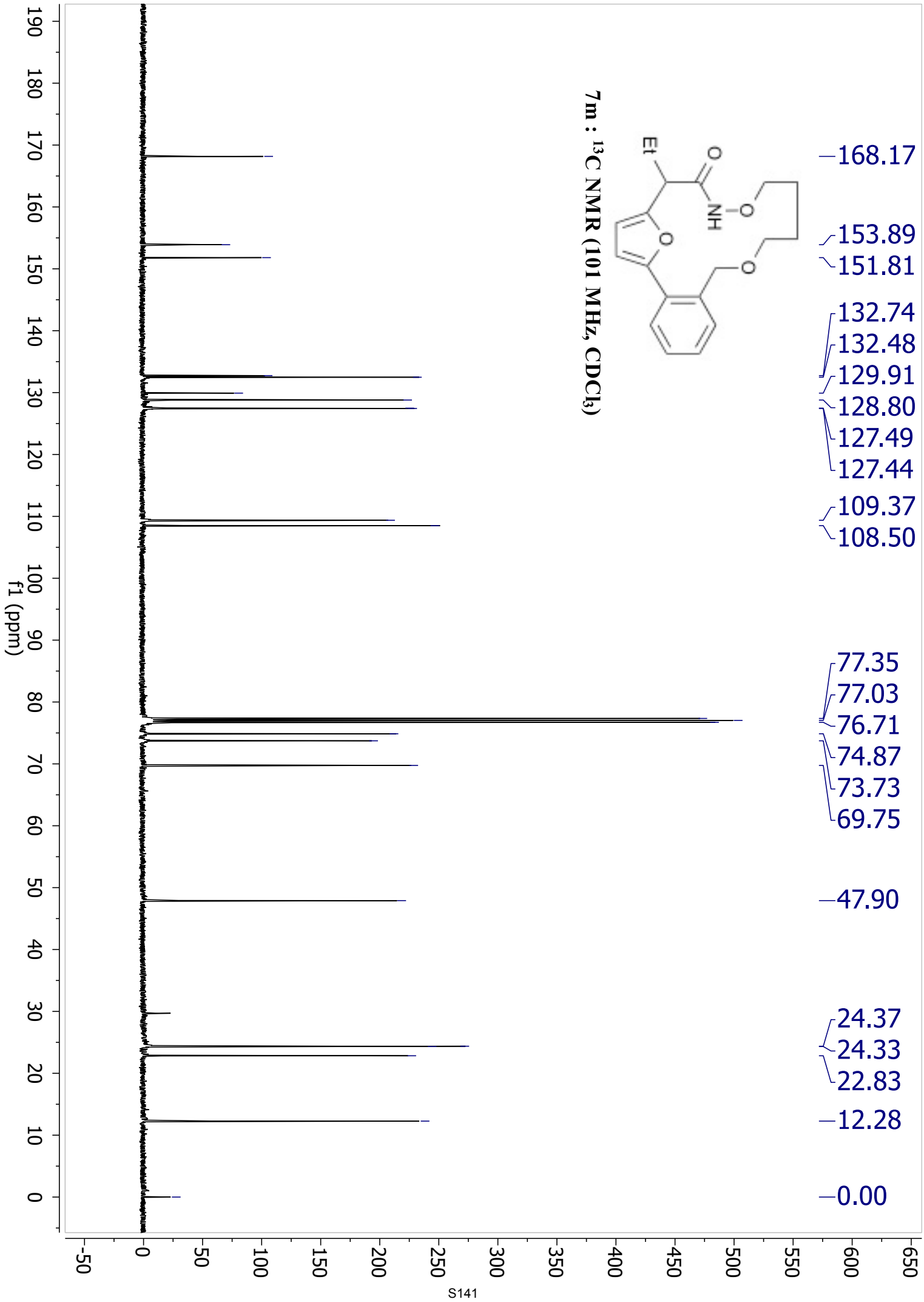
7l : ^{13}C NMR (101 MHz, $CDCl_3$)

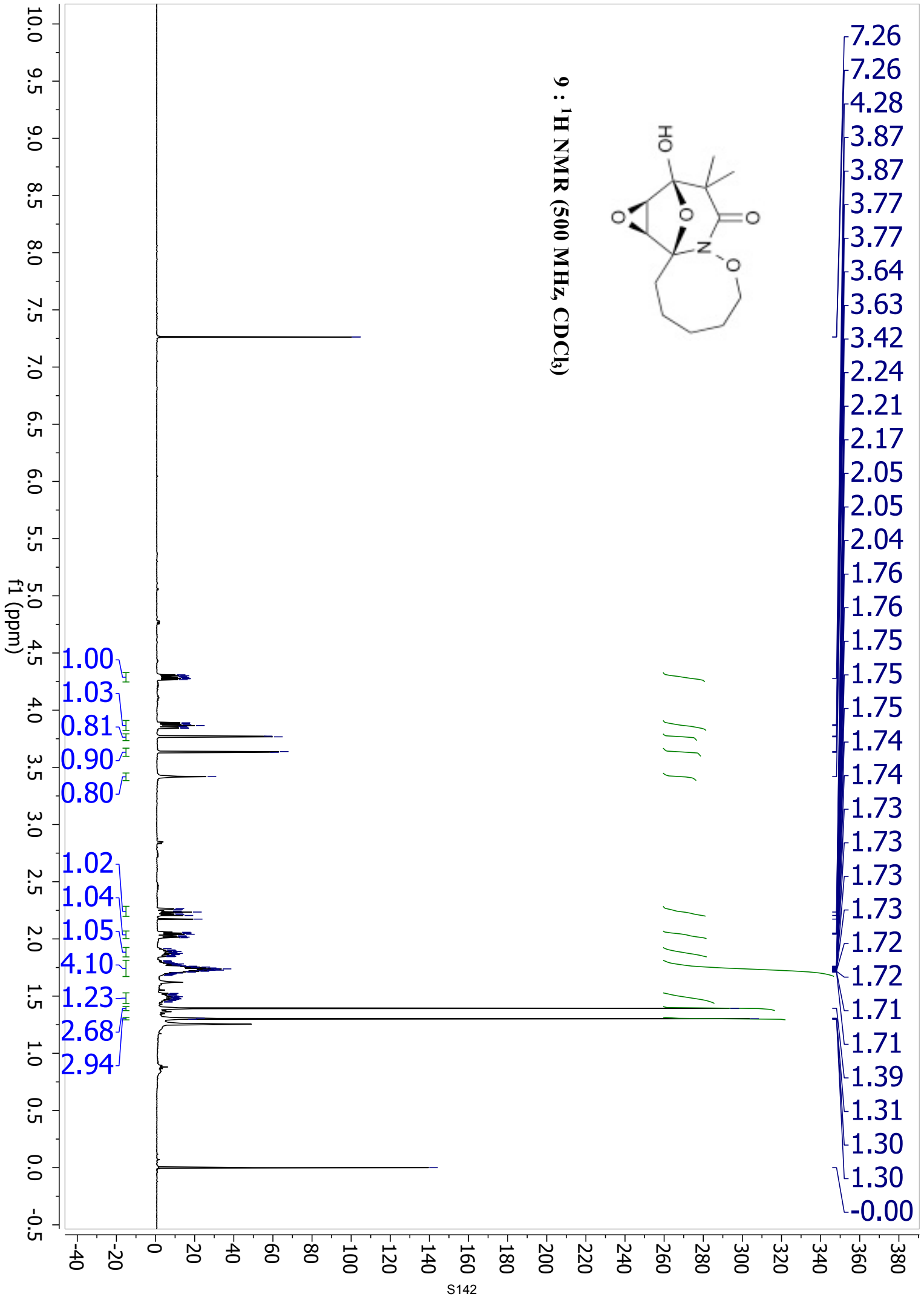


171.19
157.36
153.78
133.00
132.29
129.91
128.77
127.65
127.55
108.58
107.32
77.34
77.02
76.70
74.99
73.75
69.92
42.36
24.66
24.20
22.92
0.00

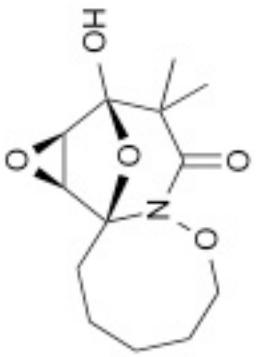
f1 (ppm)


7m : ^{1}H NMR (400 MHz, $CDCl_3$)
Et
O
NH
O
O
O
1.05
1.04
1.04
2.11
0.90
0.94
1.05
1.10
2.10
1.01
2.07
1.19
1.24
2.25
2.22
3.00
10.19
7.64
7.63
7.62
7.61
7.37
7.35
7.28
7.28
7.28
7.27
7.26
7.26
6.65
6.64
6.28
6.27
5.23
5.20
4.62
4.59
3.86
3.85
3.85
3.84
3.53
3.52
3.43
3.42
3.40
3.39
2.18
1.50
1.49
1.26
1.00
0.98
0.96
0.00
f1 (ppm)


7m : ^{13}C NMR (101 MHz, CDCl$_3$)
Et
O
NH
O
O
O
168.17
153.89
151.81
132.74
132.48
129.91
128.80
127.49
127.44
109.37
108.50
77.35
77.03
76.71
74.87
73.73
69.75
47.90
24.37
24.33
22.83
12.28
0.00
f1 (ppm)

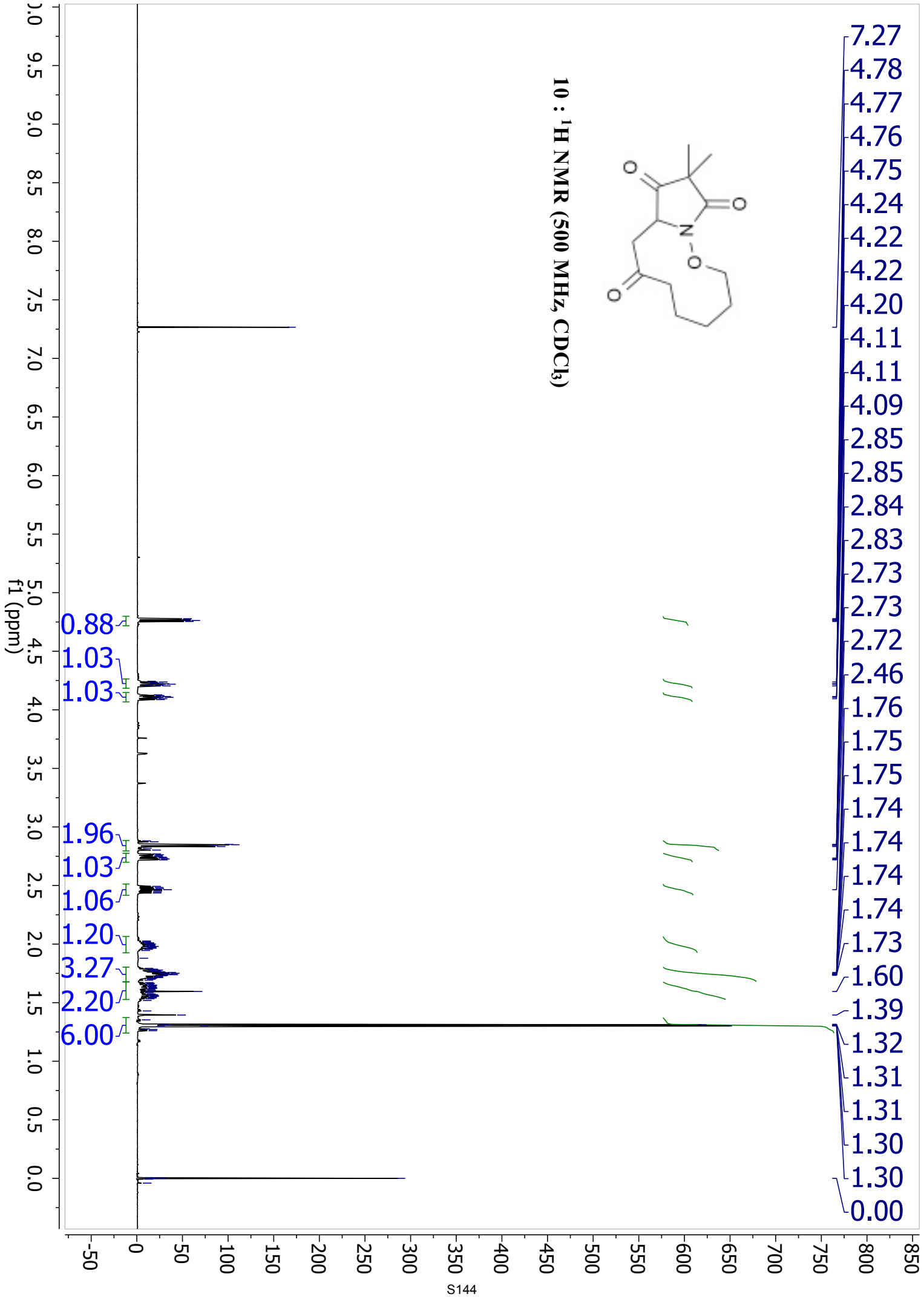

9 : ¹H NMR (500 MHz, CDCl₃)
HO
O
O
O
N
O
f1 (ppm)
1.00
1.03
0.81
0.90
0.80
1.02
1.04
1.05
4.10
1.23
2.68
2.94
7.26
7.26
4.28
3.87
3.87
3.77
3.77
3.64
3.63
3.42
2.24
2.21
2.17
2.05
2.05
2.04
1.76
1.76
1.75
1.75
1.75
1.74
1.74
1.73
1.73
1.73
1.73
1.72
1.72
1.71
1.71
1.39
1.31
1.30
1.30
-0.00

9 : ^{13}C NMR (126 MHz, $CDCl_3$)

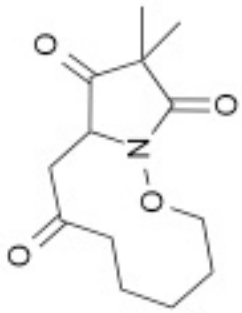


174.08
102.79
92.36
77.27
77.01
76.76
75.18
57.97
52.48
49.67
28.62
27.46
26.06
22.32
21.63
17.96
0.00

f1 (ppm)

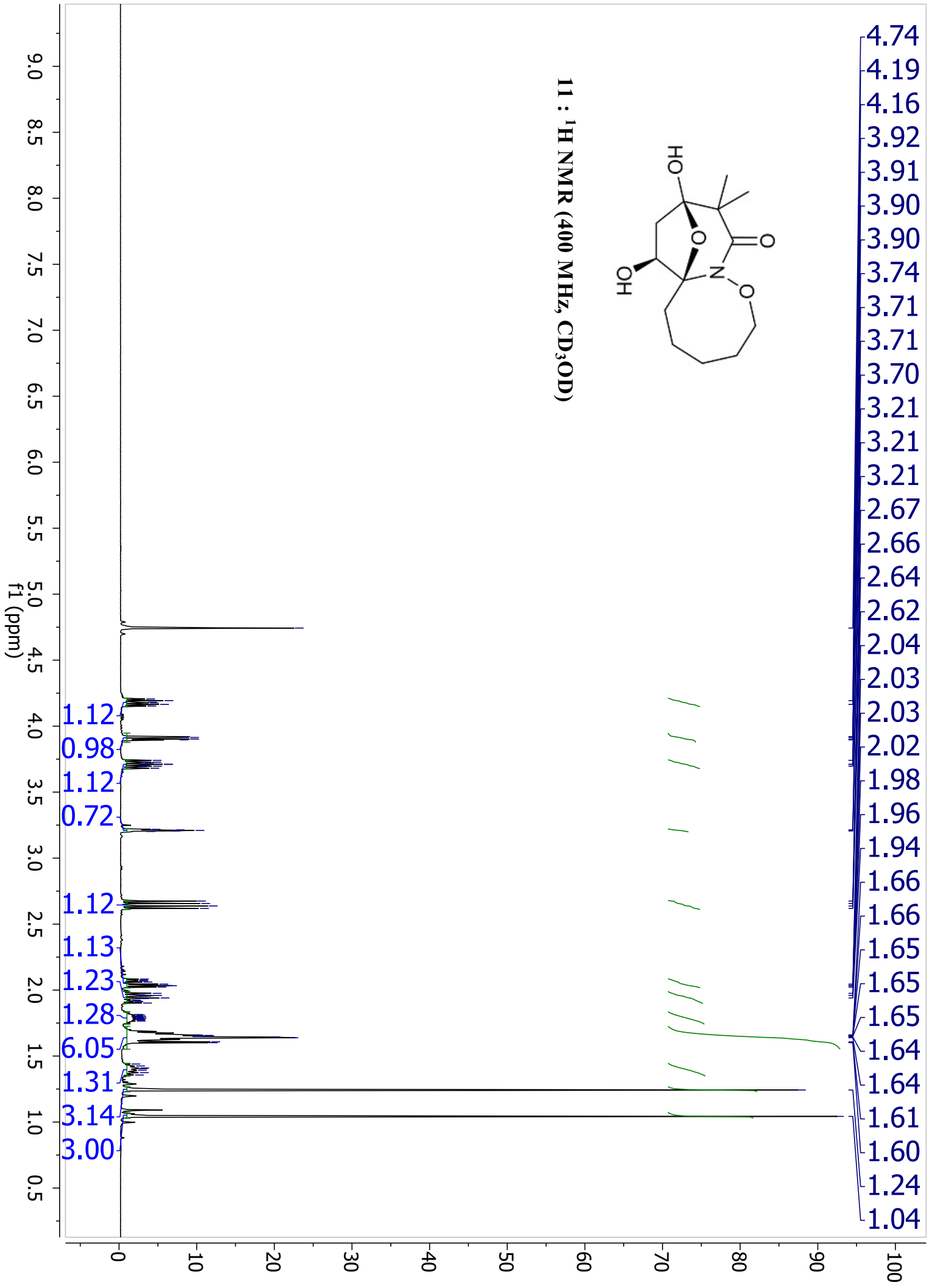

10 : ¹H NMR (500 MHz, CDCl₃)
f1 (ppm)
0.88
1.03
1.03
1.96
1.03
1.06
1.20
3.27
2.20
6.00
7.27
4.78
4.77
4.76
4.75
4.24
4.22
4.22
4.20
4.11
4.11
4.09
2.85
2.85
2.84
2.83
2.73
2.73
2.72
2.46
1.76
1.75
1.75
1.74
1.74
1.74
1.74
1.74
1.73
1.60
1.39
1.32
1.31
1.31
1.30
1.30
0.00

10 : ^{13}C NMR (126 MHz, $CDCl_3$)

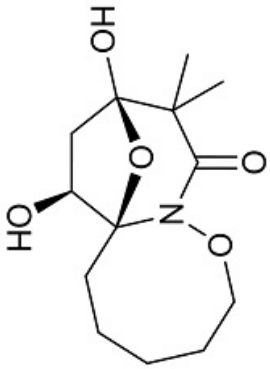


208.90
208.16
172.44
77.27
77.01
76.76
76.12
63.54
48.44
43.20
41.69
26.68
22.77
22.55
21.83
19.64
-0.00

f1 (ppm)

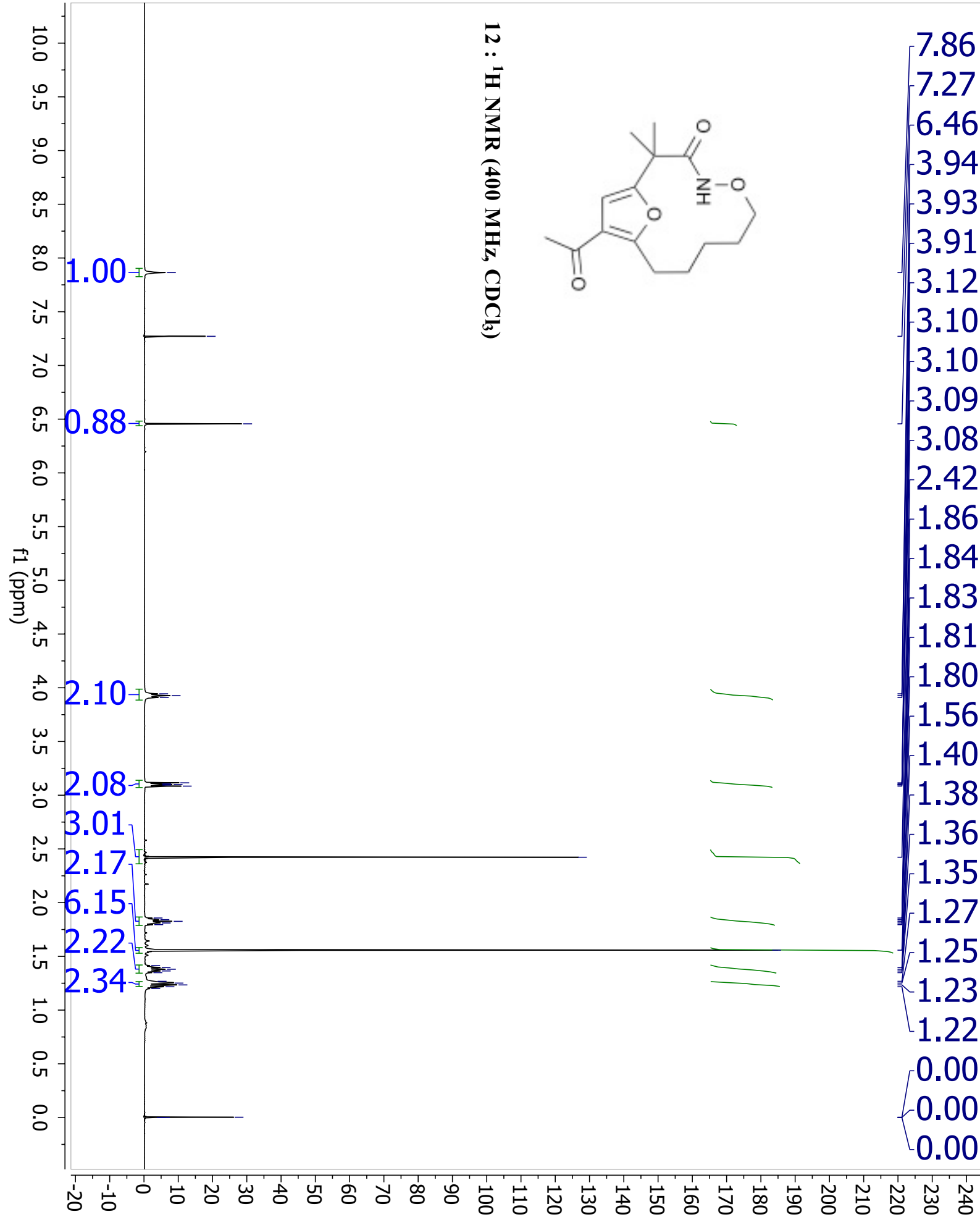

11 : ¹H NMR (400 MHz, CD₃OD)
HO
O
O
N
O
OH
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.12
0.98
1.12
0.72
1.12
1.13
1.23
1.28
6.05
1.31
3.14
3.00
4.74
4.19
4.16
3.92
3.91
3.90
3.90
3.74
3.71
3.71
3.70
3.21
3.21
3.21
2.67
2.66
2.64
2.62
2.04
2.03
2.03
2.02
1.98
1.96
1.94
1.66
1.66
1.65
1.65
1.65
1.64
1.64
1.61
1.60
1.24
1.04
0
10
20
30
40
50
60
70
80
90
100

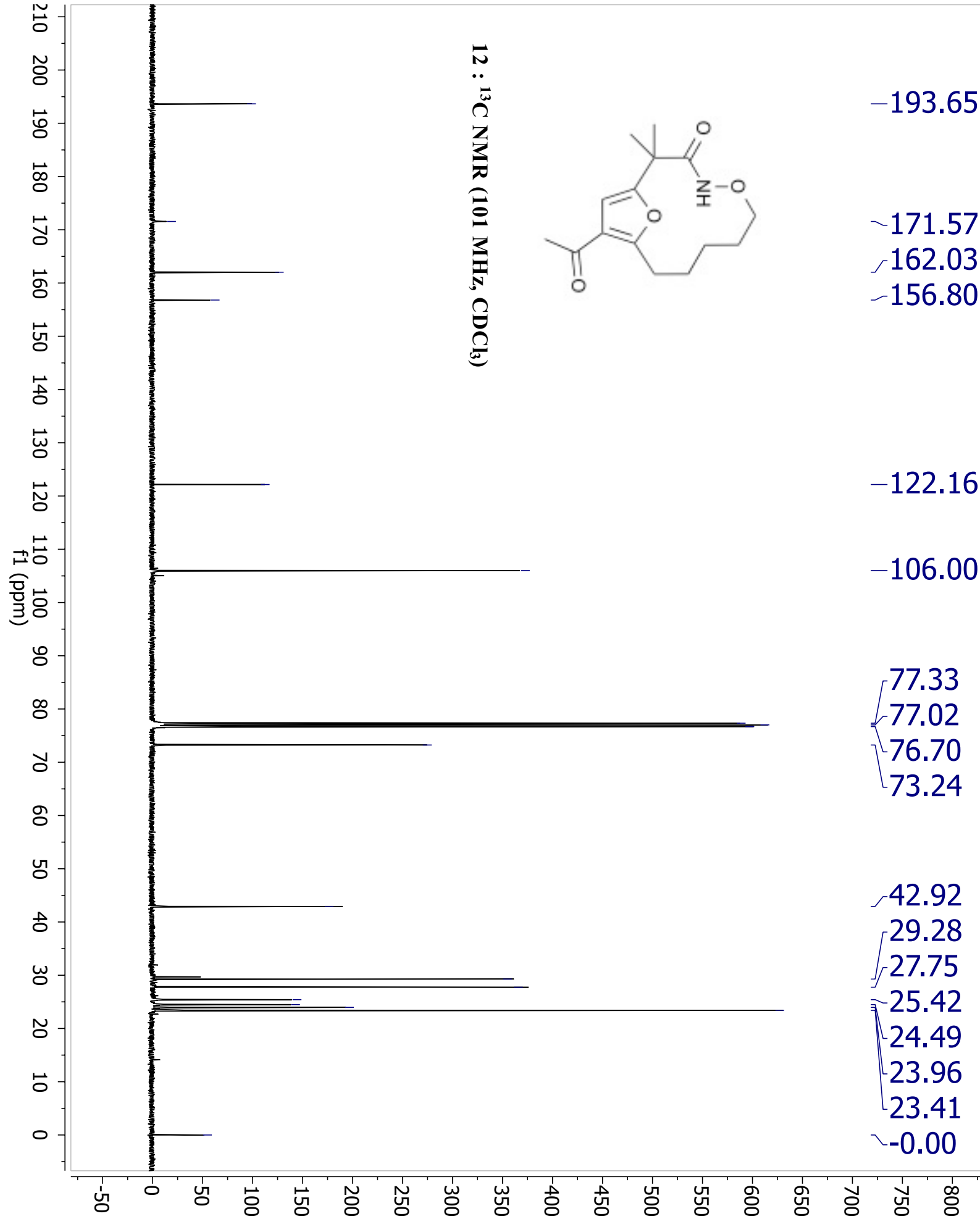
11 : ^{13}C NMR (101 MHz, CD_3OD)

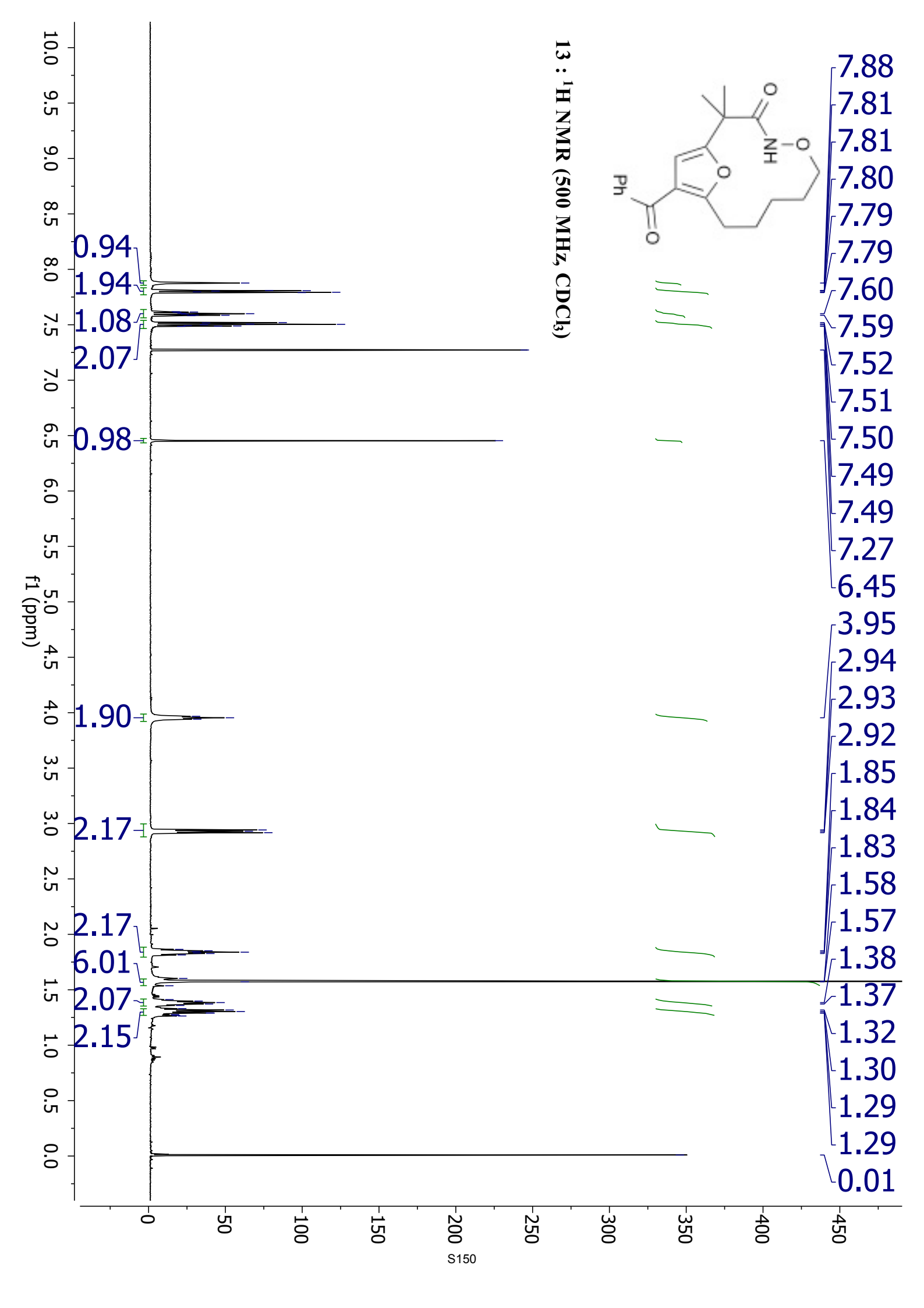


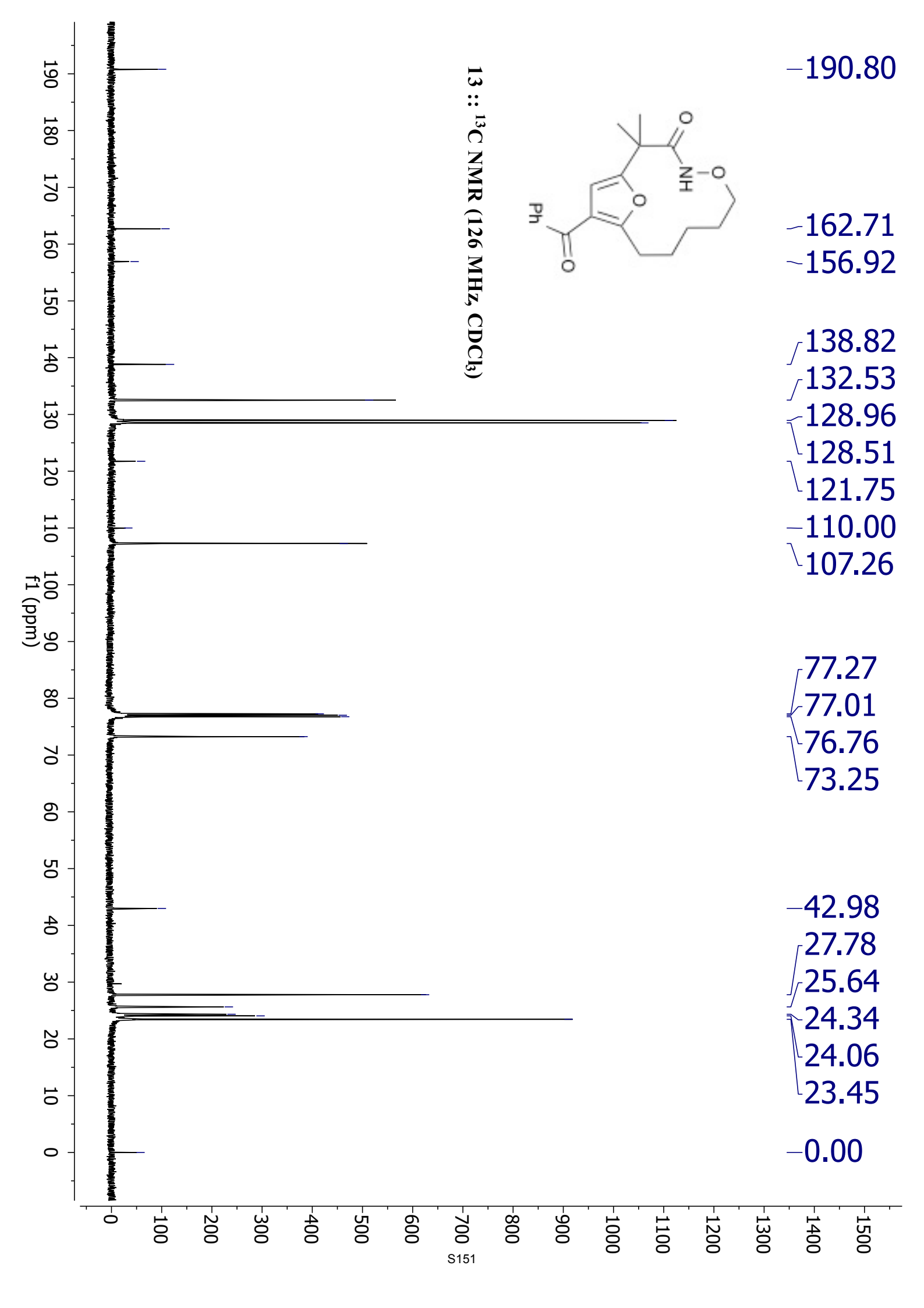
176.59
107.46
99.61
76.46
76.04
51.42
49.93
49.71
49.50
49.29
49.07
48.86
48.65
43.61
28.95
28.01
24.11
22.78
18.93

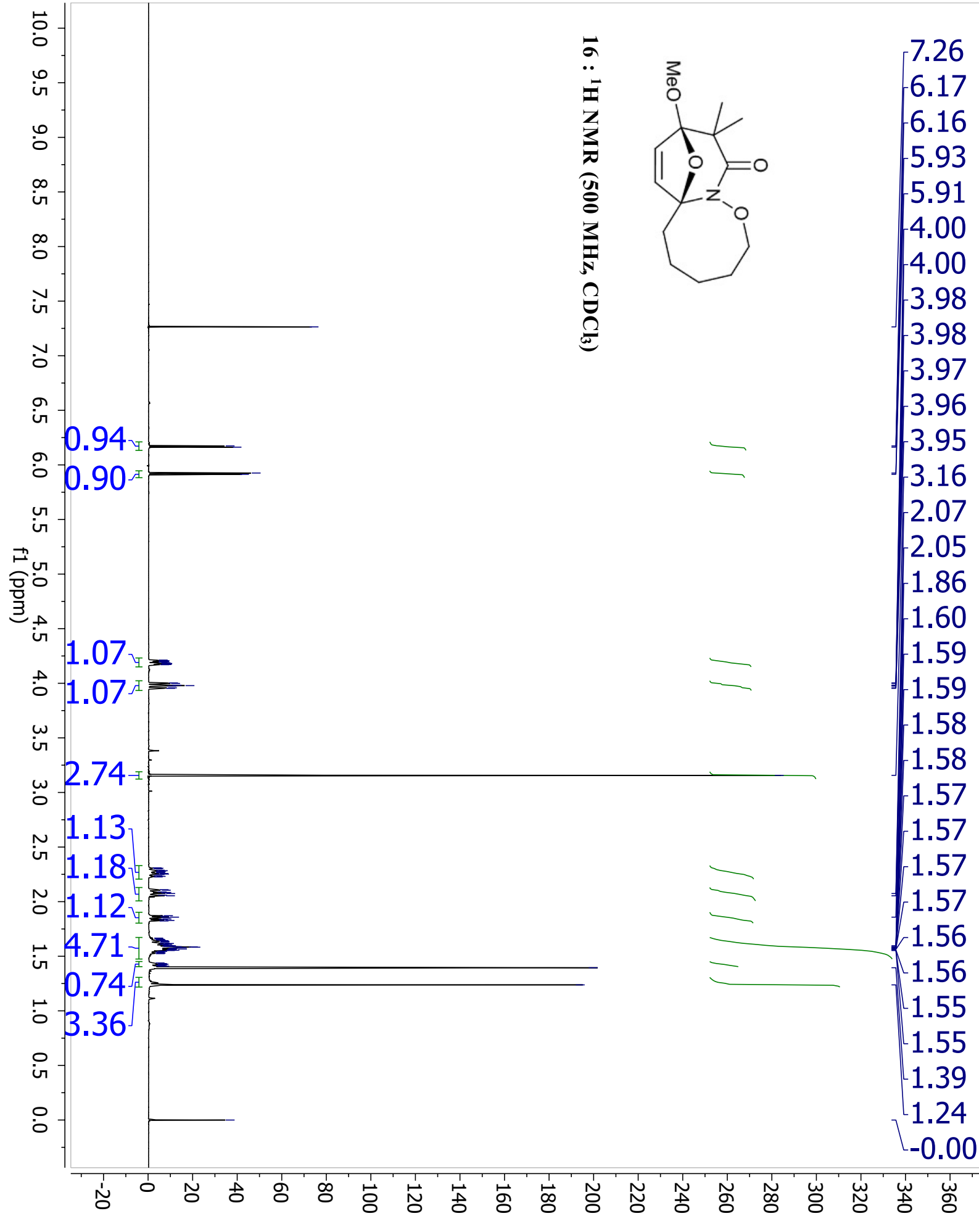
f1 (ppm)


12 : ^{1}H NMR (400 MHz, CDCl$_3$)
NH
O
O
O
O
1.00
0.88
2.10
2.08
3.01
2.17
6.15
2.22
2.34
7.86
7.27
6.46
3.94
3.93
3.91
3.12
3.10
3.10
3.09
3.08
2.42
1.86
1.84
1.83
1.81
1.80
1.56
1.40
1.38
1.36
1.35
1.27
1.25
1.23
1.22
0.00
0.00
0.00
f1 (ppm)

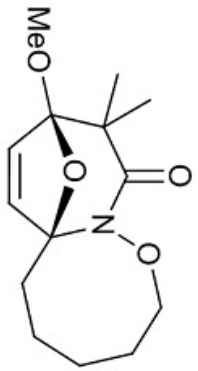

12 : 13C NMR (101 MHz, CDCl3)
193.65
171.57
162.03
156.80
122.16
106.00
77.33
77.02
76.70
73.24
42.92
29.28
27.75
25.42
24.49
23.96
23.41
-0.00
f1 (ppm)


13 : ¹H NMR (500 MHz, CDCl₃)
f1 (ppm)
0.94
1.94
1.08
2.07
0.98
1.90
2.17
2.17
6.01
2.07
2.15
7.88
7.81
7.81
7.80
7.79
7.79
7.60
7.59
7.52
7.51
7.50
7.49
7.49
7.27
6.45
3.95
2.94
2.93
2.92
1.85
1.84
1.83
1.58
1.57
1.38
1.37
1.32
1.30
1.29
1.29
0.01
Ph
O
NH
O
O
O
S150


13 :: ^{13}C NMR (126 MHz, $CDCl_3$)
190.80
162.71
156.92
138.82
132.53
128.96
128.51
121.75
110.00
107.26
77.27
77.01
76.76
73.25
42.98
27.78
25.64
24.34
24.06
23.45
0.00
f1 (ppm)
S151

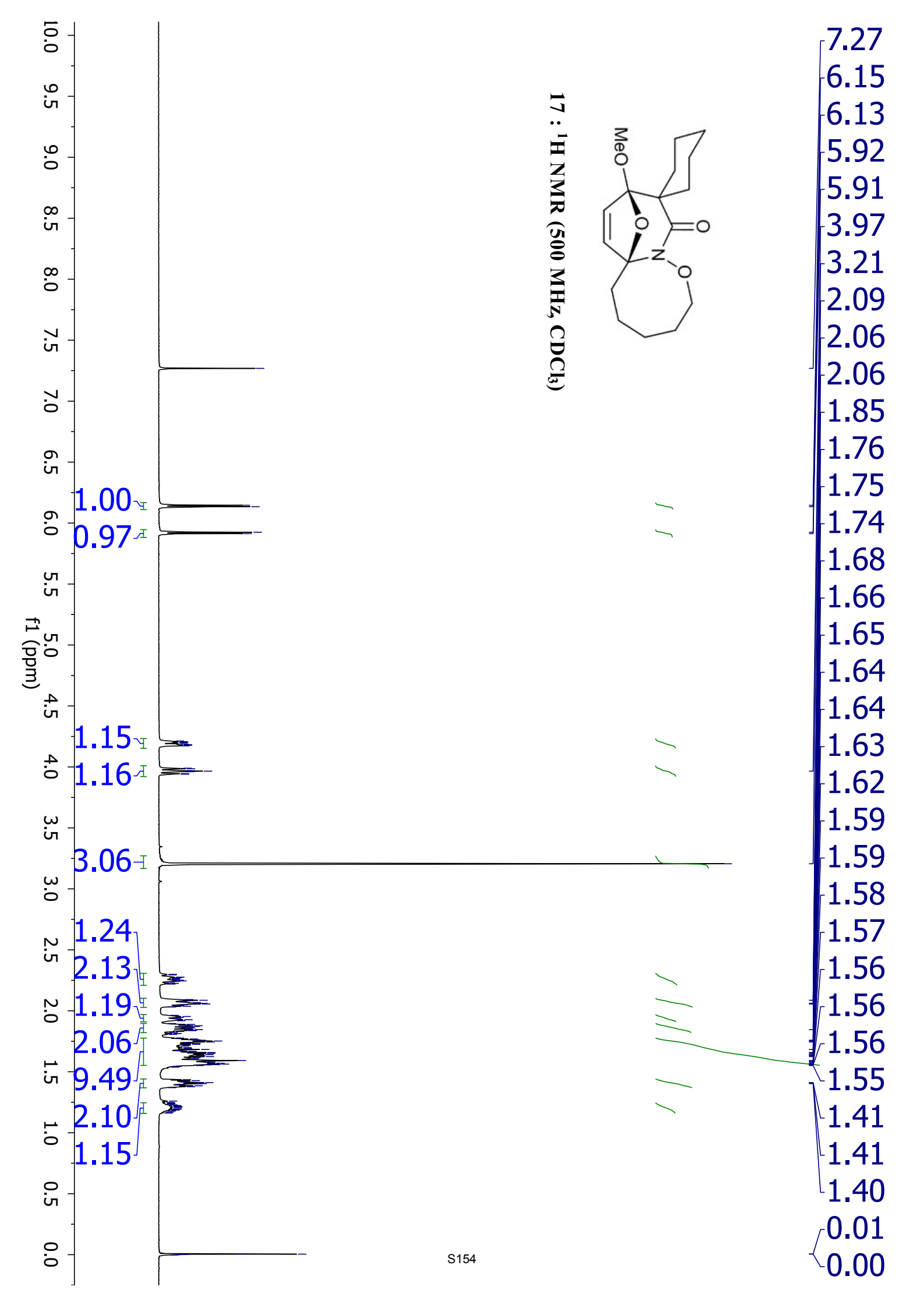

16 : ¹H NMR (500 MHz, CDCl₃)
MeO
O
O
N
O
f1 (ppm)
0.94
0.90
1.07
1.07
2.74
1.13
1.18
1.12
4.71
0.74
3.36
7.26
6.17
6.16
5.93
5.91
4.00
4.00
3.98
3.98
3.97
3.96
3.95
3.16
2.07
2.05
1.86
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.57
1.57
1.56
1.56
1.55
1.55
1.39
1.24
-0.00

16 : ^{13}C NMR (126 MHz, CDCl$_3$)



168.79
135.91
130.08
116.40
105.20
80.80
77.27
77.02
76.76
53.98
49.97
36.94
29.71
25.10
20.68
19.00
18.23

f1 (ppm)

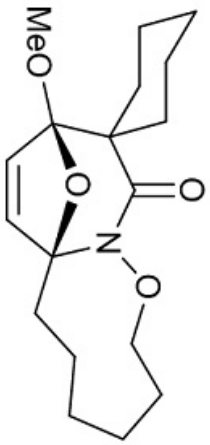

17 : ^{1}H NMR (500 MHz, $CDCl_3$)
MeO
O
O
N
O
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.00
0.97
1.15
1.16
3.06
1.24
2.13
1.19
2.06
9.49
2.10
1.15
7.27
6.15
6.13
5.92
5.91
3.97
3.21
2.09
2.06
2.06
1.85
1.76
1.75
1.74
1.68
1.66
1.65
1.64
1.64
1.63
1.62
1.59
1.59
1.58
1.57
1.56
1.56
1.56
1.55
1.41
1.41
1.40
0.01
0.00

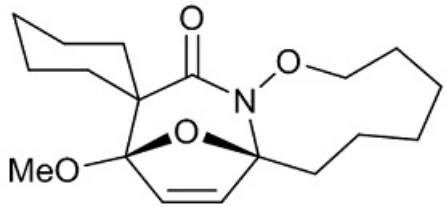
17 : ^{13}C NMR (101 MHz, $CDCl_3$)

f1 (ppm)

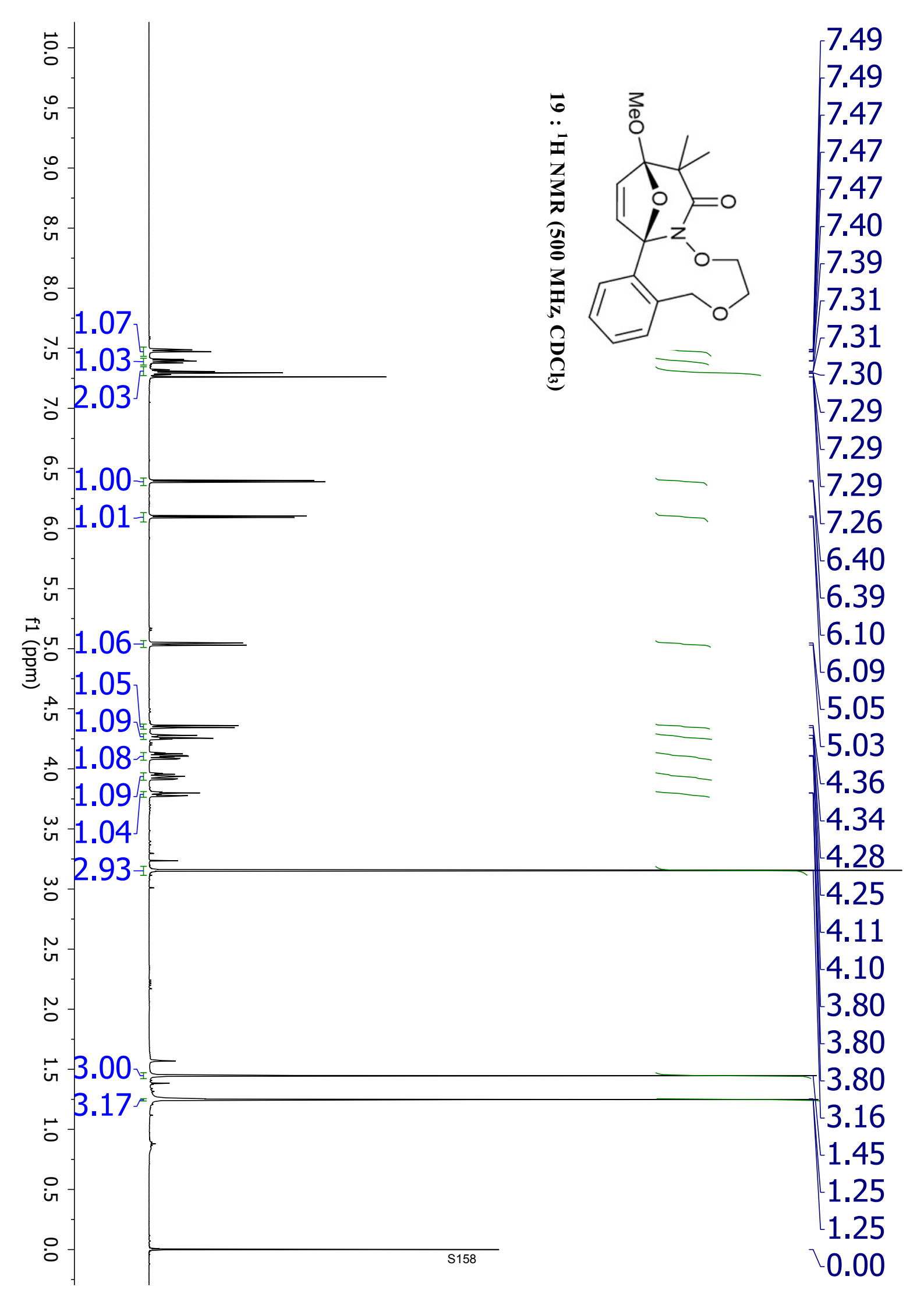
168.77
135.80
129.96
116.22
104.84
80.66
77.34
77.02
76.70
57.84
50.28
36.80
29.96
29.82
29.16
25.52
25.06
23.33
22.93
20.71
0.00

18 : ^{1}H NMR (500 MHz, $CDCl_3$)

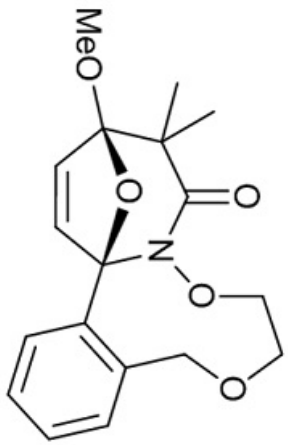




18 : ^{13}C NMR (126 MHz, $CDCl_3$)


19 : ^{1}H NMR (500 MHz, $CDCl_3$)
MeO
O
O
N
O
O
f1 (ppm)
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
1.07
1.03
2.03
1.00
1.01
1.06
1.05
1.09
1.08
1.09
1.04
2.93
3.00
3.17
7.49
7.49
7.47
7.47
7.47
7.40
7.39
7.31
7.31
7.30
7.29
7.29
7.29
7.26
6.40
6.39
6.10
6.09
5.05
5.03
4.36
4.34
4.28
4.25
4.11
4.10
3.80
3.80
3.80
3.16
1.45
1.25
1.25
0.00
S158

19 : ^{13}C NMR (126 MHz, $CDCl_3$)



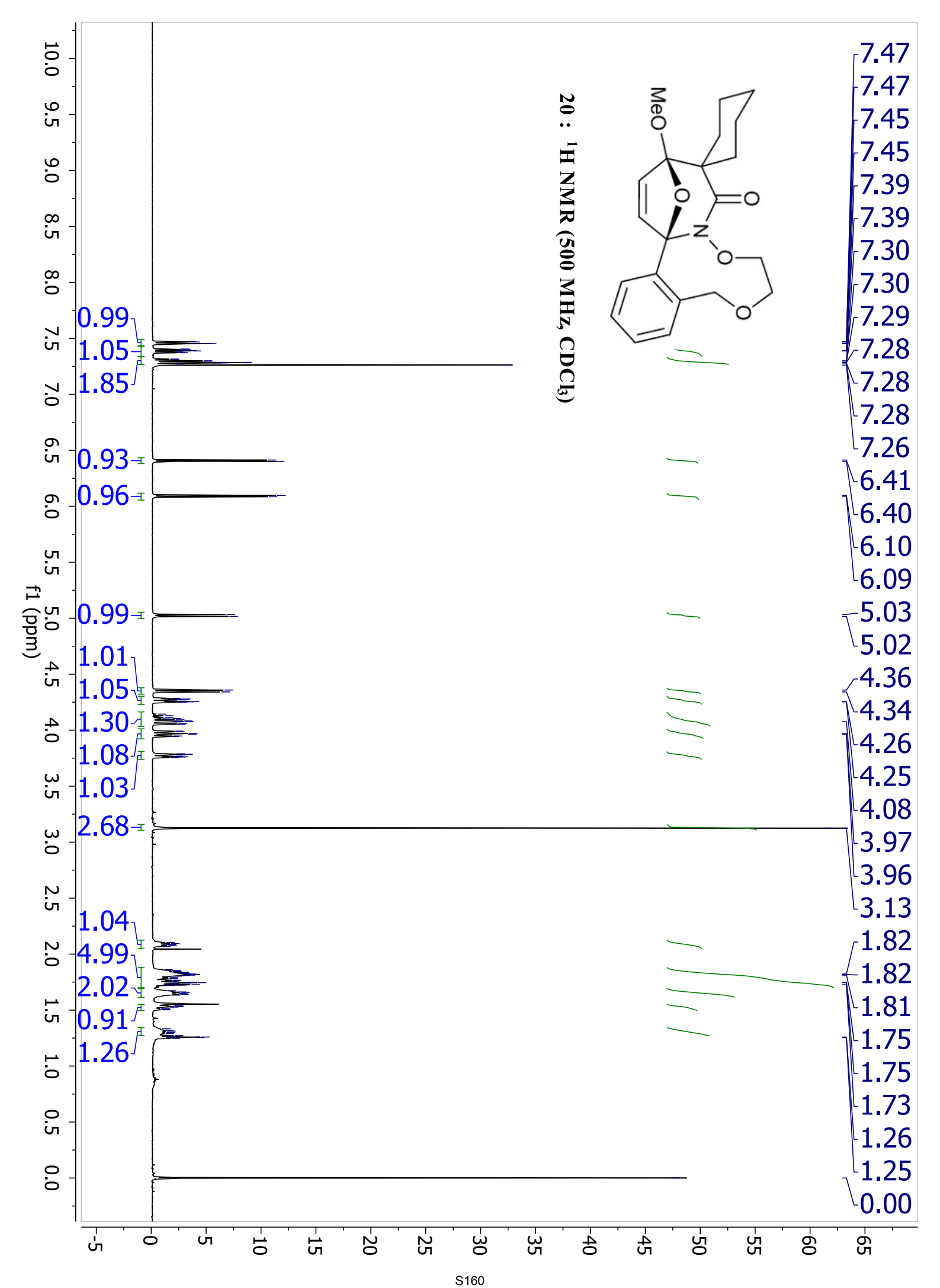
170.71
138.91
137.40
135.49
132.79
129.30
129.01
128.66
126.76
114.30
108.49

77.27
77.01
76.76
74.29
73.47
67.35
55.01
50.36

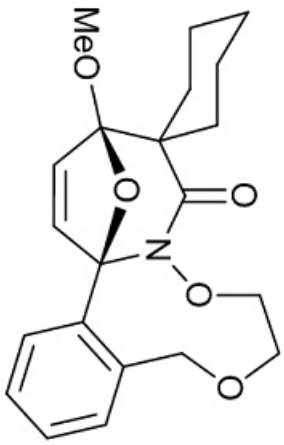
19.73
18.33

0.00

f1 (ppm)

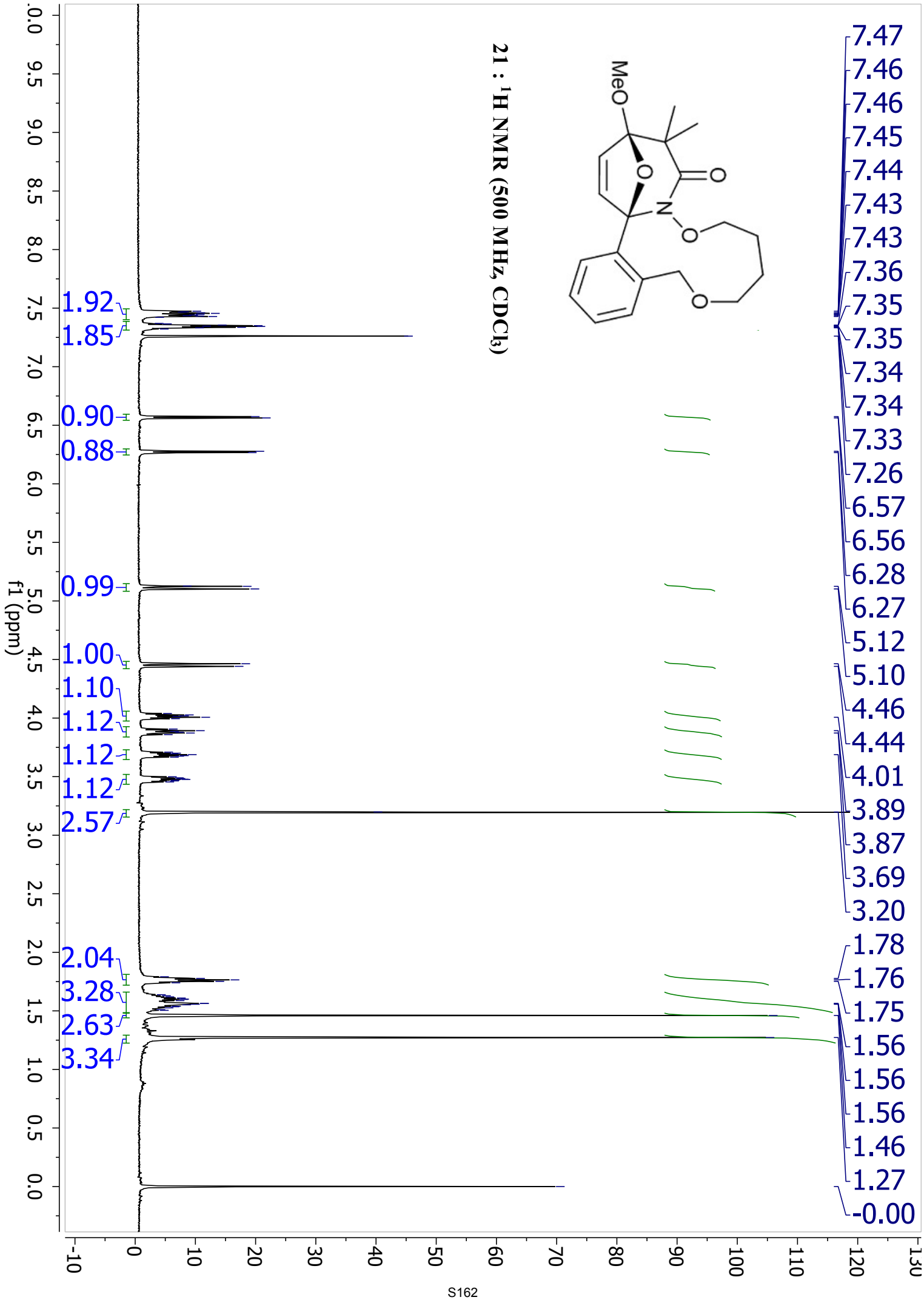

20 : ^{1}H NMR (500 MHz, CDCl$_3$)
MeO
O
O
N
O
O
O
0.99
1.05
1.85
0.93
0.96
0.99
1.01
1.05
1.30
1.08
1.03
2.68
1.04
4.99
2.02
0.91
1.26
7.47
7.47
7.45
7.45
7.39
7.39
7.30
7.30
7.29
7.28
7.28
7.28
7.26
6.41
6.40
6.10
6.09
5.03
5.02
4.36
4.34
4.26
4.25
4.08
3.97
3.96
3.13
1.82
1.82
1.81
1.75
1.75
1.73
1.26
1.25
0.00
f1 (ppm)

20 : ^{13}C NMR (101 MHz, $CDCl_3$)

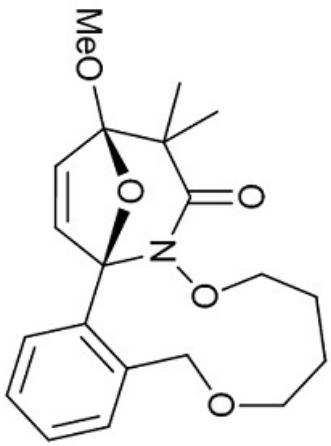


170.70
138.83
137.56
135.53
132.71
129.37
129.02
128.57
126.71
114.45
108.42
77.33
77.01
76.69
73.97
73.60
67.26
58.84
50.53
30.20
29.07
25.38
23.22
22.84
0.00

f1 (ppm)

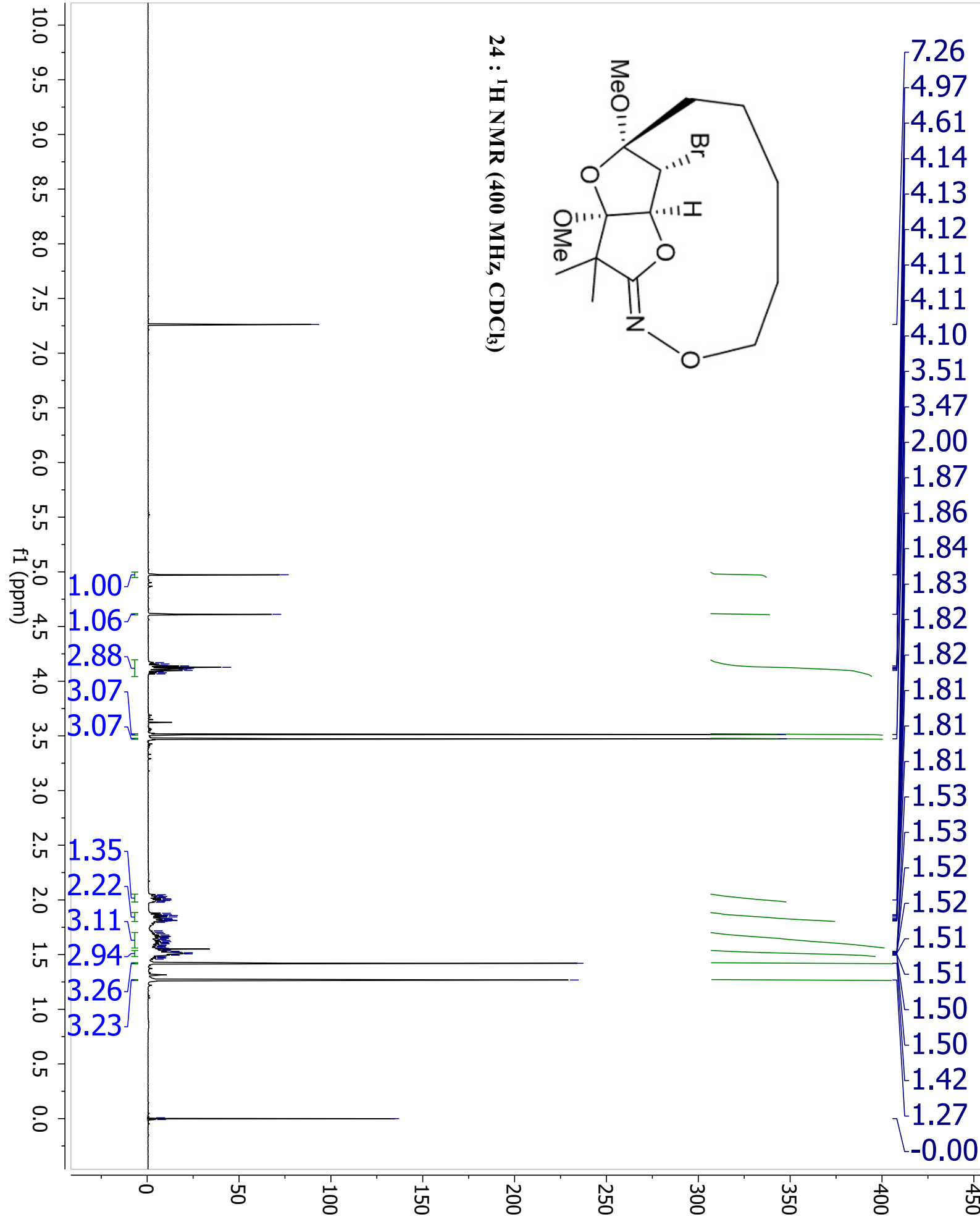

21 : ^{1}H NMR (500 MHz, CDCl$_3$)
MeO
O
O
N
O
O
1.92
1.85
0.90
0.88
0.99
1.00
1.10
1.12
1.12
1.12
2.57
2.04
3.28
2.63
3.34
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.36
7.35
7.35
7.34
7.34
7.33
7.26
6.57
6.56
6.28
6.27
5.12
5.10
4.46
4.44
4.01
3.89
3.87
3.69
3.20
1.78
1.76
1.75
1.56
1.56
1.56
1.46
1.27
-0.00
f1 (ppm)

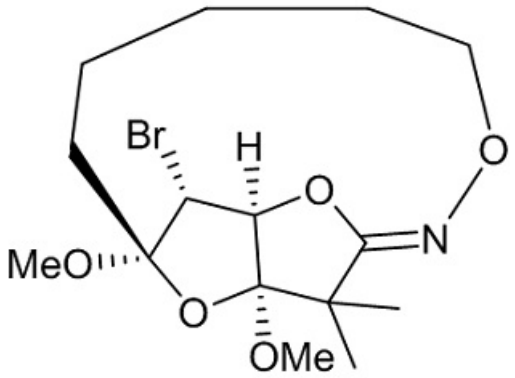
21 : ^{13}C NMR (126 MHz, $CDCl_3$)



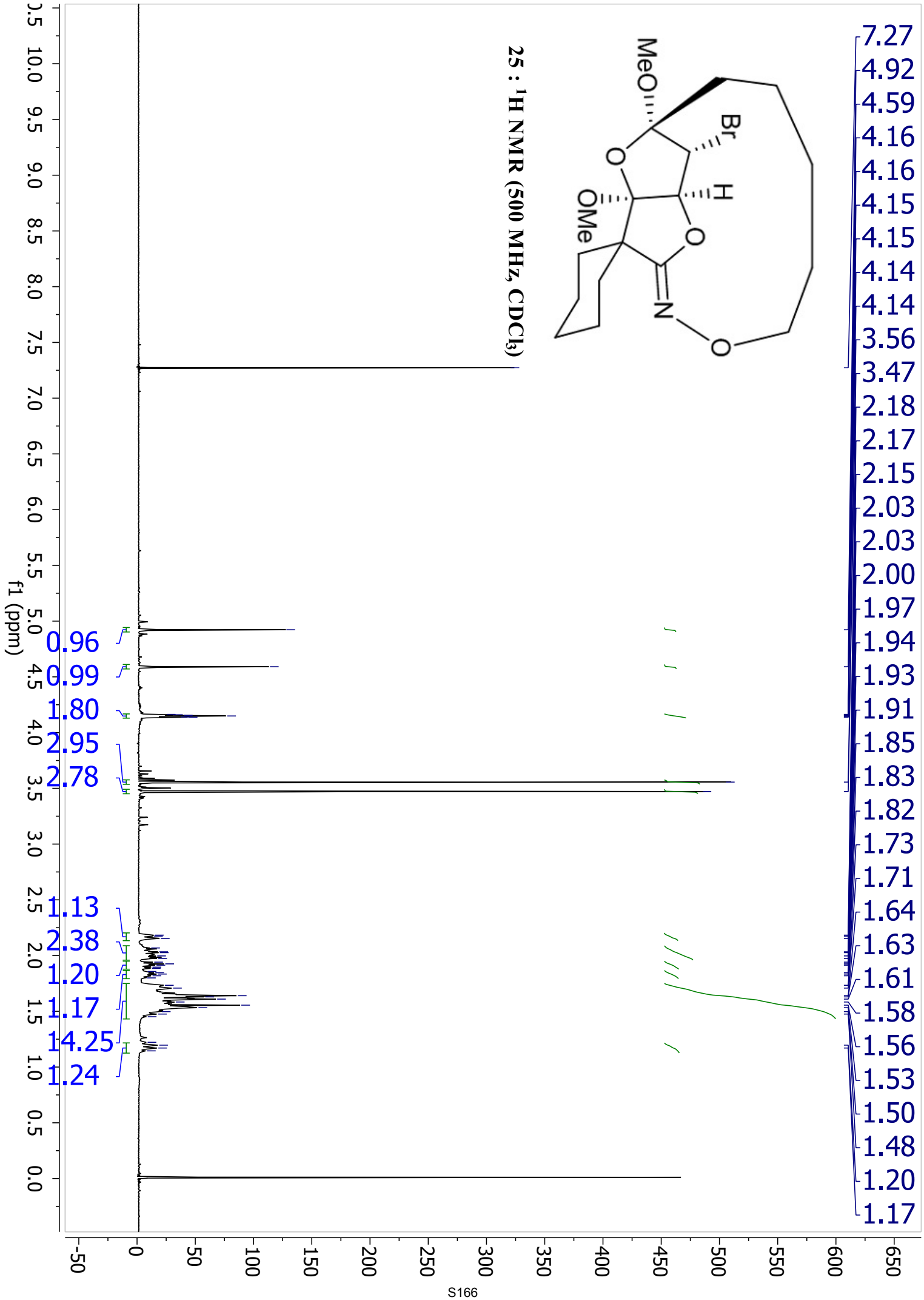
169.20
136.80
136.78
136.71
132.48
128.86
128.68
127.89
127.77
113.76
107.61
77.26
77.01
76.76
75.24
70.09
69.34
55.01
50.67
25.25
24.28
19.21
18.57
0.00

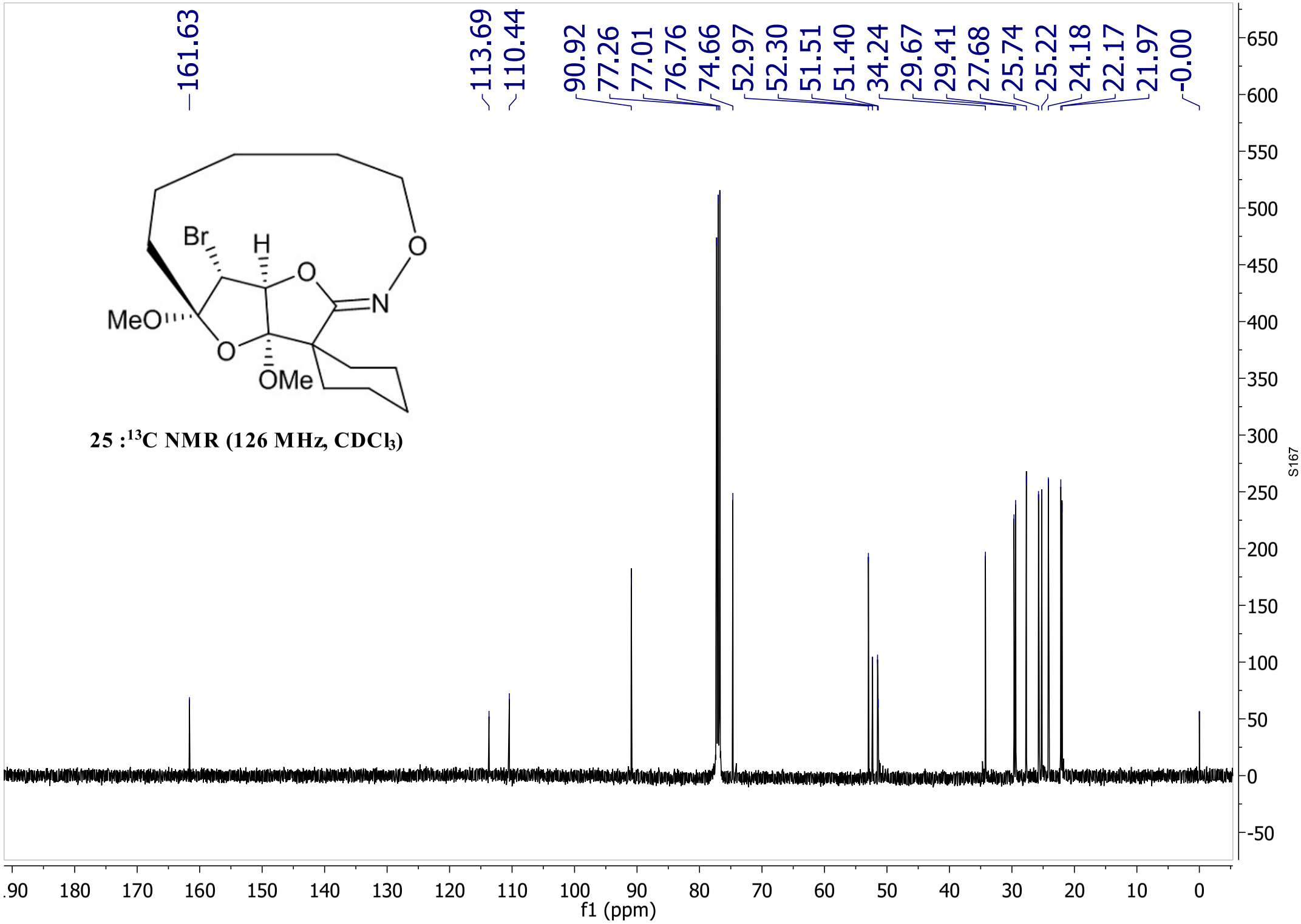
f1 (ppm)


24 : ¹H NMR (400 MHz, CDCl₃)
MeO
Br
H
O
OMe
O
N
O
7.26
4.97
4.61
4.14
4.13
4.12
4.11
4.11
4.10
3.51
3.47
2.00
1.87
1.86
1.84
1.83
1.82
1.82
1.81
1.81
1.81
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.42
1.27
-0.00
1.00
1.06
2.88
3.07
3.07
1.35
2.22
3.11
2.94
3.26
3.23
f1 (ppm)

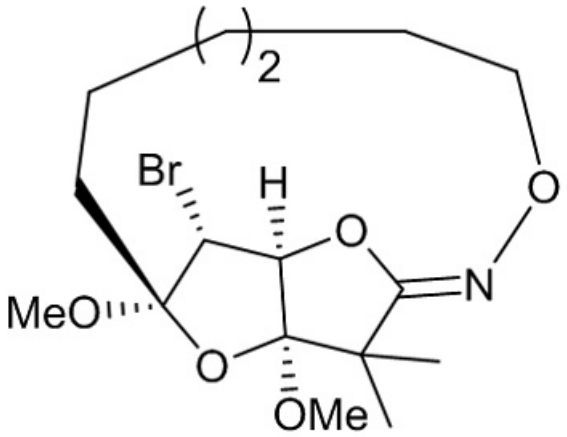


24 :^{13}C NMR (101 MHz, $CDCl_3$)

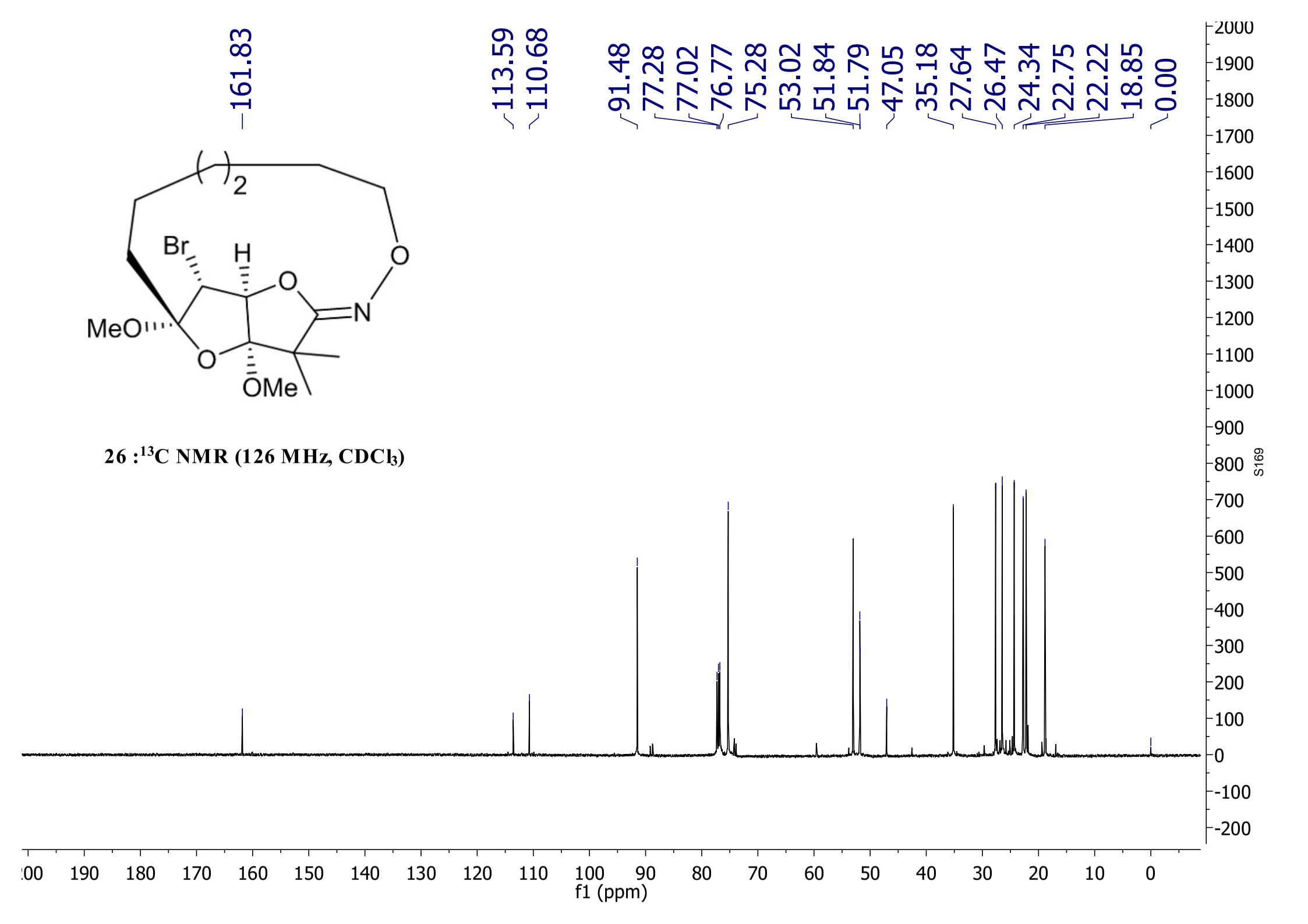

25 : 1H NMR (500 MHz, CDCl3)
MeO
Br
H
OMe
O
N
O
f1 (ppm)
0.96
0.99
1.80
2.95
2.78
1.13
2.38
1.20
1.17
4.25
1.24
7.27
4.92
4.59
4.16
4.16
4.15
4.15
4.14
4.14
3.56
3.47
2.18
2.17
2.15
2.03
2.03
2.00
1.97
1.94
1.93
1.91
1.85
1.83
1.82
1.73
1.71
1.64
1.63
1.61
1.58
1.56
1.53
1.50
1.48
1.20
1.17



25 : ^{13}C NMR (126 MHz, $CDCl_3$)

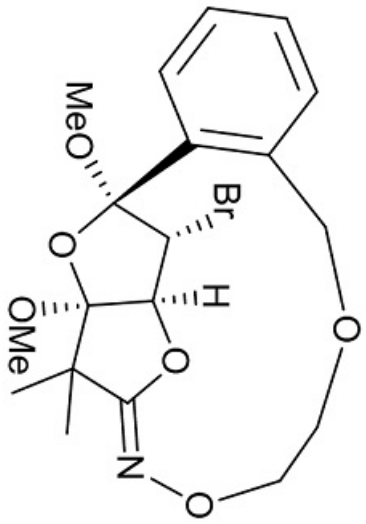


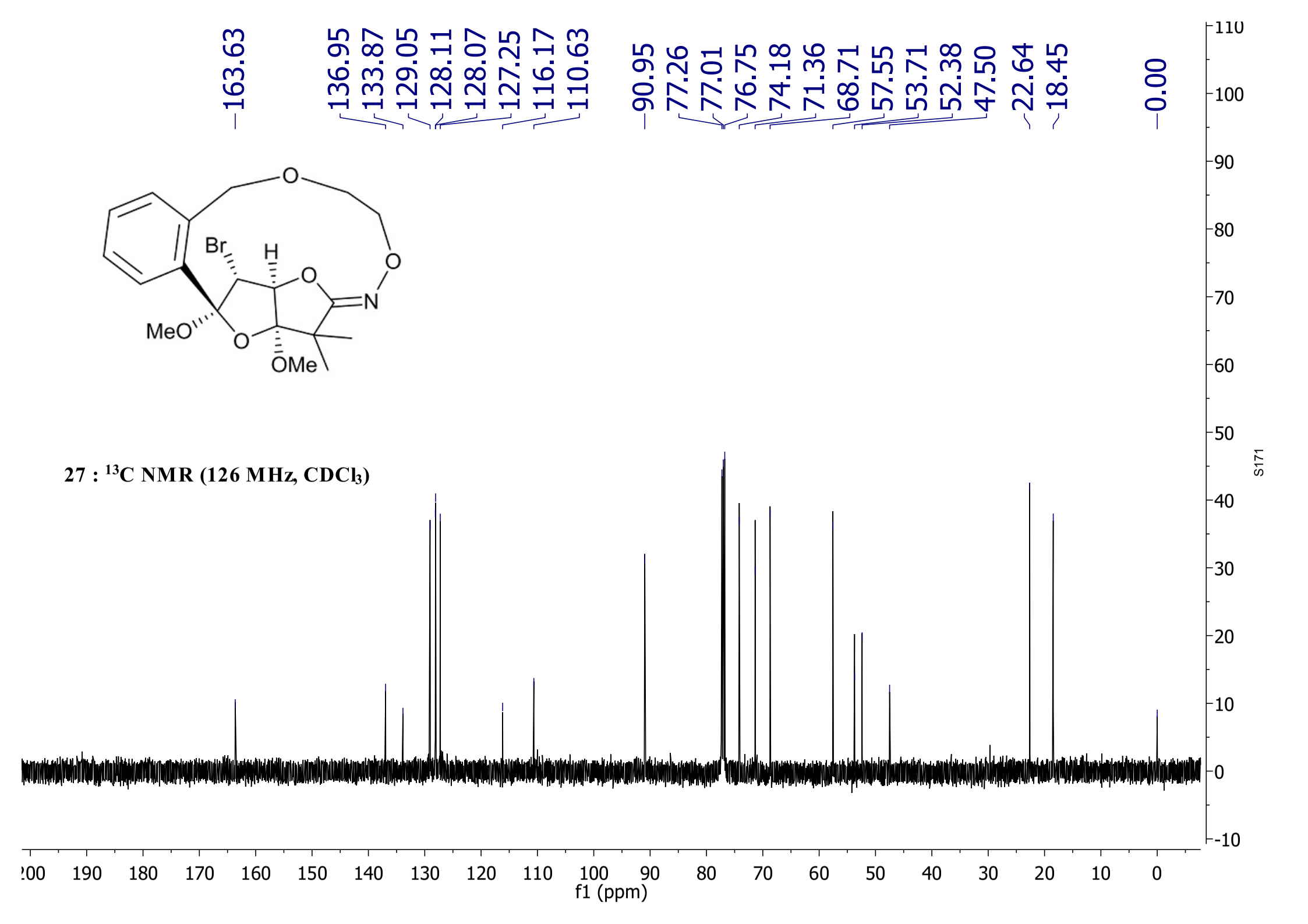
26 : ^{1}H NMR (500 MHz, $CDCl_3$)



26 :^{13}C NMR (126 MHz, $CDCl_3$)

27 : ^{1}H NMR (500 MHz, $CDCl_3$)




163.63
136.95
133.87
129.05
128.11
128.07
127.25
116.17
110.63
90.95
77.26
77.01
76.75
74.18
71.36
68.71
57.55
53.71
52.38
47.50
22.64
18.45
0.00
Br
H
O
O
N
MeO
O
OMe
27 : 13C NMR (126 MHz, CDCl3)
S171
f1 (ppm)