Supporting Information

Ritter-Enabled Catalytic Asymmetric Chloroamination of Olefins

Daniel C. Steigerwald, Bardia Soltanzadeh, Aritra Sarkar, Cecilia C. Morgenstern, Richard J. Staples, Babak Borhan*

Michigan State University, Department of Chemistry, East Lansing, MI, 48824.

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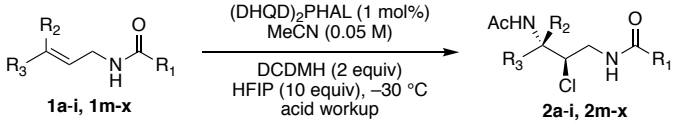
I Materials and General Instrumentations:

Commercially available reagents were purchased from Sigma-Aldrich or Alfa-Aesar and used as received. CH_2Cl_2 and acetonitrile were freshly distilled over CaH_2 prior to use. THF was distilled over sodium-benzophenone ketyl. All other solvents were used as purchased. DCDMH was purified by recrystallization in chloroform. Dichloramine-T was purchased from TCI and used without further purification. Enantiomeric excess for all products was determined by HPLC analysis using DAICEL Chiralcel® OJ-H and OD-H or Chiralpak® IA, AD-H, and AS-H columns. Optical rotations of all products were measured in chloroform. Allyl amides **1a**, **1f**, **1h**, **1i**, **1m-p**, **1r**, **1s**, **1u**, **1v** were synthesized as reported previously and analytical data matched reported values.[1] Substrates **1b-e**, **1g**, **1k**, **1l**, **1q**, **1t**, **1u**, **1x** were synthesized by the same procedure described for substrates above, and provided overall yields ranging from 40-60%. Analytical data for the new substrates can be found be low in Section **VIIIe.**

II General Procedures with DCDMH.

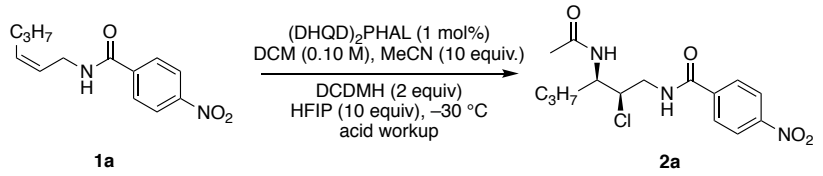
a. General procedure for the catalytic asymmetric chloroamidation of unsaturated amides with DCDMH to yield vicinal chloroamides.



The substrate (**1a-i**, **1m-x)** (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (0.8 mg, 1 mol%) were suspended in acetonitrile (2 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via syringe. The resulting suspension was cooled to –30 °C in an immersion cooler. After stirring for 10 min, DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated. To the concentrated vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 5 min. Water (3 mL) was added and the solution was

concentrated in vacuo and extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product (**2a-i**, **2m-x**).

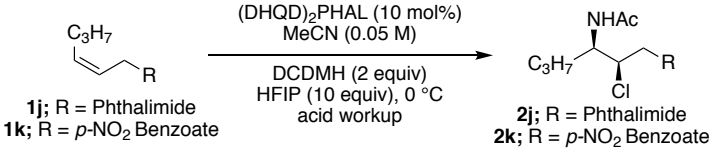
b. Procedure for the catalytic asymmetric chloroamidation of 1a with DCDMH and 10 equivalents of acetonitrile to yield vicinal chloroamides.



1a **2a**

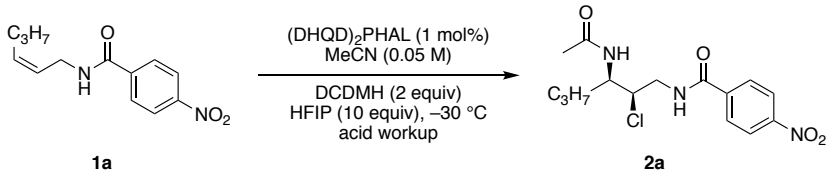
The substrate **1a** (12.4. mg, 0.05 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (0.4 mg, 1 mol%) were suspended in dichloromethane (0.5 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (50 μL, 0.50 mmol, 10 equiv) and acetonitrile (26 μL, 0.50 mmol, 10 equiv) were added via syringe. The resulting suspension was cooled to –30 °C in an immersion cooler. After stirring for 10 min, DCDMH (19.7 mg, 0.10, mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated. To the concentrated vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated in vacuo and extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **2a** (53% yield with triphenylmethane NMR standard, 99% *ee*).

c. Procedure for the chloroamidation of allyl-phthalimide (1j) and allyl-ester (1k) substrates.



The substrate (**1j, 1k)** (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (7.8 mg, 10 mol%) were suspended in acetonitrile (2 mL) HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was cooled to 0 °C in an immersion cooler. After stirring for 10 min, DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated. To the concentrated product in the vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product (**2j**, **2k**).

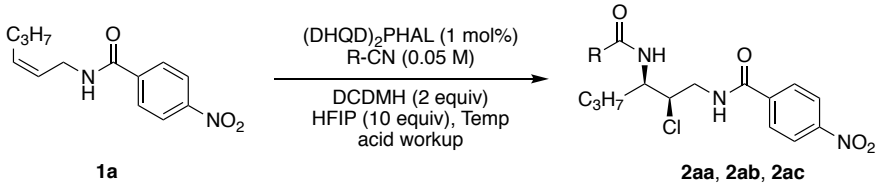
d. Procedure for the 1 mmol scale catalytic asymmetric chloroamidation of unsaturated amides with DCDMH to yield vicinal chloroamides.



The substrate **1a** (248.0 mg, 1.0 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (7.8 mg, 1 mol%) were suspended in acetonitrile (20 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (1.05 mL, 10.0 mmol, 10 equiv) was added via syringe. The resulting suspension was cooled to –30 °C in an immersion cooler. After stirring for 10 min, DCDMH (394.0 mg, 2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (10 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was

extracted with DCM (3 x 10 mL). The combined organics were concentrated. To the concentrated vial with a stir bar, acetonitrile (5 mL) and a solution of HCl (1 M, 1 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated in vacuo and extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **2a** (282.0 mg, 83% yield, 99% *ee*).

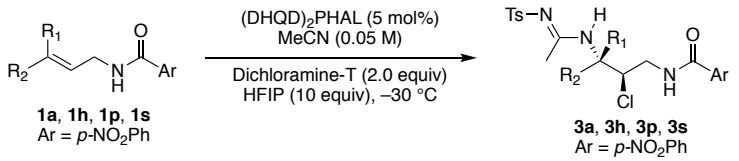
e. General procedure for the chloroamidation of allyl-amides with different nitrile solvents.



1a **2aa**, **2ab**, **2ac**

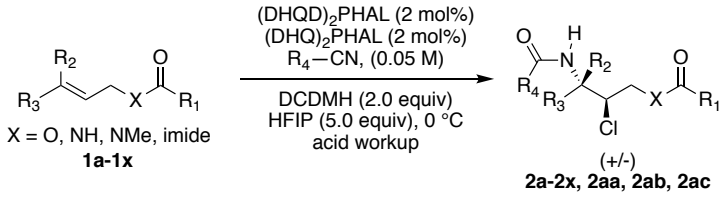
The substrate **1a** (24.8 mg, 0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (0.8 mg, 1 mol%) were suspended in a nitrile solvent (2 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via syringe. The reaction mixtures were then cooled to a temperature to accommodate the freezing point of the solvent (**2aa**: –30 °C, **2ab**: 0 °C, **2ac**: 23 °C). After stirring for 10 min, DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated. To the concentrated vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated in vacuo and extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product (**2aa**, **2ab**, **2ac)**.

III General Procedure for the Catalytic Asymmetric Chloroamidination of Unsaturated Amides with Dichloramine-T as the Chlorinating Reagent to Yield Vicinal Chlorosulfonylamidines:



The substrate (**1a**, **1h**, **1p**, **1s**) (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (3.9 mg, 5 mol%) were suspended in acetonitrile (2 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via syringe. The resulting suspension was cooled to –30 °C in an immersion cooler. After stirring for 10 min dichloramine-T (48.0 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon completion was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product (**3a**, **3h**, **3p**, **3s**).

IV Procedure for the synthesis of enantiomeric mixtures of chloroamide compounds for HPLC separations

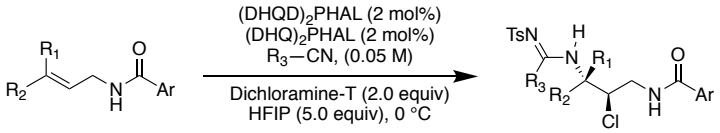


The enantiomeric mixtures used for HPLC analysis in determining enantiopurity were synthesized as follows by using the quasi-enantiomeric cinchona alkaloid dimers.

The substrate (**1a-1x**, 0.05 mmol, 1.0 equiv), $(DHQD)_2PHAL$ (0.8 mg, 2 mol%), and $(DHQ)_2PHAL$ (0.8 mg, 2 mol%) were placed in a test tube with a magnetic stir bar and dissolved in the nitrile solvent of choice (1 mL), capped with a rubber septa. HFIP (25 μ L, 0.25 mmol, 5 equiv) was added via a syringe. The resulting suspension was cooled

to 0 ^{O}C in an immersion cooler. After stirring for 10 min, DCDMH (19.7 mg, 0.1 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated under reduced pressure. To the concentrated vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 5 min. Water (3 mL) was added and the solution was concentrated in vacuo and extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired products as mixture of enantiomers (**2a-2x, 2aa, 2ab, 2ac**).

V Procedure for the synthesis of enantiomeric mixtures of chloroamidine compounds for HPLC separations



1a, **1h**, **1p**, **1s**
Ar = *p*-NO_2Ph

(+/-)
3a, **3h**, **3p**, **3s, 7a**
Ar = *p*-NO_2Ph

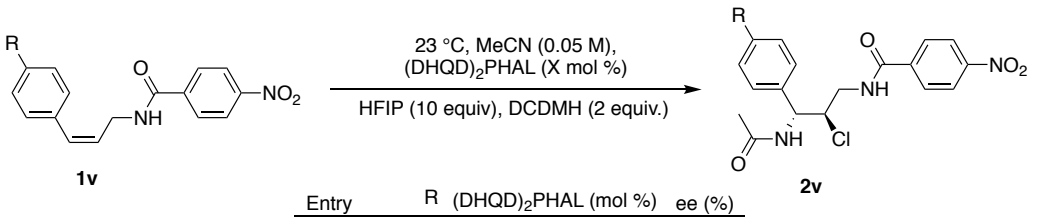
The enantiomeric mixtures used for HPLC analysis in determining enantiopurity were synthesized as follows by using the quasi-enantiomeric cinchona alkaloid dimers.

The substrate (**1a, 1h, 1p, 1s,** (0.05 mmol, 1.0 equiv), $(DHQD)_2PHAL$ (0.8 mg, 2 mol%), and $(DHQ)_2PHAL$ (0.8 mg, 2 mol%) were placed in a test tube with a magnetic stir bar and dissolved in the nitrile solvent of choice (1 mL), capped with a rubber septa. HFIP (25 μ L, 0.25 mmol, 5 equiv) was added via syringe. The resulting suspension was cooled to 0 ^{O}C in an immersion cooler. After stirring for 10 min, Dichloramine-T (24.0 mg, 0.1 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon competition was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and

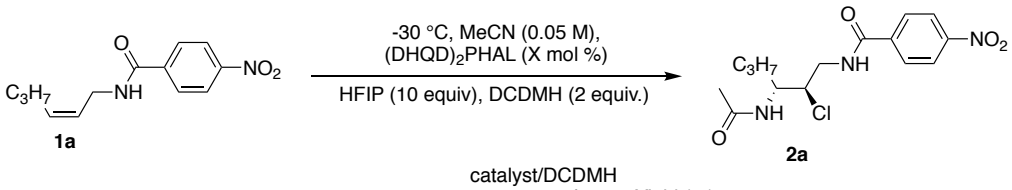
concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired products as mixture of enantiomers (**3a, 3h, 3p, 3s, 7a**).

VI Catalyst Loading Study for Less Reactive Allyl-Amide 1v:

Table S1. Catalyst loading studies with **1a** and **1v**



Entry	R	(DHQD)$_2$PHAL (mol %)	ee (%)
1	H	1	99
2	CF_3	1	54
3	CF_3	5	90
4	CF_3	10	93

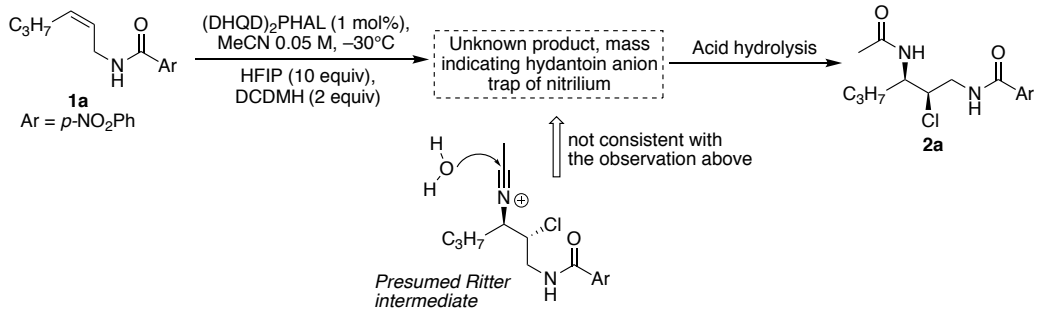


Entry	(DHQD)$_2$PHAL %	catalyst/DCDMH exposure time	Yield (%)	ee
1	1	None	76	99
2	1	48 h	48	1
3	0	NA	0	NA

Optimization studies for **1a** showed no decrease in enantioselectivity when the catalyst loading was decreased from 10 mol% to 1 mol%. Many aryl-substituted substrates (**1s**, **1u**, **1w**, **1x**) were compatible with these conditions and returned products with enantiomeric excess greater than 90%. When these reaction conditions were extended to the less reactive substrate **1v**, the enantiomeric excess decreased to 53% and the rate of the reaction decreased significantly relative to the other aryl substrates (48 h relative to 6 h). When catalyst loading was increased to 5 mol%, modest levels of enantioselectivity were restored. We hypothesized that the decrease in enantiocontrol may be the result of catalyst degradation under reaction conditions. To test this hypothesis, we subjected (DHQD)$_2$PHAL to reaction conditions for 48 h at room temperature. After 48 h, the reaction mixture was cooled to –30 °C and **1a** was added (note **1a** leads to the product **2a** in 99% *ee* under optimized conditions). These conditions provided nearly racemic product.

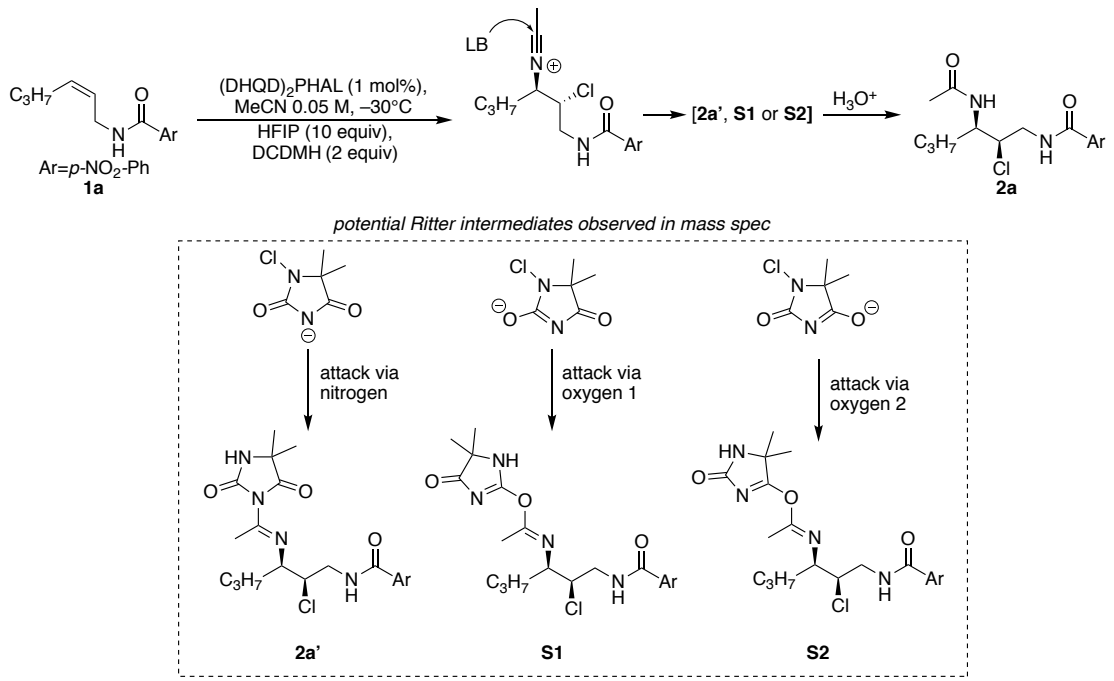
Nonetheless, the catalyst is still necessary to form the product as no reaction was observed without catalyst.

VII Structural Determination of Ritter Trapped Product:

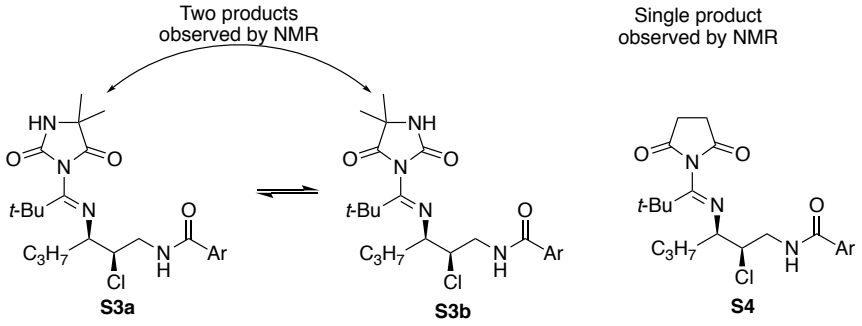


Early studies of reaction conditions on **1a** revealed that the transformation was not proceeding through a traditional Ritter-type pathway, which would undergo a nitrilium trap by water and provide **2a**. Interestingly, mass spectrometry revealed the reaction was undergoing a nitrilium trap by 3-chloro-5,5-dimethylhydantoin, the residue left after chlorenium transfer. The ^{1}H NMR was complicated, hinting at multiple products, none of which were identified as **2a**. This trapped product underwent hydrolysis to provide the amide products described in the main text. This observation leads to ambiguity of which potential nucleophilic center or centers on the chlorenium donor attacked the nitrilium cation as it could be the nitrogen atom, or either of the carbonyl oxygen atoms (see structures **2a'**, **S1**, and **S2** in figure below).

The acid lability of the Ritter intermediate obtained from acetonitrile made analysis of the intermediate challenging. The Ritter intermediate formed when pivalonitrile was employed as a nucleophile was stable under column chromatography (SiO_2/EtOAc–Hexanes gradient) and provided two products that could be isolated and analyzed by NMR. These



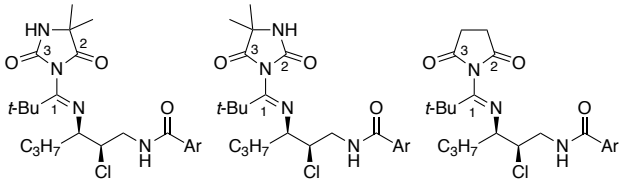
two products were determined to be in equilibrium with each other as 30 min after initial isolation, the formerly pure products began to interconvert back to being the original mixture. This led to the hypothesize that a single product with two roto-isomeric structures such as **S3a** and **S3b** were isolated. Interestingly, **S4**, obtained from the reaction of **1a** with pivalonitrile, with NCS as the chlorenium source exhibits only one rotomeric product, owing to its symmetrical nature. This provides further proof that the mixture obtained above is in fact due to rotomeric equilibria, and not the result of having a mix of products as a result of nitrogen and oxygen atoms as nucleophiles.

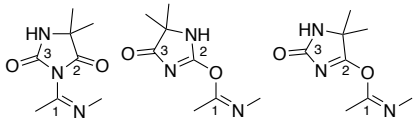


To conclusively determine the structure of the Ritter intermediates, experimentally observed ^{13}C resonances were compared to those obtained for **S4** and also computationally calculated chemical shifts anticipated for all scenarios. Comparison of the observed ^{13}C

NMR to a computationally generated (EDF2-6-31g*) NMR of simplified substrates (**S3a/b** analog, **S1**-analog, and **S2**-analog) were used to predict the structure of the Ritter intermediate. The oxygen atom attack analogs (**S1** and **S2**), lead to resonances that do not fit the observed chemical shifts for **S3a/b**. The validity of the computed chemical shifts were corroborated with examples from the literature for accuracy. The computed chemical shift for C3 in the **S1**-analog (190.2 ppm) is much further downfield as compared to other carbonyl carbons in the series investigated. Fortuitously, a similarly situated carbonyl carbon shown in structure **S5** has a chemical shift in the same range,[2] thus corroborating the calculations. The experimentally observed resonances for **S4**, along with the calculated chemicals shifts for **S3a/b** analog fit well with the observed chemical shifts for **S3a** and **S3b**, thus suggesting that not only the nitrogen atom is the nucleophilic participant, but also, the observed mixture is, as described above, a consequence of a rotomeric equilibrium.

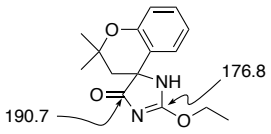
Table S2. Experimental (**S3a**, **S3b**, and **S4**) and calculated ^{13}C-NMR values for potential Ritter intermediates





	S3a	**S3b**	**S4**	**S3a/b**-analog	**S1**-analog	**S2**-analog
^{13}C-resonances (ppm)						
C1	155.4	155.3	156.5	151.7	153.3	151.7
C2	175.3	153.5	175.1	173.5	176.3	179.0
C3	154.9	177.0	176.6	155.6	190.2	166.0

outlier chemical shifts

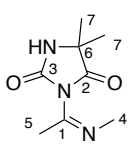


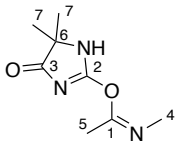
S5
known chemical shifts
see reference 2

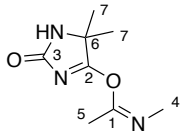
Computational details for NMR calculations:

All calculations presented in this article were performed using the Spartan'18 (Spartan 18; Wavefunction Inc.: Irvine, CA) software package. NMR calculations for **S1**-analog, **S2**-analog, and **S3a/b**-analog commenced with finding optimum geometry using a MonteCarlo search function. The best conformer was then subject to DFT optimization at the B3LYP/6-31G* level. The geometry optimized structures were then recalculated with EDF2-6-31G* to obtain NMR values. The table below lists the calculated ^{13}C-NMR values for the three analogs.

Table S3. ^{13}C-Chemical shifts for **S3a/b** and **S1**/**S2**-analogs



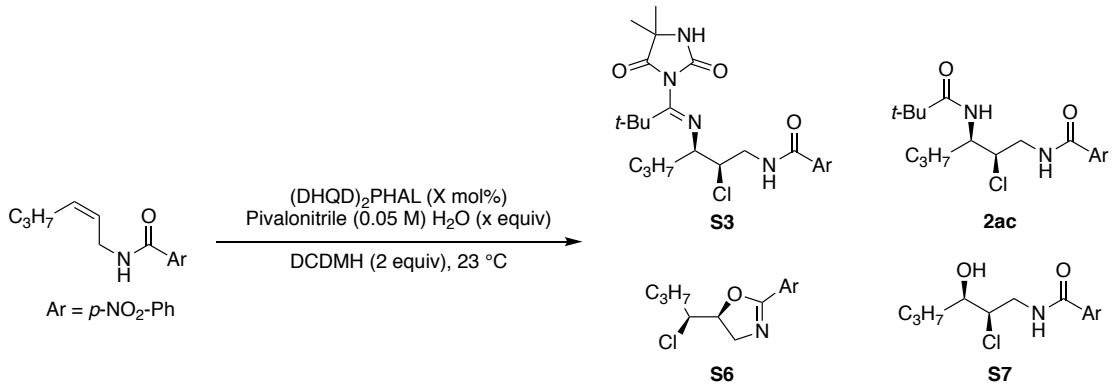




	S3a/b-analog	**S1**-analog	**S2**-analog
1	151.7	153.3	151.7
2	173.5	176.3	179.0
3	155.6	190.2	166.0
4	40.6	36.4	35.6
5	22.4	19.3	18.5
6	57.3	63.9	58.0
7	25.5	24.5	24.5

VIII Catalyst Control of Product Formation:

Table S4. Catalyzed vs non-catalyzed chloroamidation in absence and presence of water.



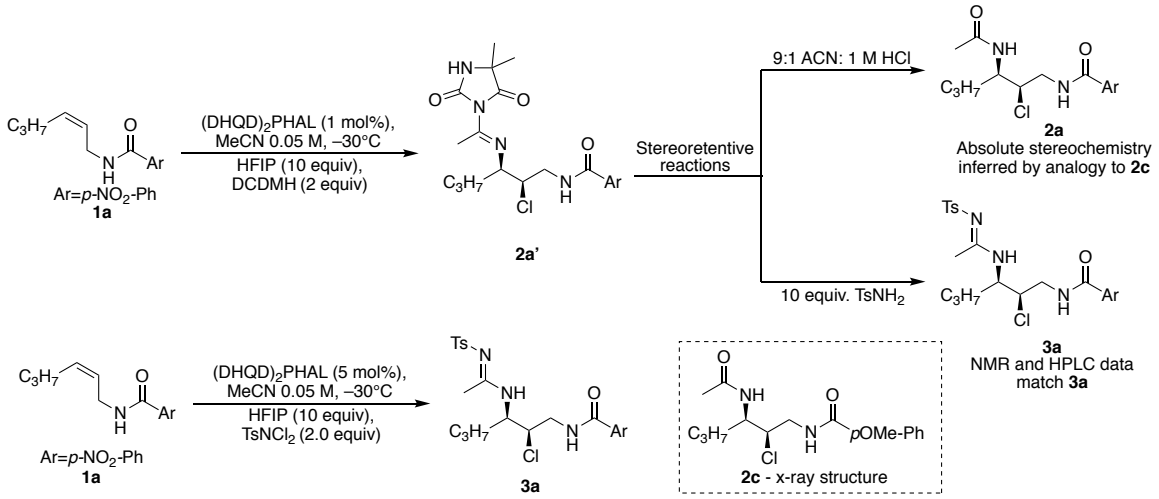
Entry	Catalyst loading (mol %)	H_2O (equiv)	**S3**:**2ac**:**S6**:**S7**
1	0	0	0:37:63:0
2	10	0	83:6:11:0
3	10	10	64:11:11:14
4	10	20	31:5:4:60
5	10	40	25:5:4:66

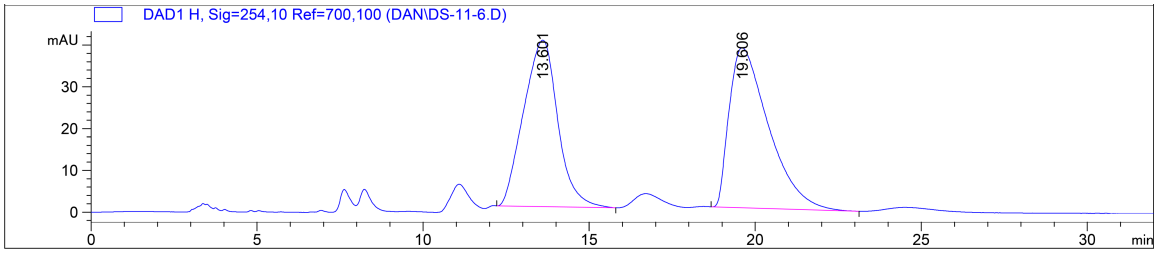
As discussed in Section VII, under standard reaction conditions the Lewis base of the chlorenium donor traps the nitrilium ion intermediate (entry 1) to yield **S3** before acid workup. However, when **1a** was exposed to pivalonitrile and DCDMH without $(DHQD)_2PHAL$ (entry 2), **S3** was not observed. In fact, Ritter product **2ac**, the result of trapping the nitrilium ion by water, along with the cyclized **S6**, product of the non-Ritter intramolecular pathway were isolated. This divergent reaction path hints at an associative complex between the $(DHQD)_2PHAL$ and DCDMH. [3]

IX Procedure for the Determination of the Absolute and Relative Stereochemistry of Vicinal Chlorosulfonylamidine Products:

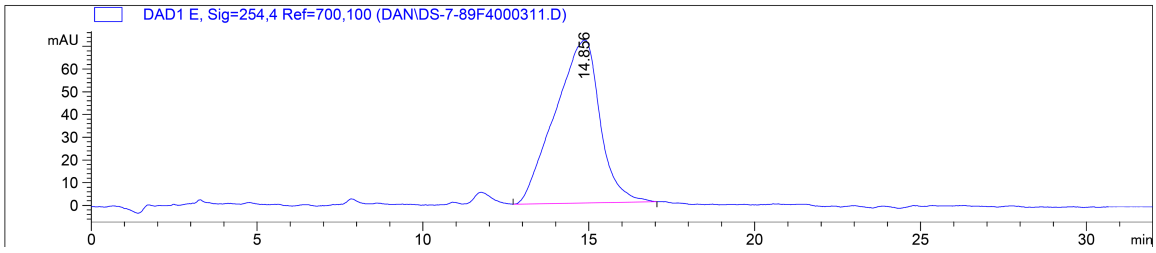
The absolute and relative stereochemistry of chloroamide products **2c** and **2i** were determined by single crystal X-ray diffraction. The stereochemistry of other chloroamide products were inferred. We were unable to obtain crystals for vicinal chlorosulfonylamidine products and resorted to chemical transformations. We observed that the Ritter intermediate **2a'** obtained from the hydantoin mediated reaction could be converted to the sulfonylamidine product **3a** with the addition of para-toluene sulfonamide (10 equiv) in a stereoretentive reaction. The HPLC trace for **3a** obtained by the procedure

described in Section **III** and the HPLC trace of presumed **3a**, obtained via the derivatization of **2a'** matched, and thus confirmed the absolute stereochemistry of **3a** as illustrated. The relative and absolute stereochemistries of **3h**, **3p**, **3s**, **4h**, **5a**, **6a**, **7a**, and **8a** were inferred as a result of this observation.

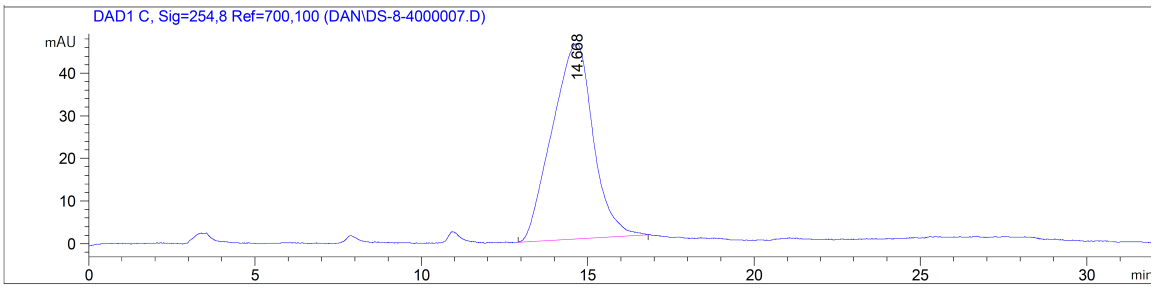




HPLC trace of **3a** and *ent*-**3a**



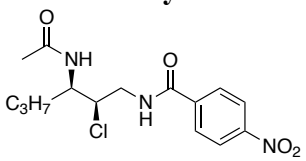
HPLC trace of **3a** following procedure for the chlorosulfonylamidation of allyl amides.



HPLC trace of **3a** obtained from derivatization of **2a'**

X Analytical Data:

a. Analytical data for vicinal chloroamide products:



2a, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)-4-nitrobenzamide

Compound **2a** (30.7 mg, 90% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1a** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.14 (60% EtOAC/Hex)

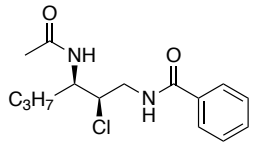
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.27 (m, 3H), 8.08 (d, *J* = 8.6 Hz, 2H), 5.72 (d, *J* = 9.3 Hz, 1H), 4.38 – 4.25 (m, 2H), 4.13 (ddd, *J* = 11.0, 5.2, 1.7 Hz, 1H), 2.93 (ddd, *J* = 13.7, 11.0, 4.3 Hz, 1H), 2.15 (s, 3H), 1.67 (dtd, *J* = 13.8, 8.6, 6.7 Hz, 1H), 1.61 – 1.52 (m, 1H), 1.41 – 1.32 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 164.8, 149.7, 139.2, 128.4, 123.9, 61.2, 49.4, 42.6, 34.7, 23.3, 19.3, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 10% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=10.6 min, RT 2 (minor) =12.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{21}ClN_3O4$: 342.1221; Found: 342.1223

Optical activity: $[\alpha]_D^{20}$ = -35.2 (c = 0.4, $CHCl_3$, 99% *ee*)



2b, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)benzamide

Compound **2b** (24.1 mg, 81% yield, 98% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1b** (20.3 mg, 0.10 mmol) as starting material.

R_f: 0.16 (50% EtOAC/Hex)

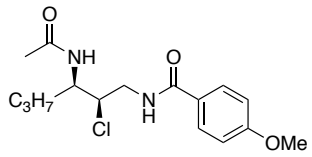
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.7, 4.5 Hz, 1H),7.92 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 5.69 (d, *J* = 9.4 Hz, 1H), 4.43 – 4.22 (m, 2H), 4.15 (ddd, *J* = 10.8, 5.1, 1.7 Hz, 1H), 2.93 (ddd, *J* = 13.6, 10.8, 4.5 Hz, 1H), 2.14 (s, 3H), 1.69 – 1.60 (m, 1H), 1.54 (dtd, *J* = 13.6, 7.9, 5.5 Hz, 1H), 1.36 (dq, *J* = 15.0, 7.6 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 167.0, 133.7, 131.7, 128.6, 127.1, 61.7, 49.2, 42.5, 34.8, 23.2, 19.2, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 10% IPA/Hexane 1ml/min, 254nm, RT 1 (major)=8.8 min, RT 2 (minor) =10.2 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{22}ClN_2O_2$: 297.1370; Found: 297.1369

Optical Activity: $[\alpha]_D^{20}$ = -31.2 (c = 0.40, $CHCl_3$, 98% *ee*)



2c, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)-4-methoxybenzamide

Compound **2c** (29.0 mg, 89% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1c** (22.3 mg, 0.10 mmol) as starting material.

R_f: 0.12 (50% EtOAC/Hex)

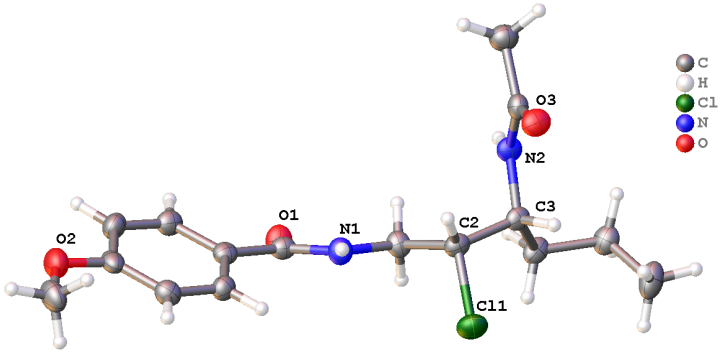
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.58 (d, *J* = 9.5 Hz, 1H), 4.38 – 4.24 (m, 2H), 4.14 (ddd, *J* = 10.8, 5.2, 1.7 Hz, 1H), 3.85 (s, 3H), 2.90 (ddd, *J* = 13.7, 10.8, 4.5 Hz, 1H), 2.14 (s, 3H), 1.68 – 1.60 (m, 1H), 1.54 (dtd, *J* = 13.7, 7.9, 5.5 Hz, 1H), 1.37 (ddd, *J* = 15.0, 8.0, 6.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 166.6, 162.3, 129.0, 126.0, 113.8, 61.8, 55.4, 49.2, 42.4, 34.8, 23.3, 19.3, 13.7.

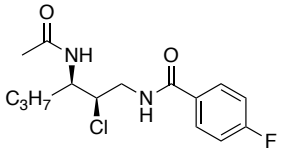
Resolution of enantiomers: DAICEL Chiralpak®, IA 10% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=13.9 min, RT 2 (minor) =17.8 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{16}H_{24}ClN_2O_3$: 327.1476; Found: 327.1475

Optical activity: $[\alpha]_D^{20}$ = -19.8 (c = 0.10, $CHCl_3$, 99% *ee*)



Single colorless needle-shaped crystals of **2c** were obtained from a mixture of methanol and hexanes by slow evaporation in a silicone coated NMR tube.



2d, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)-4-fluorobenzamide

Compound **2d** (26.7 mg, 85% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1d** (22.1 mg, 0.10 mmol) as starting material.

R_f: 0.25 (50% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.6, 4.4 Hz, 1H), 7.93 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 5.69 (d, *J* = 9.4 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.13 (ddd, *J* = 10.9, 5.1, 1.7 Hz, 1H), 2.90 (ddd, *J* = 13.6, 10.9, 4.4 Hz, 1H), 2.14 (s, 3H), 1.70 – 1.59 (m, 1H), 1.60 – 1.49 (m, 1H), 1.41 – 1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 165.9, 164.9 (d, *J* = 251.8 Hz).

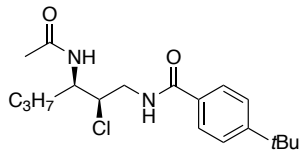
129.9 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 9.0 Hz), 115.7 (d, *J* = 21.9 Hz), 61.5, 49.2, 42.5, 34.8, 23.3, 19.3, 13.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ -108.06.

Resolution of enantiomers: DAICEL Chiralpak®, IA 5% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=20.9 min, RT 2 (minor) =22.1 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{21}ClN_2O_2$: 315.1276; Found: 315.1274

Optical Activity: $[\alpha]_D^{20}$ = -23.9 (c = 0.10, $CHCl_3$, 99% *ee*)



2e, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)-4-(*tert*-butyl)benzamide

Compound **2e** (27.8 mg, 79% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1e** (25.9 mg, 0.10 mmol) as starting material.

R_f: 0.21 (70% EtOAC/Hex)

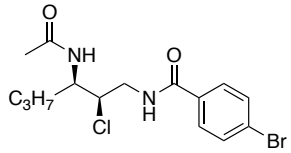
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 5.59 (s, 1H), 4.37 – 4.24 (m, 2H), 4.19 – 4.05 (m, 1H), 2.91 (ddd, *J* = 13.6, 10.8, 4.5 Hz, 1H), 2.13 (s, 3H), 1.68 – 1.58 (m, 1H), 1.53 (dtd, *J* = 13.6, 7.9, 5.5 Hz, 1H), 1.38-1.32 (m, 2H), 1.32 (s, 9H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 171.7, 166.9, 155.1, 130.9, 127.0, 125.6, 61.8, 49.2, 42.4, 34.9, 34.9, 31.2, 23.3, 19.3, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, IA 10% IPA/Hexane 1ml/min, 254nm, RT 1 (major)=8.2 min, RT 2 (minor) =11.7 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{30}ClN_2O_2$: 353.1996; Found: 353.1989

Optical activity: $[\alpha]_D^{20}$ = -27.1 (c = 0.10, $CHCl_3$, 99% *ee*)



2f, *N*-((2*R*,3*R*)-3-acetamido-2-chlorohexyl)-4-bromobenzamide

R_f: 0.21 (50% EtOAC/Hex)

Compound **2f** (34.2 mg, 91% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1f** (28.2 mg, 0.10 mmol) as starting material.

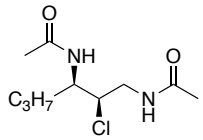
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.6, 4.7 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 5.65 (d, *J* = 9.4 Hz, 1H), 4.29 (ddd, *J* = 13.7, 8.8, 5.2 Hz, 2H), 4.12 (ddd, *J* = 10.9, 5.1, 1.7 Hz, 1H), 2.90 (ddd, *J* = 13.5, 10.9, 4.4 Hz, 1H), 2.14 (s, 3H), 1.70 – 1.59 (m, 1H), 1.54 (dtd, *J* = 13.6, 7.8, 5.5 Hz, 1H), 1.36 (h, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 166.0, 132.5, 131.9, 128.8, 126.5, 61.5, 49.2, 42.5, 34.8, 23.3, 19.3, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 15% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=6.1 min, RT 2 (minor) =7.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{21}BrClN_2O_2$: 375.0475; Found: 375.0473

Optical activity: $[\alpha]_D^{20}$ = -13.2 (c = 0.40, $CHCl_3$, 99% *ee*)



2g, *N*,*N*'-((2*R*,3*R*)-2-chlorohexane-1,3-diyl)diacetamide

Compound **2g** (13.6 mg, 58% yield, 94% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1g** (14.1 mg, 0.10 mmol) as starting material.

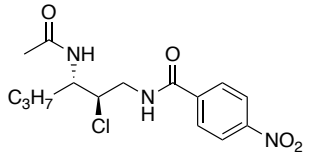
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 5.57 (d, *J* = 9.5 Hz, 1H), 4.25 (tdd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 4.07 – 3.90 (m, 2H), 2.85 – 2.68 (m, 1H), 2.07 (s, 3H), 2.00 (s, 3H), 1.67 – 1.57 (m, 1H), 1.58 – 1.48 (m, 1H), 1.36 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 170.4, 61.9, 49.0, 42.39, 35.9, 23.3, 23.2, 19.2, 13.7.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 8% IPA/Hexane 1 ml/min, 214 nm, RT 1 (minor)=10.5 min, RT 2 (major) =11.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{10}H_{20}ClN_2O_2$: 235.1213; Found: 235.1208

Optical activity: $[\alpha]_D^{20}$ = -22.3 (c = 0.10, $CHCl_3$, 94% *ee*)



2h, *N*-((2*R*,3*S*)-3-acetamido-2-chlorohexyl)-4-nitrobenzamide

Compound **2h** (27.7 mg, 81% yield, 97% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1h** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.16 (50% EtOAC/Hex)

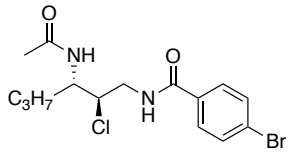
^{1}H NMR (500 MHz, C_2D_6SO) δ 9.05 (t, *J* = 5.7 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 4.23 (dt, *J* = 8.3, 4.9 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.70 (dt, *J* = 14.0, 5.2 Hz, 1H), 3.48 (ddd, *J* = 14.3, 8.4, 6.1 Hz, 1H), 1.85 (s, 3H), 1.61 (dddd, *J* = 12.9, 9.6, 6.7, 2.9 Hz, 1H), 1.51 – 1.41 (m, 1H), 1.41 – 1.32 (m, 1H), 1.29 – 1.13 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, C_2D_6SO) δ 169.5, 164.8, 149.1, 149.8, 128.7, 123.7, 64.8, 50.6, 43.2, 30.8, 22.5, 18.8, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 10% IPA/Hexane 1ml/min, 254 nm, RT 1 (minor)=10.8 min, RT 2 (major) =12.0 min. (97% *ee*)

HRMS analysis (ESI): calculated for [M+H]+: $C_{15}H_{21}ClN_3O_4$: 342.1221; Found: 342.1220.

Optical activity: $[\alpha]_D^{20}$ = +63.3 (c = 0.4, $CHCl_3$, 97% *ee*)



2i, *N*-((2*R*,3*S*)-3-acetamido-2-chlorohexyl)-4-bromobenzamide

Compound **2i** (22.1 mg, 59% yield, 95% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1i** (28.2 mg, 0.10 mmol) as starting material.

R_f: 0.23 (70% EtOAC/Hex)

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.80 (t, *J* = 5.7 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 4.22 (dt, *J* = 8.1, 5.0 Hz, 1H), 4.06 – 3.97

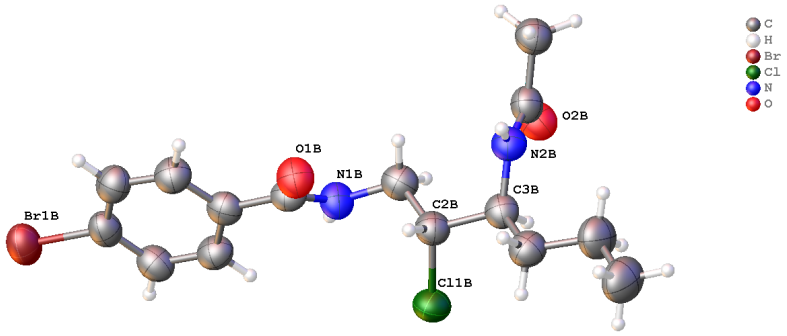
(m, 1H), 3.68 (dt, *J* = 14.0, 5.3 Hz, 1H), 3.44 (ddd, *J* = 14.2, 8.2, 6.1 Hz, 1H), 1.85 (s, 3H), 1.62 (dddd, *J* = 12.8, 9.5, 6.6, 2.9 Hz, 1H), 1.51 – 1.42 (m, 1H), 1.36 (dd, *J* = 6.5, 3.1 Hz, 1H), 1.28 – 1.18 (m, 1H), 0.7 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 169.5, 165.5, 133.3, 131.4, 129.3, 125.1, 64.9, 50.5, 43.0, 30.8, 22.5, 18.8, 13.7.

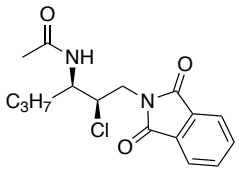
Resolution of enantiomers: DAICEL Chiralpak®, ad-h 10% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=8.1 min, RT 2 (minor) =10.2 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{21}BrClN_2O_2$: 375.0475; Found: 375.0477

Optical activity: $[\alpha]_D^{20}$ = +32.8 (c = 0.1, $CHCl_3$, 96% *ee*)



Single colorless needle-shaped crystals of **2i** were recrystallized from a mixture of dichloromethane and hexanes by slow evaporation in a silicone coated NMR tube.



2j, *N*-((2*R*,3*R*)-2-chloro-1-(1,3-dioxoisoindolin-2-yl)hexan-3-yl)acetamide

Compound **2j** (19.1 mg, 67% yield, 29% *ee*) was synthesized following the procedure detailed in Section **IIb** using **1j** (22.9 mg, 0.10 mmol) as starting material.

R_f: 0.21 (50% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.61 (d, *J* = 9.7 Hz, 1H), 4.58 (ddd, *J* = 10.2, 4.2, 1.8 Hz, 1H), 4.43 (dddd, *J* = 10.1,

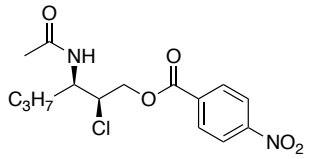
8.2, 5.9, 1.8 Hz, 1H), 4.02 (dd, *J* = 14.5, 10.2 Hz, 1H), 3.91 (dd, *J* = 14.5, 4.2 Hz, 1H), 2.10 (s, 3H), 1.67 – 1.53 (m, 2H), 1.44 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 168.0, 134.2, 131.8, 123.5, 63.0, 49.7, 42.5, 35.8, 23.4, 19.0, 13.8.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 10% IPA/Hexane 1 ml/min, 230 nm, RT 1 (minor)=13.0 min, RT 2 (major) = 15.8 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{16}H_{20}ClN_2O_3$: 323.1162; Found: 323.1162

Optical activity: $[\alpha]_D^{20}$ = +2.1 (c = 0.10, $CHCl_3$, 29% *ee*)



2k, (2*S*,3*R*)-3-acetamido-2-chlorohexyl 4-nitrobenzoate

Compound **2k** (23.3 mg, 68% yield, 60% *ee*) was synthesized following the procedure detailed in Section **IIb** using **1k** (24.9 mg, 0.10 mmol) as starting material.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 5.50 (d, *J* = 9.7 Hz, 1H), 4.57 – 4.43 (m, 3H), 4.35 (ddd, *J* = 7.6, 6.5, 1.8 Hz, 1H), 2.05 (s, 3H), 1.71 – 1.52 (m, 2H), 1.44 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

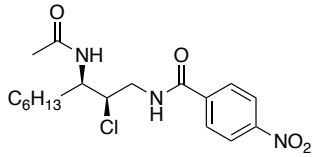
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 164.1, 150.7, 135.0, 131.0, 123.7, 66.1, 62.0, 48.7, 35.3, 23.3, 19.1, 13.8.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=11.6 min, RT 2 (minor) =15.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{15}H_{20}ClN_2O_5$: 343.1061; Found: 343.1058

Optical activity: $[\alpha]_D^{20}$ = +3.0 (c = 0.1, $CHCl_3$, 60% *ee*)

R_f: 0.23 (50% EtOAC/Hex)



2m, *N*-((2*R*,3*R*)-3-acetamido-2-chlorononyl)-4-nitrobenzamide

R_f: 0.22 (50% EtOAC/Hex).

Compound **2m** (30.3 mg, 79% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1m** (29.0 mg, 0.10 mmol) as starting material.

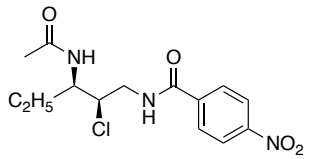
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.23 (m, 3H), 8.08 (d, *J* = 8.8 Hz, 2H), 5.58 (d, *J* = 9.4 Hz, 1H), 4.34 (ddd, *J* = 13.8, 8.8, 5.2 Hz, 1H), 4.26 (tdd, *J* = 8.7, 5.7, 1.7 Hz, 1H), 4.13 (ddd, *J* = 11.1, 5.2, 1.7 Hz, 1H), 2.92 (ddd, *J* = 13.7, 11.0, 4.3 Hz, 1H), 2.15 (s, 3H), 1.71 – 1.54 (m, 2H), 1.36 – 1.16 (m, 8H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 164.8, 149.7, 139.2, 128.4, 123.9, 61.1, 49.7, 42.5, 32.8, 31.5, 28.9, 26.0, 23.3, 22.5, 14.0.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 4% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=28.1 min, RT 2 (major) =31.0 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{27}ClN_3O_4$: 384.1690; Found: 384.1688

Optical activity: $[\alpha]_D^{20}$ = -35.3 (c = 0.20, $CHCl_3$, 99% *ee*)



2n, *N*-((2*R*,3*R*)-3-acetamido-2-chloropentyl)-4-nitrobenzamide

Compound **2n** (23.3 mg, 73% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1n** (23.4 mg, 0.10 mmol) as starting material.

R_f: 0.16 (50% EtOAC/Hex)

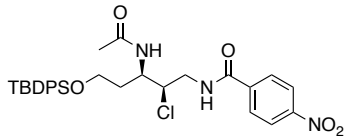
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.27 (m, 3H), 8.10 (d, *J* = 9.0 Hz, 2H), 5.62 (d, *J* = 9.3 Hz, 1H), 4.35 (ddd, *J* = 13.8, 8.8, 5.1 Hz, 1H), 4.23 – 4.09 (m, 2H), 2.94 (ddd, *J* = 13.6, 11.0, 4.3 Hz, 1H), 2.17 (s, 3H), 1.78 – 1.58 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 164.8, 149.7, 139.2, 128.4, 123.9, 60.8, 51.3, 42.5, 25.9, 23.3, 10.6.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 15% IPA/Hexane 1 ml/min, 214 nm, RT 1 (major)=7.8 min, RT 2 (minor) =9.4 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{14}H_{19}ClN_3O_4$: 328.1064; Found: 328.1061

Optical activity: $[\alpha]_D^{20}$ = -40.5 (c = 0.2, $CHCl_3$, 99% *ee*)



2o, *N*-((2*R*,3*R*)-3-acetamido-5-((*tert*-butyldiphenylsilyl)oxy)-2-chloropentyl)-4-nitrobenzamide

Compound **2o** (36.1 mg, 62% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1o** (48.8 mg, 0.10 mmol) as starting material.

R_f: 0.36 (50% EtOAC/Hex)

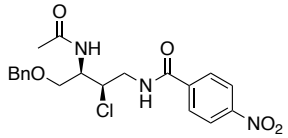
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.9, 4.2 Hz, 1H), 8.25 (d, *J* = 8.9 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.51-7.55 (m, *J* = 9.7, 6.7, 1.5 Hz, 4H), 7.45 – 7.39 (m, 2H), 7.39-7.34 (m, 4H), 5.61 (d, *J* = 9.3 Hz, 1H), 4.77 (dtd, *J* = 8.9, 6.9, 1.7 Hz, 1H), 4.40 (ddd, *J* = 13.9, 8.9, 5.1 Hz, 1H), 4.17 (ddd, *J* = 11.2, 5.1, 1.7 Hz, 1H), 3.76 – 3.58 (m, 2H), 2.93 (ddd, *J* = 13.7, 11.2, 4.2 Hz, 1H), 2.11 (s, 3H), 1.84 (q, *J* = 6.4 Hz, 2H), 0.89 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 164.7, 149.7, 139.1, 135.5, 135.4, 133.0, 133.0, 129.8, 129.8, 128.4, 127.8, 127.8, 123.8, 61.5, 59.5, 46.4, 42.4, 35.6, 26.7, 23.3, 19.0.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 7% IPA/Hexane 1ml/min, 254nm, RT 1 (minor)=21.5 min, RT 2 (major) =26.4 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{30}H_{37}ClN_3O_5Si$: 582.2191; Found: 582.2188

Optical activity: $[\alpha]_D^{20}$ = -173.2 (c = 0.05, $CHCl_3$, 99% *ee*)



2p, *N*-((2*R*,3*R*)-3-acetamido-4-(benzyloxy)-2-chlorobutyl)-4-nitrobenzamide

The substrate **1p** (32.6 mg, 0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (1.6 mg, 2 mol%) were suspended in acetonitrile (1 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was stirred at 23 °C. After stirring for 10 min DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and $(DHQD)_2PHAL$ (1.6 mg, 2 mol%) was added every 12 h until the reaction reached completion. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 4 mL). The combined organics were concentrated. To the concentrated product in the vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **2p** in a 23 % yield (9.7 mg, 99% *ee*)

R_f: 0.10 (50% EtOAC/Hex)

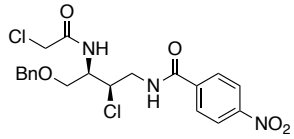
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.19 – 8.12 (m, 1H), 8.08 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.27 (m, 5H), 5.73 (d, *J* = 9.2 Hz, 1H), 4.62 – 4.44 (m, 3H), 4.38 – 4.25 (m, 2H), 3.59 (d, *J* = 6.8 Hz, 2H), 3.00 (ddd, *J* = 15.2, 12.1, 4.5 Hz, 1H), 2.14 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 164.8, 149.7, 139.2, 137.2, 128.6, 128.4, 128.1, 127.9, 123.8, 73.5, 69.3, 58.5, 49.4, 42.2, 23.3.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 10% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=42.7 min, RT 2 (minor) =66.8 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{20}H_{23}ClN_3O_5$: 420.1326; Found: 420.1328

Optical activity: $[\alpha]_D^{20}$ = -21.5 (c = 0.1, $CHCl_3$, 99% *ee*)



2p', *N*-((2*R*,3*R*)-4-(benzyloxy)-2-chloro-3-(2-chloroacetamido)butyl)-4-nitrobenzamide
The substrate **1p** (32.6 mg, 0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (1.6 mg, 2 mol%) were suspended in acetonitrile (1 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was stirred at 23 °C. After stirring for 10 min DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and $(DHQD)_2PHAL$ (1.6 mg 2 mol%) was added every 12 h until the reaction reached completion. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 4 mL). The combined organics were concentrated. To the concentrated product in the vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided product **2p'** in a 20.8 mg yield (46% yield, 99% *ee*).

R_f: 0.35 (50% EtOAC/Hex)

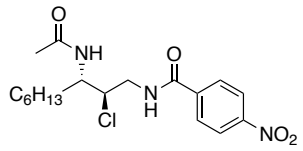
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.77 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.38 – 7.29 (m, 5H), 6.78 (d, *J* = 9.3 Hz, 1H), 4.61 – 4.51 (m, 3H), 4.40 (ddd, *J* = 10.2, 5.6, 2.0 Hz, 1H), 4.26 (ddd, *J* = 13.9, 8.2, 5.7 Hz, 1H), 4.17 (d, *J* = 1.9 Hz, 2H), 3.65 (d, *J* = 6.7 Hz, 2H), 3.09 (ddd, *J* = 13.9, 10.2, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 164.9, 149.8, 139.1, 137.1, 128.6, 128.4, 128.1, 127.8, 123.9, 73.6, 69.0, 58.2, 50.0, 42.4, 42.4.

Resolution of enantiomers: DAICEL Chiralpak®, IA 20% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=11.8 min, RT 2 (minor) =15.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{20}H_{22}Cl_2N_3O_5$: 454.0937; Found: 454.0938

Optical activity: $[\alpha]_D^{20}$ = +15.1 (c = 0.1, $CHCl_3$, 99% *ee*)



2q, *N*-((2*R*,3*S*)-3-acetamido-2-chlorononyl)-4-nitrobenzamide

R_f: 0.28 (70% EtOAC/Hex)

Compound **2q** (31.7 mg, 83% yield, 94% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1q** (29.0 mg, 0.10 mmol) as starting material.

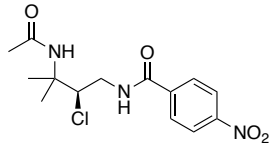
^{1}H NMR (500 MHz, C_2D_6SO) δ 9.04 (t, *J* = 5.7 Hz, 1H), 8.33 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 4.22 (dt, *J* = 8.3, 4.9 Hz, 1H), 4.10 – 3.89 (m, 1H), 3.69 (dt, *J* = 14.1, 5.2 Hz, 1H), 3.48 (ddd, *J* = 14.3, 8.4, 6.1 Hz, 1H), 1.85 (s, 3H), 1.60-1.68 (m, 1H), 1.53 – 1.40 (m, 1H), 1.37 – 1.15 (m, 8H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, C_2D_6SO) δ 170.0, 165.3, 149.6, 140.2, 129.2, 124.1, 65.2, 51.3, 43.5, 31.6, 29.2, 28.9, 25.9, 22.9, 22.5, 14.4.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 5% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=17.1 min, RT 2 (minor) =23.0 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{27}ClN_3O_4$: 384.1690; Found: 384.1689

Optical activity: $[\alpha]_D^{20}$ = +72.1 (c = 0.20, $CHCl_3$, 95% *ee*)



2r, (*R*)-*N*-(3-acetamido-2-chloro-3-methylbutyl)-4-nitrobenzamide

Compound **2r** (25.9 mg, 79% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1r** (23.4 mg, 0.10 mmol) as starting material.

R_f: 0.13 (70% EtOAC/Hex)

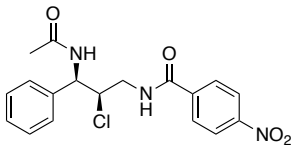
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 1H), 5.54 (s, 1H), 4.90 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.21 – 4.10 (m, 1H), 3.57 – 3.47 (m, 1H), 1.98 (s, 3H), 1.54 (s, 3H), 1.50 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 165.5, 149.7, 139.6, 128.2, 123.9, 66.6, 56.6, 42.9, 24.5, 24.4, 24.0.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 10% IPA/Hexane 1 ml/min, 254nm, RT 1 (major)=17.5 min, RT 2 (minor) =22.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{14}H_{19}ClN_3O_4$: 328.1064; Found: 328.1064

Optical activity: $[\alpha]_D^{20}$ = +62.4 (c = 0.10, $CHCl_3$, 99 % *ee*)



2s, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-phenylpropyl)-4-nitrobenzamide

Compound **2s** (35.6 mg, 95% yield, 65:35 *dr*, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1s** (28.2 mg, 0.10 mmol) as starting material.

R_f: 0.11 (50% EtOAC/Hex)

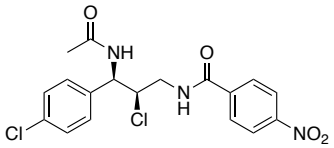
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 2H), 8.11 (m, 3H), 7.42 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 6.29 (d, *J* = 9.7 Hz, 1H), 5.63 (dd, *J* = 9.6, 1.8 Hz, 1H), 4.56 (ddd, *J* = 10.5, 5.4, 1.8 Hz, 1H), 4.39 (ddd, *J* = 13.8, 8.3, 5.4 Hz, 1H), 3.14 (ddd, *J* = 13.8, 10.5, 4.7 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 165.0, 149.8, 139.1, 137.1, 128.8, 128.4, 128.3, 126.6, 123.9, 61.2, 52.2, 43.0, 23.4.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 20% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=12.1 min, RT 2 (minor) = 16.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{19}ClN_3O_4$: 376.1064; Found: 376.1057.

Optical activity: $[\alpha]_D^{20}$ = -33.5 (c = 0.2, $CHCl_3$, 99% *ee*)



2t, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-(4-chlorophenyl)propyl)-4-nitrobenzamide

Compound **2t** (37.6 mg, 92% yield, 64:36 *dr*, 97% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1t** (31.6 mg, 0.10 mmol) as starting material.

R_f: 0.08 (50% EtOAC/Hex)

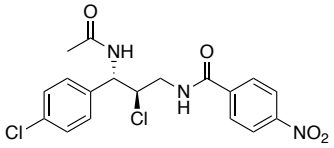
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 8.01 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.23 (m, 2H), 6.29 (d, *J* = 9.7 Hz, 1H), 5.61 (dd, *J* = 9.8, 1.9 Hz, 1H), 4.52 (ddd, *J* = 10.3, 5.5, 1.9 Hz, 1H), 4.35 (ddd, *J* = 13.8, 8.1, 5.4 Hz, 1H), 3.14 (ddd, *J* = 13.9, 10.3, 4.8 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 165.1, 149.8, 138.9, 135.6, 134.2, 129.0, 128.4, 128.1, 123.9, 61.0, 51.7, 43.0, 23.4.

Resolution of enantiomers: DAICEL Chiralpak®, IA 20% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=10.8 min, RT 2 (major) =17.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{18}Cl_2N_3O_4$: 410.0674; Found: 410.0668.

Optical activity: $[\alpha]_D^{20}$ = -28.2 (c = 0.2, $CHCl_3$, 97% *ee*)



2t-Diastereomer, *N*-((2*R*,3*S*)-3-acetamido-2-chloro-3-(4-chlorophenyl)propyl)-4-nitrobenzamide

R_f: 0.15 (70% EtOAC/Hex)

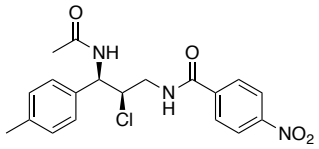
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.55 (dd, *J* = 8.3, 3.9 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.26 (d, *J* = 8.7 Hz, 1H), 5.23 (t, *J* = 8.5 Hz, 1H), 4.46 – 4.37 (m, 2H), 3.34 (ddd, *J* = 15.4, 5.9, 3.8 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 165.6, 149.7, 139.4, 136.1, 134.7, 129.3, 128.9, 128.3, 123.9, 62.0, 55.6, 42.7, 23.4.

Resolution of enantiomers: DAICEL Chiralcel®, OJ-H 8% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=22.2 min, RT 2 (minor) =31.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{18}Cl_2N_3O_4$: 410.0674; Found: 410.0666.

Optical activity: $[\alpha]_D^{20}$ = +90.8 (c = 0.2, $CHCl_3$, 98% *ee*)



2u, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-(*p*-tolyl)propyl)-4-nitrobenzamide

Compound **2u** (30.3 mg, 78% yield, 50:50 *dr*, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1u** (29.6 mg, 0.10 mmol) as starting material.

R_f: 0.08 (50% EtOAC/Hex)

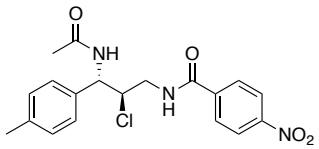
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.13 (dd, *J* = 8.3, 4.8 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.19 (s, 4H), 6.27 (d, *J* = 9.7 Hz, 1H), 5.57 (d, *J* = 9.7 Hz, 1H), 4.52 (ddd, *J* = 10.5, 5.4, 1.9 Hz, 1H), 4.37 (ddd, *J* = 13.8, 8.3, 5.4 Hz, 1H), 3.11 (ddd, *J* = 13.8, 10.5, 4.7 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 165.0, 149.8, 139.1, 138.1, 134.0, 129.5, 128.4, 126.5, 123.9, 61.3, 52.0, 43.0, 23.4, 21.0.

Resolution of enantiomers: DAICEL Chiralpak®, IA 15% IPA/Hexane 1 ml/min, 254nm, RT 1 (minor)=17.6 min, RT 2 (major) = 23.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{21}ClN_3O_4$: 390.1221; Found: 390.1214.

Optical activity: $[\alpha]_D^{20}$ = +157.3 (c = 0.1, $CHCl_3$, 99% *ee*)



2u-Diastereomer, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-(*p*-tolyl)propyl)-4-nitrobenzamide

R_f: 0.22 (70% EtOAC/Hex)

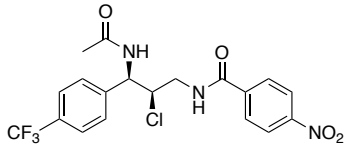
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.17 (m, 4H), 6.00 (d, *J* = 8.4 Hz, 1H), 5.19 (t, *J* = 8.7 Hz, 1H), 4.50 (ddd, *J* = 14.5, 8.9, 3.5 Hz, 1H), 4.43 (ddd, *J* = 8.5, 4.7, 3.5 Hz, 1H), 3.37 (ddd, *J* = 14.6, 4.7, 3.7 Hz, 1H), 2.37 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 165.5, 149.7, 139.6, 138.8, 134.6, 129.8, 128.4, 127.3, 123.8, 62.2, 56.1, 42.5, 23.4, 21.2.

Resolution of enantiomers: DAICEL Chiralcel®, OJ-H 5% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=39.7 min, RT 2 (minor) =49.4 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{21}ClN_3O_4$: 390.1221; Found: 390.1212.

Optical activity: +80.1 (90% *ee*) (c = 0.1, $CHCl_3$, 99% *ee)*



2v, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-(4-(trifluoromethyl)phenyl)propyl)-4-nitrobenzamide

The substrate **1v** (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (1.6 mg, 2 mol%) were suspended in acetonitrile (1 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was stirred at 23 °C. After stirring for 10 min DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and $(DHQD)_2PHAL$ (1.6 mg 2 mol%) was added every 12 h until the reaction reached completion. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 4 mL). The combined organics were concentrated. To the concentrated product in the vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was concentrated and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **2v** (5.1 mg, 12% yield, 89% *ee*).

R_f: 0.28 (50% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.95 (t, *J* = 6.8 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.27 (d, *J* = 9.9 Hz, 1H), 5.71 (d, *J* = 9.8 Hz, 1H), 4.58 (ddd, *J* = 10.3, 5.5, 1.8 Hz, 1H), 4.39 (ddd, *J* = 13.8, 8.2, 5.5 Hz, 1H), 3.17 (ddd, *J* = 13.7, 10.3, 4.8 Hz, 1H), 2.28 (s, 3H).

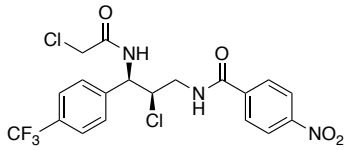
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 165.1, 149.9, 140.6, 138.5, 130.8 (q, J_{CF} = 31.25 Hz), 128.4, 127.1, 125.7 (q, J_{CF} = 3.75 Hz), 123.8 (q, J_{CF} = 145.00 Hz), 124.0, 60.9, 51.9, 43.1, 23.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.72.

Resolution of enantiomers: DAICEL Chiralcel®, IA 20% IPA/Hexane 1 ml/min, 254nm, RT 1 (minor)=8.4 min, RT 2 (major) =15.1 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{18}ClF_3N_3O_4$: 444.0938; Found: 444.0932.

Optical activity: $[\alpha]_D^{20}$ = -18.2 (c = 0.1, $CHCl_3$, 89% *ee*)



2v', *N*-((2*R*,3*R*)-2-chloro-3-(2-chloroacetamido)-3-(4-(trifluoromethyl)phenyl)propyl)-4-nitrobenzamide

The substrate **1v** (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (1.6 mg, 2 mol%) were suspended in acetonitrile (1 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was stirred at 23 °C. After stirring for 10 min DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and $(DHQD)_2PHAL$ (1.6 mg 2 mol%) was added every 12 h until the reaction reached completion. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 4 mL). The combined organics were concentrated. To the concentrated product in the vial with a stir bar, acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added and stirred for 15 min. Water (3 mL) was added and the solution was

concentrated and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **2v'** (30.5 mg, 64% yield, 87% *ee*).

R_f: 0.54 (50% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 3H), 5.67 (d, *J* = 9.7 Hz, 1H), 4.62 (ddd, *J* = 8.8, 6.1, 2.1 Hz, 1H), 4.27 (d, *J* = 5.0 Hz, 2H), 4.26 – 4.19 (m, 1H), 3.34 (ddd, *J* = 14.3, 9.3, 5.3 Hz, 1H).

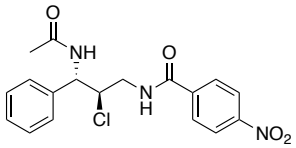
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 165.2, 149.9, 140.6, 138.8, 130.8 (q, J_{CF} = 31.25 Hz), 128.4, 127.0, 126.0 (q, J_{CF} = 3.75 Hz), 124.3 (q, J_{CF} = 145.00 Hz), 124.0, 61.2, 52.7, 43.4, 42.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.8.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=22.2 min, RT 2 (minor) =29.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{17}Cl_2F_3N_3O_4$: 478.0548; Found: 478.0558.

Optical activity: $[\alpha]_D^{20}$ = -14.3 (c = 0.1, $CHCl_3$, 87% *ee*)



2w, *N*-((2*R*,3*S*)-3-acetamido-2-chloro-3-phenylpropyl)-4-nitrobenzamide

Compound **2w** (19.8 mg, 53% yield, 74:26 *dr*, 99% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1w** (28.2 mg, 0.10 mmol) as starting material.

R_f: 0.19 (70% EtOAC/Hex)

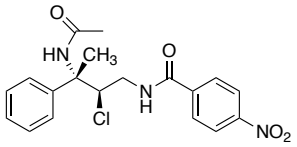
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.68 (dd, *J* = 8.7, 3.7 Hz, 1H), 7.44 – 7.31 (m, 5H), 6.16 (d, *J* = 8.5 Hz, 1H), 5.23 (t, *J* = 8.6 Hz, 1H), 4.54 – 4.39 (m, 2H), 3.47 – 3.30 (m, 1H), 2.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 165.5, 149.7, 139.6, 137.6, 129.2, 128.9, 128.4, 127.5, 123.8, 62.1, 56.3, 42.5, 23.4.

Resolution of enantiomers: DAICEL Chiralcel®, OJ-H 10% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=18.7 min, RT 2 (minor) =23.5 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{19}ClN_3O_4$: 376.1064; Found: 376.1057.

Optical activity: $[\alpha]_D^{20}$ = +86.8 (c = 0.1, $CHCl_3$, 99% *ee*)



2x, *N*-((2*R*,3*S*)-3-acetamido-2-chloro-3-phenylbutyl)-4-nitrobenzamide

R_f: 0.23 (70% EtOAC/Hex)

Compound **2x** (22.2 mg, 57% yield, 61:39 *dr*, 97% *ee*) was synthesized following the procedure detailed in Section **IIa** using **1x** (29.6 mg, 0.10 mmol) as starting material. Following column chromatography (SiO_2/EtOAc–Hexanes gradient), though inseparable by column chromatography, the diastereomers were able to be separated by HPLC (IA, 10% IPA/Hexanes).

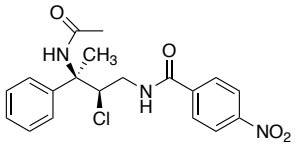
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.71 (t, *J* = 5.8 Hz, 1H), 6.13 (s, 1H), 4.90 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.85 (ddd, *J* = 14.5, 6.3, 5.2 Hz, 1H), 3.49 (ddd, *J* = 14.2, 8.0, 6.0 Hz, 1H), 2.14 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 165.2, 149.6 (HMBC correlation), 140.5, 139.2, 128.6, 128.1, 127.7, 125.9, 123.7, 67.4, 61.6, 43.5, 29.7, 24.5.

Resolution of enantiomers: DAICEL Chiralcel®, IA 10% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=15.8 min, RT 2 (minor) =18.0 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{21}ClN_3O_4$: 390.1221; Found: 390.1215.

Optical activity: $[\alpha]_D^{20}$ = -19.2 (c = 0.1, $CHCl_3$, 97% *ee*)



2x-Diastereomer-, *N*-((2*R*,3*R*)-3-acetamido-2-chloro-3-phenylbutyl)-4-nitrobenzamide

R_f: 0.23 (70% EtOAC/Hex)

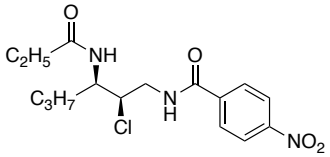
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.34 – 7.29 (m, 1H), 6.32 (t, *J* = 5.4 Hz, 1H), 6.24 (s, 1H), 4.73 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.92 (ddd, *J* = 14.4, 6.6, 3.5 Hz, 1H), 3.39 (ddd, *J* = 14.5, 9.3, 5.3 Hz, 1H), 2.04 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 165.4, 149.8, 141.2, 139.2, 128.8, 128.2, 128.1, 126.0, 123.9, 68.7, 61.4, 42.7, 24.4, 20.3.

Resolution of enantiomers: DAICEL Chiralcel®, IA 10% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=22.1 min, RT 2 (minor) =28.1 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{19}H_{21}ClN_3O_4$: 390.1221; Found: 390.1187.

Optical activity: $[\alpha]_D^{20}$ = -35.6 (c = 0.05, $CHCl_3$, 97% *ee*)



2aa, *N*-((2*R*,3*R*)-2-chloro-3-propionamidohexyl)-4-nitrobenzamide

Compound **2aa** (31.2 mg, 88% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IId** using **1a** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.29 (50% EtOAC/Hex)

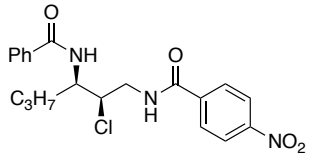
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.25 (m, 3H), 8.09 (d, *J* = 9.0 Hz, 2H), 5.56 (d, *J* = 9.3 Hz, 1H), 4.40 – 4.22 (m, 2H), 4.13 (ddd, *J* = 11.0, 5.2, 1.7 Hz, 1H), 2.89 (ddd, *J* = 13.6, 11.0, 4.3 Hz, 1H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.71 – 1.61 (m, 1H), 1.61 – 1.51 (m, 1H), 1.41 – 1.32 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 164.8, 149.7, 139.2, 128.4, 123.9, 61.2, 49.0, 42.5, 34.8, 29.9, 19.3, 13.7, 10.2.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{16}H_{23}ClN_3O_4$: 356.1377; Found: 356.1378.

Resolution of enantiomers: DAICEL Chiralpak®, AS-H 10% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=13.5 min, RT 2 (major) = 28.7 min.

Optical Activity: $[\alpha]_D^{20}$ = -40.8 (c = 0.40, $CHCl_3$, 99% *ee*)



2ab, *N*-((2*R*,3*R*)-3-benzamido-2-chlorohexyl)-4-nitrobenzamide

Compound **2ab** (35.0 mg, 86% yield, 98% *ee*) was synthesized following the procedure detailed in Section **IId** using **1a** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.65 (50% EtOAC/Hex)

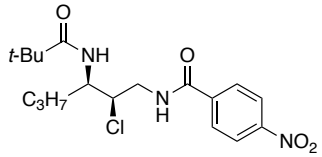
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 – 8.36 (m, 1H), 8.33 (d, *J* = 8.9 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.86 – 7.81 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 6.23 (d, *J* = 9.4 Hz, 1H), 4.53 (tdd, *J* = 9.2, 5.4, 1.7 Hz, 1H), 4.35 (ddd, *J* = 13.8, 8.7, 5.2 Hz, 1H), 4.24 (ddd, *J* = 10.9, 5.2, 1.7 Hz, 1H), 3.00 (ddd, *J* = 13.7, 10.9, 4.4 Hz, 1H), 1.81 (dtd, *J* = 14.0, 8.5, 6.6 Hz, 1H), 1.74 – 1.63 (m, 1H), 1.49 – 1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 164.9, 149.7, 139.2, 133.2, 132.4, 129.0, 128.4, 128.0, 123.9, 61.5, 50.0, 42.7, 34.9, 19.4, 13.7.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=15.4 min, RT 2 (major) =30.0 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{20}H_{23}ClN_3O_4$: 404.1377; Found: 404.1383.

Optical activity: $[\alpha]_D^{20}$ = -119.2 (c = 0.39, $CHCl_3$), 98% *ee*)



2ac, *N*-((2*R*,3*R*)-2-chloro-3-pivalamidohexyl)-4-nitrobenzamide

Compound **2ac** (33.0 mg, 86% yield, 99% *ee*) was synthesized following the procedure detailed in Section **IId** (heated to 80 °C during hydrolysis) using **1a** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.65 (30% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 – 8.27 (m, 3H), 8.11 (d, *J* = 9.0 Hz, 2H), 5.72 (d, *J* = 9.3 Hz, 1H), 4.38 – 4.25 (m, 2H), 4.14 (ddd, *J* = 11.0, 5.1, 1.7 Hz, 1H), 2.81 (ddd, *J* = 13.6, 11.0, 4.3 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.61 – 1.52 (m, 1H), 1.37 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.29 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H).

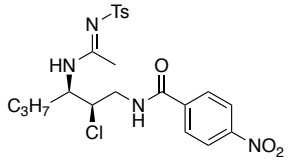
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.7, 164.8, 149.7, 139.3, 128.4, 123.9, 61.5, 48.7, 42.6, 39.2, 34.8, 27.7, 19.3, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, IA 7% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=8.9 min, RT 2 (major) = 10.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{27}ClN_3O_4$: 384.1690; Found: 384.1683.

Optical activity: $[\alpha]_D^{20}$ = -38.9 (c = 0.2, $CHCl_3$) (99% *ee*)

b. Analytical data for vicinal chloroamidine products:



3a, *N*-((2*R*,3*R*)-2-chloro-3-*N*'-tosylacetimidamido)hexyl)-4-nitrobenzamide

Compound **3a** (35.1 mg, 71% yield, 99% *ee*) was synthesized following the procedure detailed in Section **III** using **1a** (24.8 mg, 0.10 mmol) as starting material.

R_f: 0.26 (50% EtOAC/Hex)

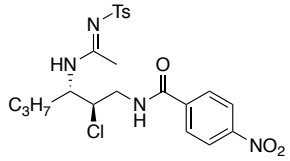
^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, CDCl3) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 8.00 (t J=6.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.63 (d, *J* = 9.1 Hz, 1H), 4.54 (td, *J*= 9.1, 5.5 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.06 (ddd, *J* = 14.5, 12.2, 5.1 Hz, 1H).2.41 (s, 3H), 2.41 (s, 3H), 1.69 (dtd, *J* = 15.2, 9.0, 7.1 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.31 (q, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 165.6, 149.8, 143.3, 139.1, 138.5, 129.7, 128.9, 126.4, 123.7, 60.8, 51.2, 43.3, 34.6, 21.5, 20.9, 19.1, 13.5.

Resolution of enantiomers: DAICEL Chiralpak®, IA 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=13.6 min, RT 2 (minor) =19.6 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{22}H_{28}ClN_4O_5S$: 495.1469; Found: 495.1473.

Optical activity: $[\alpha]_D^{20}$ = +39.7 (c = 0.2, $CHCl_3$) (99% *ee*)



3h, *N*-((2*R*,3*S*)-2-chloro-3-*N*'-tosylacetimidamido)hexyl)-4-nitrobenzamide

R_f: 0.10 (50% EtOAC/Hex)

Compound **3h** (32.1 mg, 65% yield, 95% *ee*) was synthesized following the procedure detailed in Section **III** using **1a** (24.8 mg, 0.10 mmol) as starting material.

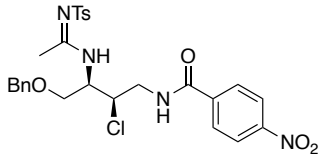
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 7.0, 4.8 Hz, 1H), 5.99 (d, *J* = 8.7 Hz, 1H), 4.37 (tt, *J* = 10.3, 8.4, 3.1 Hz, 1H), 4.24 (q, *J* = 5.7 Hz, 1H), 4.14 (ddd, *J* = 13.7, 7.8, 5.6 Hz, 1H), 3.49 (ddd, *J* = 14.3, 6.1, 4.5 Hz, 1H), 2.39 (s, *J* = 1.8 Hz, 6H), 1.81 (dddd, *J* = 13.6, 9.8, 6.8, 2.9 Hz, 1H), 1.56 (dtd, *J* = 14.6, 10.1, 4.6 Hz, 1H), 1.45 – 1.32 (m, 1H), 1.32-1.22 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 166.1, 149.7, 142.9, 139.7, 139.3, 129.5, 128.5, 126.3, 123.8, 62.5, 53.3, 42.9, 31.8, 21.5, 21.2, 19.0, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, IA 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=11.4 min, RT 2 (major) =17.3 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{22}H_{28}ClN_4O_5S$: 495.1469; Found: 495.1470.

Optical activity: $[\alpha]_D^{20}$ = -15.8 (c = 0.1, $CHCl_3$, 95% *ee*)



3p, *N*-((2*R*,3*R*)-4-(benzyloxy)-2-chloro-3-(*N*'-tosylacetimidamido)butyl)-4-nitrobenzamide

The substrate **1p** (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (3.9 mg, 5 mol%) were suspended in acetonitrile (2 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via syringe. The resulting suspension was cooled to 0 °C in an immersion cooler. After stirring for 10 min Dichloramine-T (48.0 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon completion was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **3p** in a 65% yield (34.3 mg, 96% *ee*).

R_f: 0.10 (50% EtOAC/Hex)

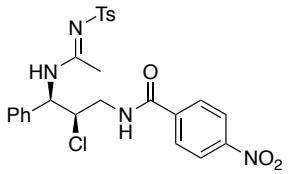
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.93 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.20 (m, 4H), 5.79 (d, *J* = 8.8 Hz, 1H), 4.78 (dtd, *J* = 8.6, 6.7, 1.5 Hz, 1H), 4.51 – 4.42 (m, 2H), 4.37 (ddd, *J* = 11.0, 4.7, 1.5 Hz, 1H), 4.22 (ddd, *J* = 13.6, 7.5, 4.8 Hz, 1H), 3.60 (qd, *J* = 10.0, 6.6 Hz, 2H), 3.13 (ddd, *J* = 13.7, 10.9, 5.1 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 165.6, 149.8, 143.3, 138.9, 138.6, 136.9, 129.7, 128.9, 128.6, 128.2, 127.8, 126.5, 123.7, 73.4, 69.3, 58.1, 51.2, 43.1, 21.5, 20.9.

Resolution of enantiomers: DAICEL Chiralcel®, OD-H 17.5% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=27.1 min, RT 2 (minor) =42.8 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{27}H_{30}ClN_4O_6S$: 573.1575; Found: 573.1577.

Optical activity: $[\alpha]_D^{20}$ = +29.5 (c = 0.1, $CHCl_3$, 95% *ee*)



3s, *N*-((2*R*,3*S*)-2-chloro-3-phenyl-3-((*N*'-tosylacetimidamido)propyl)-4-nitrobenzamide

R_f: 0.20 (50% EtOAC/Hex)

Compound **3s** (17.2 mg, 54% yield, 99% *ee*) was synthesized following the procedure detailed in Section **III** using **1s** (14.1 mg, 0.05 mmol) as starting material.

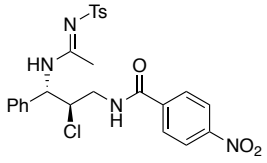
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 8.00 – 7.88 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.31 (m, 3H), 7.31 – 7.22 (m, 4H), 6.13 (d, *J* = 9.3 Hz, 1H), 5.82 (d, *J* = 9.0 Hz, 1H), 4.68 (ddd, *J* = 10.8, 4.9, 1.5 Hz, 1H), 4.28 (ddd, *J* = 13.7, 7.1, 4.9 Hz, 1H), 3.25 (ddd, *J* = 13.8, 10.7, 5.3 Hz, 1H), 2.51 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 165.8, 149.8, 143.4, 138.9, 138.5, 136.2, 129.7, 129.0, 128.9, 128.7, 126.7, 126.5, 123.8, 60.6, 53.9, 43.8, 21.5, 21.3.

Resolution of enantiomers: DAICEL Chiralpak®, IA 20% IPA/Hexane 1 ml/min, 254 nm, RT 1 (major)=32.0 min, RT 2 (minor) =41.3 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{25}H_{26}ClN_4O_5S$: 529.1312; Found: 592.1312.

Optical activity: $[\alpha]_D^{20}$ = +120.2 (c = 0.1, $CHCl_3$, 99% *ee*)



3s-Diastereomer, *N*-((2*R*,3*R*)-2-chloro-3-phenyl-3-(*N*'-tosylacetimidamido)propyl)-4-nitrobenzamide

R_f: 0.12 (50% EtOAC/Hex)

^{1}H NMR (500 MHz, CD_3CN) δ 8.27 (d, *J* = 8.9 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.46 – 7.34 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.44 (dd, *J* = 8.4, 6.5 Hz, 1H), 4.70 (td, *J* = 6.8, 4.6 Hz, 1H), 3.91 (dt, *J* = 14.4, 5.4 Hz, 1H), 3.51 (dt, *J* = 14.3, 6.4 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H).

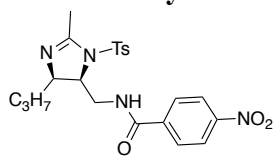
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.8, 149.8, 142.7, 139.6, 139.0, 136.2, 129.4, 129.0, 128.9, 128.4, 127.7, 126.4, 123.8, 61.6, 57.8, 43.2, 21.5, 21.3.

Resolution of enantiomers: DAICEL Chiralpak®, IA 22% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=11.9 min, RT 2 (minor) =35.3 min

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{25}H_{26}ClN_4O_5S$: 529.1312; Found: 592.1312.

Optical activity: $[\alpha]_D^{20}$ = +54.2 (c = 0.1, $CHCl_3$, 97% *ee*)

c. Analytical data for derivatives:



5a, *N*-(((4*R*,5*S*)-2-(methyl)-4-propyl-1-tosyl-4,5-dihydro-1*H*-imidazol-5-yl)methyl)-4-nitrobenzamide

To a solution of **3a** (49.4 mg, 0.1 mmol, 1 equiv) in acetonitrile (1 mL) at room temperature, Cs_2CO_3 was added and allowed to stir for 48 h. The reaction was quenched with the addition of water (3 mL) and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuo. Column chromatography (SiO_2/EtOAc–Hexanes gradient) gave the desired product **5a** in a 57% yield (26.2 mg).

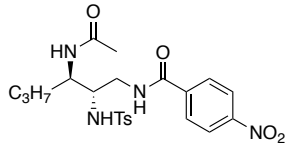
R_f: 0.55 (60% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.39 – 7.32 (m, 2H), 4.18 (ddd, *J* = 11.2, 8.3, 2.7 Hz, 1H), 3.81 (ddd, *J* = 13.9, 6.4, 2.7 Hz, 1H), 3.46 – 3.35 (m, 1H), 3.27 (ddd, *J* = 14.2, 11.3, 3.0 Hz, 1H), 2.45 (s, 3H), 2.37 (d, *J* = 2.2 Hz, 3H), 1.62 – 1.46 (m, 2H), 1.38 – 1.28 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 155.7, 149.7, 145.4, 139.6, 135.6, 130.5, 128.4, 126.7, 123.9, 67.6, 62.4, 39.8, 31.3, 21.7, 20.9, 17.9, 14.0.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{22}H_{27}N_4O_5S$: 459.1702; Found: 459.1700.

Optical activity: $[\alpha]_D^{20}$ = +183.2 (c = 0.5, $CHCl_3$, 99% *ee*)



6a, *N*-((2*S*,3*R*)-3-acetamido-2-((4-methylphenyl)sulfonamido)hexyl)-4-nitrobenzamide

R_f: 0.25 (60% EtOAC/Hex)

Imidazoline **5a** (26.2 mg, 0.57 mmol), acetonitrile (1 mL) and a solution of HCl (1 M, 0.2 mL) were added to a vial and stirred for 15 min. Water (3 mL) was added and the solution was concentrated in vacuo and extracted with DCM (3 x 4 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **6a** in a 99% yield (27.1 mg, 99% *ee*).

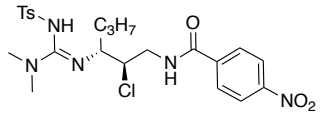
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.77 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 6.6 Hz, 1H), 5.66 (d, *J* = 7.8 Hz, 1H), 3.69 (dq, *J* = 8.7, 4.4 Hz, 1H), 3.60 (dd, *J* = 10.7, 6.6 Hz, 1H), 3.35 – 3.17 (m, 2H), 2.43 (s, 3H), 2.00 (s, 3H), 1.63-1.57 (m, 1H), 1.44 – 1.33 (m, 1H), 1.23 – 1.13 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 166.3, 149.8, 143.9, 139.0, 136.8, 129.9, 128.4, 127.3, 123.9, 57.6, 52.3, 40.5, 33.6, 23.1, 21.6, 19.3, 13.4.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 15% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=15.2 min, RT 2 (major) =22.8 min

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{22}H_{29}ClN_4O_5S$: 477.1808; Found: 477.1804.

Optical activity: $[\alpha]_D^{20}$ = +65.2 (c = 0.2, $CHCl_3$, 99% *ee*)



7a, *N*-((2*R*,3*R*)-2-chloro-3-(((*Z*)-(dimethylamino)((4-methylphenyl)sulfonamido)methylene)amino)hexyl)-4-nitrobenzamide

The substrate **1a** (24.8 mg, 0.1 mmol, 1.0 equiv), $(DHQD)_2PHAL$ (0.8 mg, 1 mol%), and MS4Å (20 mg) were suspended in dimethylcyanamide (1 mL) in a test tube with a

magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via syringe. The resulting suspension was cooled to 0 °C in an immersion cooler. After stirring for 10 min dichloramine-T (48.0 mg, 0.2 mmol, 2 equiv) was added. The reaction was monitored by TLC and upon completion was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **7a** in an 82% yield (42.9 mg, 98% *ee*).

R_f: 0.35 (70% EtOAC/Hex)

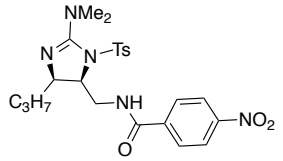
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 – 8.54 (m, 1H), 8.25 (d, *J* = 8.9 Hz, 2H), 8.17 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.09 (d, *J* = 9.9 Hz, 1H), 4.67 – 4.54 (m, 1H), 4.33 – 4.18 (m, 2H), 3.30 (ddd, *J* = 13.3, 10.1, 4.9 Hz, 1H), 3.05 (s, 6H), 2.37 (s, 3H), 1.67 – 1.53 (m, 2H), 1.42 – 1.29 (m, 1H), 1.28 – 1.17 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 165.8, 156.7, 149.6, 142.1, 141.8, 139.1, 129.3, 128.9, 125.4, 123.6, 61.5, 53.7, 42.7, 39.3, 36.3, 21.4, 19.1, 13.7.

Resolution of enantiomers: DAICEL Chiralpak®, IA 16% IPA/Hexane 1ml/min, 254 nm, RT 1 (major)=43.8 min, RT 2 (minor) =51.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{23}H_{31}N_5O_5S$: 524.1735; Found: 524.1732.

Optical activity: $[\alpha]_D^{20}$ = -31.9 (c = 0.50, $CHCl_3$) (98% *ee*)



8a, *N*-(((4*R*,5*S*)-2-(dimethylamino)-4-propyl-1-tosyl-4,5-dihydro-1*H*-imidazol-5-yl)methyl)-4-nitrobenzamide

7a (26.2 mg, 0.05 mmol) was added to a 10 mL test tube with a magnetic stir bar. DMF (0.5 mL) was added via syringe. The reaction was heated to 80 °C and monitored by TLC. After the reaction reached competition reaction, it was cooled, quenched with water

(5 mL) and extracted with dichloromethane (3x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuo. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided the desired product **8a** in a 62% yield (15.1 mg).

R_f: 0.30 (100% EtOAC)

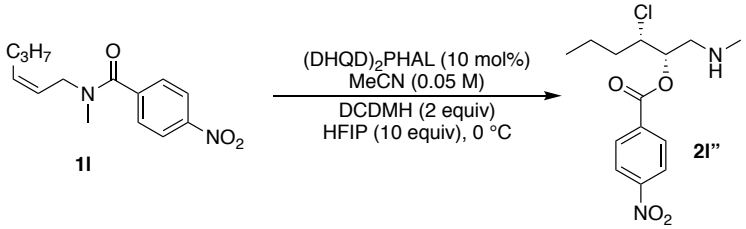
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 4.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.87 (dt, *J* = 11.1, 2.9 Hz, 1H), 3.59 (ddd, *J* = 13.9, 5.8, 3.3 Hz, 1H), 3.38 (ddd, *J* = 14.2, 11.0, 3.5 Hz, 1H), 3.25 (ddd, *J* = 8.8, 6.1, 2.2 Hz, 1H), 2.92 (s, 6H), 2.46 (s, 3H), 1.20 – 0.93 (m, 2H), 0.63 (t, *J* = 7.3 Hz, 3H), 0.57 (ddd, *J* = 16.5, 9.0, 5.3 Hz, 1H), -0.16 (dtd, *J* = 14.0, 9.6, 5.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 156.0, 149.6, 145.5, 139.6, 133.3, 130.0, 128.4, 127.9, 123.9, 66.6, 64.5, 44.7, 41.6, 38.0, 21.6, 18.9, 13.7.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{23}H_{30}N_5O_5S$: 488.1968; Found: 488.1978.

Optical activity: $[\alpha]_D^{20}$ = +40.2 (c = 0.25, $CHCl_3$)

d. Analytical data for miscellaneous products/byproducts:



2l", *N*-((2*R*,3*R*)-3-chloro-2-hydroxyhexyl)-*N*-methyl-4-nitrobenzamide

1l (0.1 mmol, 1.0 equiv) and $(DHQD)_2PHAL$ (7.8 mg, 10 mol%) were suspended in acetonitrile (2 mL) in a test tube with a magnetic stir bar and capped with a rubber septa. HFIP (105 μL, 1.0 mmol, 10 equiv) was added via a syringe. The resulting suspension was cooled to 0 °C in an immersion cooler. After stirring for 10 min, DCDMH (39.4 mg, 0.2 mmol, 2 equiv) was added. Upon completion, the reaction was quenched by the addition of saturated $Na_2S_2O_3$ (2 mL). The reaction was concentrated to remove the acetonitrile and the resultant aqueous layer was extracted with DCM (3 x 5 mL). The combined organics were concentrated. The combined organic layers were dried with

anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided **2l"** (25.1 mg, 80% yield, 19% *ee*).

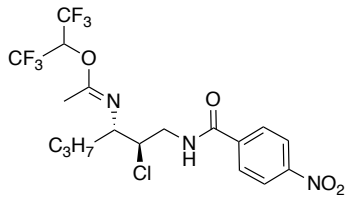
R_f 0.68 (20% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.0 Hz, 2H), 8.27 (d, *J* = 9.0 Hz, 2H), 5.68 (td, *J* = 6.2, 2.2 Hz, 1H), 4.30 (ddd, *J* = 8.2, 5.8, 2.2 Hz, 1H), 3.31 (dd, *J* = 6.1, 1.7 Hz, 2H), 3.01 (s, 3H), 1.84 – 1.69 (m, 2H), 1.69 – 1.55 (m, 2H), 1.56 – 1.42 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 150.8, 134.9, 131.1, 123.7, 73.5, 66.2, 61.6, 53.7, 37.0, 19.8, 13.4.

Resolution of enantiomers: DAICEL Chiralpak®, AD-H 5% IPA/Hexane 1 ml/min, 254 nm, RT 1 (minor)=6.6 min, RT 2 (major) =7.9 min.

HRMS analysis (ESI): calculated for $[M+H]^+$: C14H20ClN2O4: 315.1111; Found: 315.1108



4h, 1,1,1,3,3,3-hexafluoropropan-2-yl-*N*-((2*R*,3*S*)-2-chloro-1-(4-nitrobenzamido)hexan-3-yl)acetimidate

R_f: 0.39 (25% EtOAC/Hex)

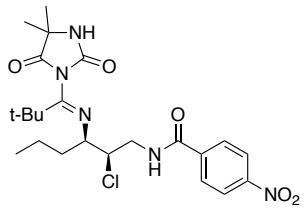
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 6.54 (s, 1H), 6.34 (hept, *J* = 6.5 Hz, 1H), 4.32 – 4.21 (m, 2H), 3.69 (dt, *J* = 9.2, 4.0 Hz, 1H), 3.34 (ddd, *J* = 13.8, 9.6, 4.0 Hz, 1H), 2.08 (s, 3H), 1.75 (tdd, *J* = 10.1, 6.2, 3.0 Hz, 1H), 1.64 (ddt, *J* = 18.7, 9.6, 5.0 Hz, 1H), 1.34 – 1.17 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 158.7, 149.8, 139.6, 128.2, 124.0, 65.5, 62.5, 42.3, 35.9, 19.4, 14.7, 13.9 (note the trifluoromethyl carbons and the methine of the HFIP addition are not listed since they could not be assigned with confidence, presumably due to their splitting, which led to small intensity in the NMR spectrum.

^{19}F NMR (470 MHz, $CDCl_3$) δ -73.01 – -73.10 (m), -73.29 – -73.44 (m).

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{18}H_{21}ClF_6N_3O_4$: 492.1125, found: 492.1110

Optical activity: $[\alpha]_D^{20} = 27.9$ (c = 0.20, $CHCl_3$)



S3a/b, *N*-((2*R*,3*R*)-2-chloro-3-(((1-(4,4-dimethyl-2,5-dioxoimidazolidin-1-yl)-2,2-dimethylpropylidene)amino)hexyl)-4-nitrobenzamide

Less polar rotamer

R_f: 0.25 (30% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.77 (t, 1H, *J* = 7.5 Hz), 6.23 (s, 1H), 4.20 (ddd, *J* = 9.8, 4.8, 1.9 Hz, 1H), 4.15 – 4.04 (m, 1H), 3.45 (ddd, *J* = 9.2, 5.1, 1.9 Hz, 1H), 3.35 (ddd, *J* = 13.4, 9.9, 5.1 Hz, 1H), 1.89 (dtd, *J* = 13.2, 9.3, 4.4 Hz, 1H), 1.56 (s, 3H), 1.48 (s, 3H), 1.27 (s, 9H), 1.32-1.11 (m, 3H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 165.5, 155.4, 154.9, 149.3, 139.6, 128.8, 123.6, 60.1, 60.0, 59.4, 43.4, 41.3, 34.3, 28.4, 25.4, 25.3, 18.8, 14.0.

S3a/b, *More polar rotamer*

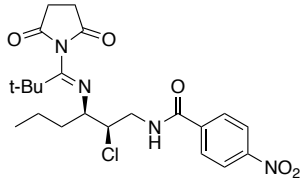
R_f: 0.25 (30% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 6.3 Hz, 1H), 5.79 (s, 1H), 4.22 (ddd, *J* = 8.9, 5.7, 2.2 Hz, 1H), 3.98 (ddd, *J* = 13.7, 6.8, 5.7 Hz, 1H), 3.48 (td, *J* = 8.7, 4.5 Hz, 1H), 3.35 (td, *J* = 5.6, 2.7 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.68 (s, 3H), 1.52 (s, 3H), 1.41 – 1.28 (m, 3H), 1.25 (s, 9H), 0.85 (t, *J* = 7.2, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 165.6, 155.3, 153.5, 149.6, 139.5, 128.6, 123.6, 60.6, 59.7, 59.7, 43.5, 41.2, 33.5, 28.4, 25.6, 25.2, 18.7, 13.8.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{23}H_{33}ClN_5O_5$: 494.2170; Found: 494.2149

Optical activity: $[\alpha]_D^{20} = +40.2$ (c = 0.25, $CHCl_3$)



S4, *N*-((2*R*,3*R*)-2-chloro-3-(((1-(2,5-dioxopyrrolidin-1-yl)-2,2-dimethylpropylidene)amino)hexyl)-4-nitrobenzamide

R_f: 0.20 (30% EtOAC/Hex)

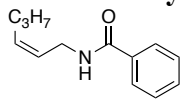
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.09 (m, 1H), 4.19 (ddd, *J* = 8.2, 6.4, 2.2 Hz, 1H), 3.85 (dt, *J* = 13.9, 6.4 Hz, 1H), 3.57 (ddd, *J* = 13.8, 8.0, 5.7 Hz, 1H), 3.24 (ddd, *J* = 8.0, 5.4, 2.3 Hz, 1H), 2.97 – 2.62 (m, 4H), 1.94 – 1.81 (m, 1H), 1.33 – 1.23 (m, 3H), 1.21 (s, 9H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 175.1, 165.4, 156.5, 149.6, 139.5, 128.5, 123.7, 61.3, 60.3, 43.6, 40.8, 33.6, 28.7, 28.7, 28.4, 18.7, 13.9.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{22}H_{30}ClN_4O_5$: 465.1905; Found; 465.1907

Optical activity: $[\alpha]_D^{20} = +63.8$ (c = 0.35, $CHCl_3$)

e. Analytical data for starting materials:



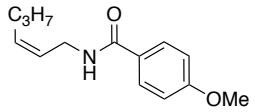
1b, (*Z*)-*N*-(hex-2-en-1-yl)benzamide

R_f: 0.26 (20% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46-7.41 (m, 2H), 6.06 (s, 1H), 5.64 (dtt, *J* = 10.3, 7.4, 1.4 Hz, 1H), 5.53 (dtt, *J* = 10.7, 7.0, 1.5 Hz, 1H), 4.11 (t, *J* = 6.1 Hz, 2H), 2.13 (q, *J* = 7.4 Hz, 2H), 1.43 (dt, *J* = 14.8, 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 134.7, 134.3, 131.5, 128.7, 127.0, 125.3, 37.3, 29.6, 22.8, 13.9.

HRMS analysis (ESI): calculated for $[M+H]^+$: C13H18NO: 204.1388; Found: 204.1386



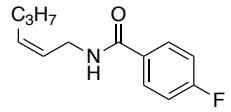
1c, (*Z*)-*N*-(hex-2-en-1-yl)-4-methoxybenzamide

R_f: 0.38 (20% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.94 (s, 1H), 5.63 (dtt, *J* = 10.4, 7.3, 1.4 Hz, 1H), 5.56 – 5.46 (m, 1H), 4.10 (, *J* = 6.1 Hz, 2H), 3.86 (s, 3H), 2.13 (q, *J* = 6.7 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 162.1, 134.0, 128.6, 126.9, 125.2, 113.7, 55.4, 37.1, 29.4, 22.7, 13.7.

HRMS analysis (ESI): calculated for $[M+H]^+$: C14H20NO2: 234.1494; Found: 234.1490



1d, (*Z*)-4-fluoro-*N*-(hex-2-en-1-yl)benzamide

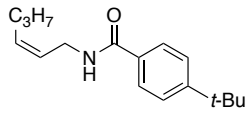
R_f: 0.15 (10% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.11 (s, 1H), 5.67 – 5.56 (m, 1H), 5.56 – 5.46 (m, 1H), 4.08 (t, *J* = 6.1 Hz, 2H), 2.11 (q, *J* = 7.4 2H), 1.41 (h, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 164.7 (d, *J* = 251.8 Hz), 134.2, 130.7 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 9.0 Hz), 124.9, 115.6 (d, *J* = 21.9 Hz), 37.3, 29.4, 22.6, 13.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ -108.40.

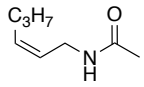
HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{13}H_{17}FNO$: 222.1294; Found: 222.1287



1e, (*Z*)-4-(*tert*-butyl)-*N*-(hex-2-en-1-yl)benzamide

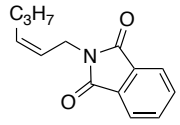
R_f: 0.33 (20% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 5.99 (s, 1H), 5.63 (dtt, *J* = 10.4, 7.3, 1.4 Hz, 1H), 5.57 – 5.48 (m, 1H), 4.11 (t, *J* = 6.1 Hz, 2H), 2.13 (q, *J* = 7.6, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 1.34 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 154.9, 134.1, 131.7, 126.7, 125.5, 125.2, 37.1, 34.9, 31.2, 29.4, 22.7, 13.7.
HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{17}H_{26}NO$: 260.2014; Found: 260.2011

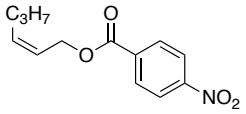


1g, (*Z*)-*N*-(hex-2-en-1-yl)acetamide
R_f: 0.23 (70% EtOAC/Hex)

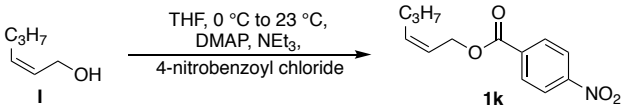
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (dtt, *J* = 10.6, 7.5, 1.6 Hz, 1H), 5.46 (s, 1H), 5.40 (dtt, *J* = 10.8, 7.0, 1.6 Hz, 1H), 3.88 (t, *J* = 6.0 Hz, 2H), 2.04 (q, *J* = 7.6 Hz, 2H), 1.98 (s, 3H), 1.38 (h, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 133.8, 125.1, 36.8, 29.3, 23.3, 22.6, 13.7.
HRMS analysis (ESI): calculated for $[M+H]^+$: $C_8H_{16}NO$: 142.1232; Found: 142.1229.



1j, (*Z*)-2-(hex-2-en-1-yl)isoindoline-1,3-dione
R_f: 0.17 (10% EtOAC/Hex)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.64 – 5.55 (m, 1H), 5.47 (dtd, *J* = 10.8, 7.0, 1.5 Hz, 1H), 4.32 (d, *J* = 7.0 Hz, 2H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.44 (p, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 134.4, 133.9, 132.3, 123.2, 123.0, 34.9, 29.3, 22.6, 13.8.
HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{14}H_{16}NO_2$: 230.1181; Found: 230.1181



1k, (*Z*)-hex-2-en-1-yl 4-nitrobenzoate

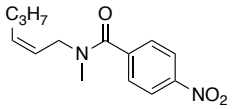


Alcohol **I** (400 mg, 4.0 mmol, 1.0 equiv) was placed in an oven-dried round bottom flask with stir bar under argon. THF (20 mL) and DMAP (12 mg, 0.1 mmol, 0.05 equiv) was added and the reaction was cooled to 0 °C, after which, 4-nitrobenzoyl chloride (814 mg, 4.4 mmol, 1.1 equiv) was added. Reaction progress was monitored by TLC and quenched at 2 h by the addition of water (5 mL). The reaction was concentrated in vacuo to remove THF. The aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided **1j** in a 91% yield (909 mg).

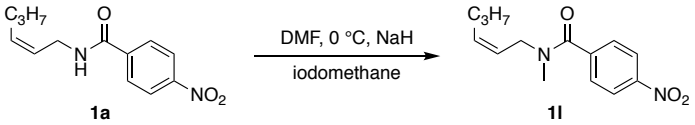
R_f: 0.33 (10% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.1 Hz, 2H), 8.22 (d, *J* = 9.0 Hz, 2H), 5.75 (dtt, *J* = 11.0, 7.1, 1.0 Hz, 1H), 5.67 (dtt, *J* = 11.0, 6.9, 1.3 Hz, 1H), 4.92 (d, *J* = 6.4 Hz, 2H), 2.21 – 2.11 (m, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 150.5, 136.3, 135.7, 130.7, 123.5, 122.7, 61.7, 29.6, 22.5, 13.7.



1l, (*Z*)-*N*-(hex-2-en-1-yl)-*N*-methyl-4-nitrobenzamide



1a (124 mg, 0.5 mmol, 1.0 equiv) was added to a flame dried round bottom flask with stir bar under argon. Distilled DMF (5 mL) was added and the reaction was cooled to 0 °C. After stirring for 5 min, iodomethane (0.047 mL, 0.75 mmol, 1.5 equiv) was added via syringe and the reaction was slowly warmed to room temperature. The reaction was

monitored by TLC and reached completion at 1 h. It was again cooled to 0 °C. Water (1 mL) was added dropwise to quench the reaction. After the exotherm was complete, water (10 mL) and dichloromethane (5 mL) were added, and the organic layer was separated. The organics were washed with water (3 x 5 mL) and then concentrated. Column chromatography (SiO_2/EtOAc–Hexanes gradient) provided **1l** in a 88% yield (121.8 mg).

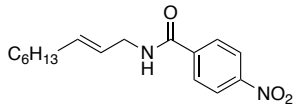
1l exists as two rotamers in chloroform at room temperature in a ratio of 0.56:0.44.

***Major rotamer*: ^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 5.61 (dd, *J* = 12.5, 5.9 Hz, 1H), 5.37 (dt, *J* = 11.0, 6.6 Hz, 1H), 3.83 (d, *J* = 6.6 Hz, 2H), 3.08 (s, 3H), 1.85 (q, *J* = 7.4 Hz, 2H), 1.33 (q, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

***Minor rotamer*: ^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 5.72 (q, *J*= 8.3 Hz, 1H), 5.47 (dd, *J* = 10.0, 7.5 Hz, 1H), 4.23 (d, *J* = 7.1 Hz, 2H), 2.87 (s, 3H), 2.14 (t, *J* = 7.4 Hz, 2H), 1.44 (q, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

Carbon NMR of the mixture is not reported since it was not possible to assign peaks to the major and minor components with confidence.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{14}H_{20}N_2O_3$: 263.1396; Found: 263.1406



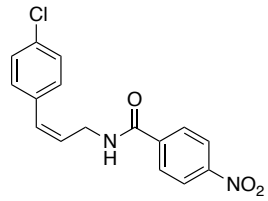
1q, (*E*)-4-nitro-*N*-(non-2-en-1-yl)benzamide

R_f: 0.53 (40% EtOAc/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 6.15 (s, 1H), 5.78-5.71 (m, 1H), 5.60 – 5.51 (m, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.06 (q, *J* = 8.1, 7.5 Hz, 2H), 1.38 (q, *J* = 7.2, 6.7 Hz, 2H), 1.35 – 1.24 (m, 6H), 0.89 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 149.6, 140.2, 135.3, 128.1, 124.7, 123.9, 42.4, 32.3, 31.7, 29.0, 28.9, 22.6, 14.1.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{16}H_{23}N_2O_3$: 291.1709; Found: 291.1706.



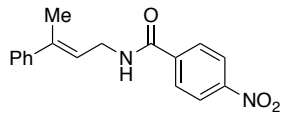
1t, (*Z*)-*N*-(3-(4-chlorophenyl)allyl)-4-nitrobenzamide

R_f: 0.25 (30% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 11.5 Hz, 1H), 6.25 (s, 1H), 5.78 (dt, *J* = 11.5, 6.7 Hz, 1H), 4.36 (ddd, *J* = 7.0, 5.5, 1.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 149.7, 139.8, 134.4, 133.4, 131.3, 130.0, 128.7, 128.1, 127.6, 123.9, 38.6.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{16}H_{14}ClN_2O_3$: 317.0693; Found: 317.0693.



1x, (*E*)-4-nitro-*N*-(3-phenylbut-2-en-1-yl)benzamide

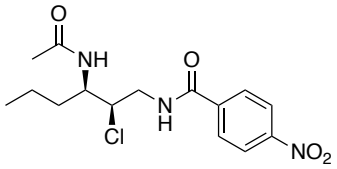
R_f: 0.43 (40% EtOAC/Hex)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 6.22 (s, 1H), 5.88 (td, *J* = 7.1, 1.5 Hz, 1H), 4.31 (t, *J*=6.3 2H), 2.18 (s, 3H).

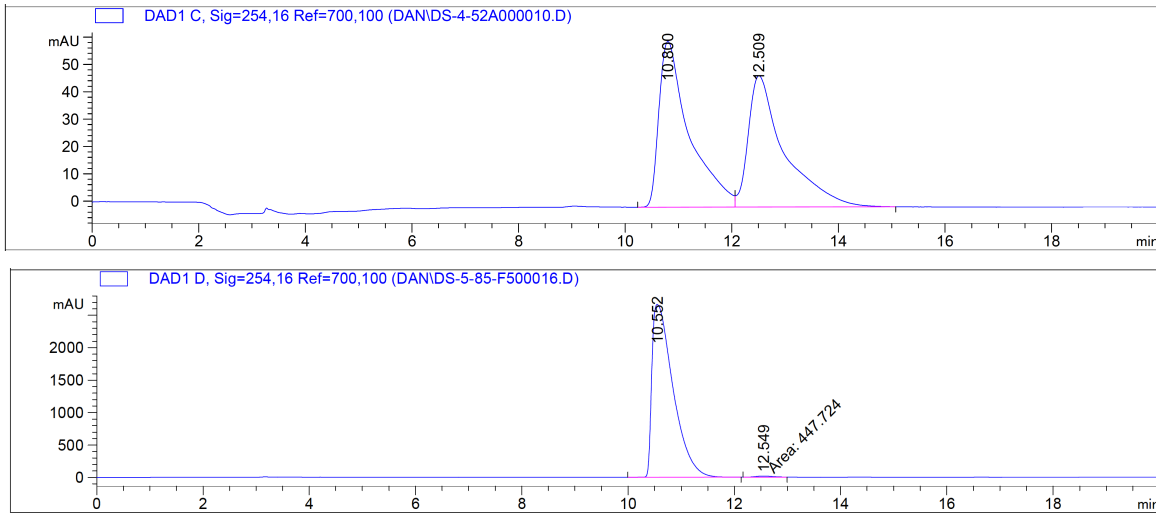
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 149.6, 142.5, 140.1, 139.7, 128.4, 128.1, 127.6, 125.8, 123.9, 122.3, 38.9, 16.2.

HRMS analysis (ESI): calculated for $[M+H]^+$: $C_{17}H_{17}N_2O_3$: 297.1239; Found: 297.1238

f. HPLC traces:

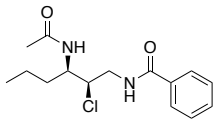


2a

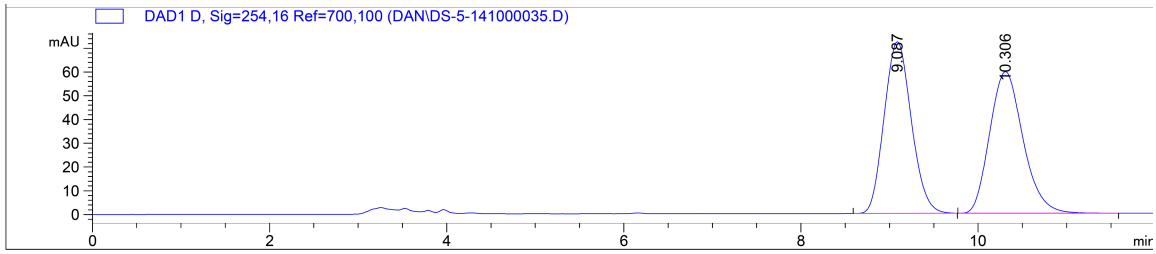


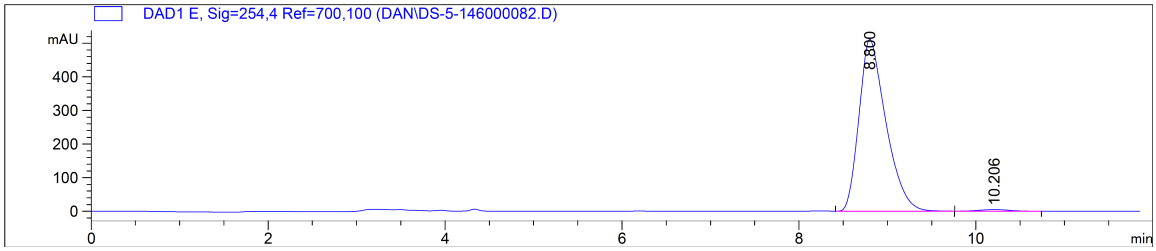
Signal 4: DAD1 D, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.552	BB	0.4176	7.34487e4	2664.31372	99.3941
2	12.549	MM	0.4103	447.72388	18.18661	0.6059



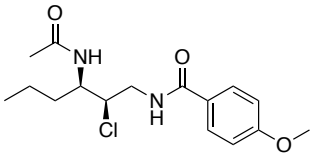
2b



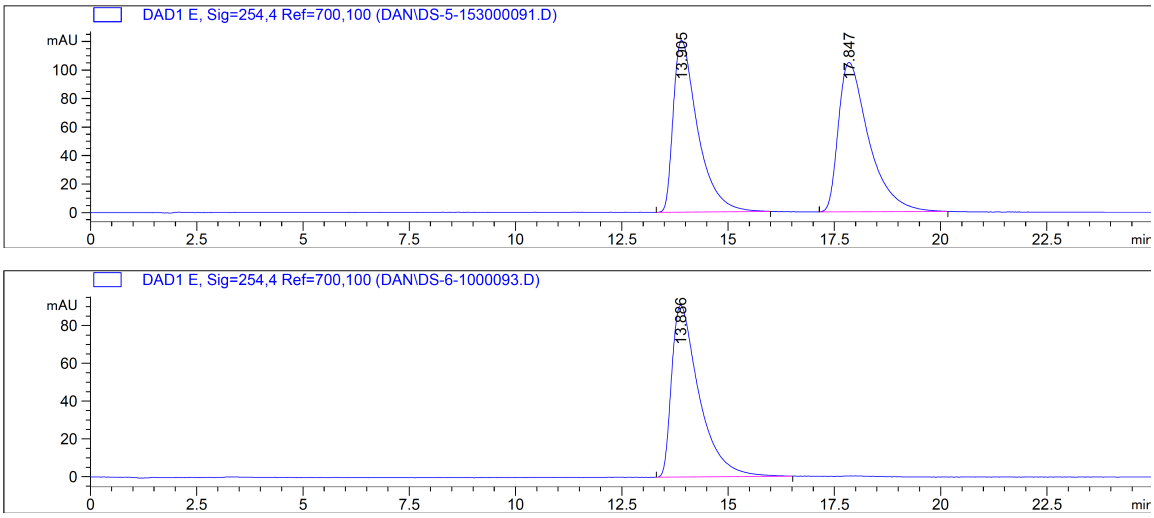


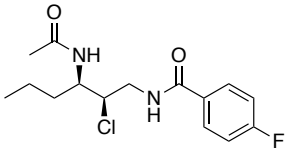
Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.800	BB	0.3100	1.07800e4	511.33914	98.9854
2	10.206	BB	0.3232	110.49004	4.71902	1.0146

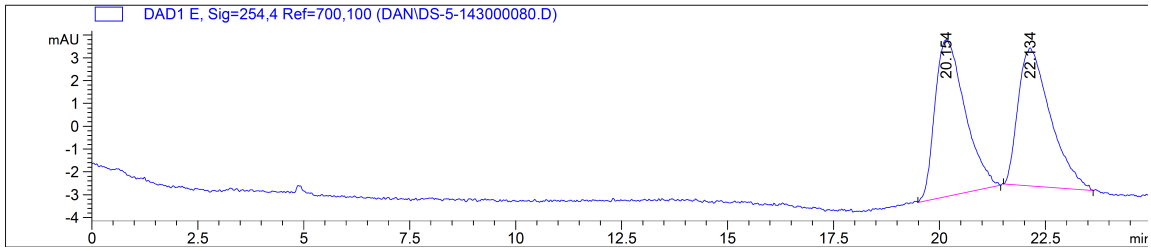

O
NH
O
N
H
Cl
O

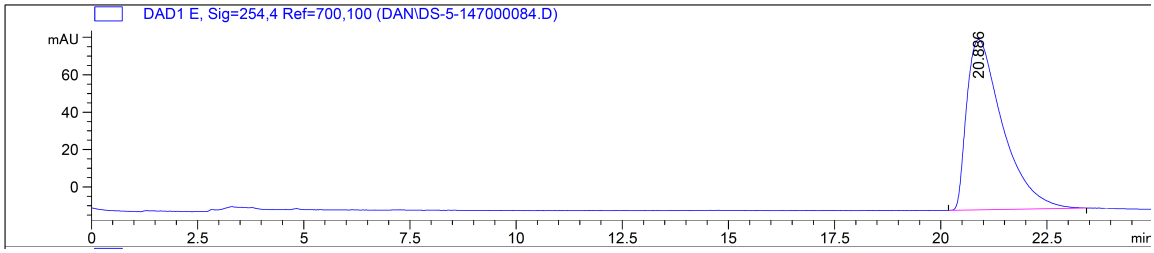
2c

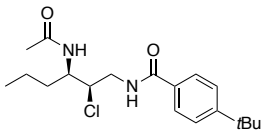

DAD1 E, Sig=254,4 Ref=700,100 (DAN\DS-5-153000091.D)
mAU
13.905
17.847
min
DAD1 E, Sig=254,4 Ref=700,100 (DAN\DS-6-1000093.D)
mAU
13.886
min


O
NH
O
N
H
Cl
F

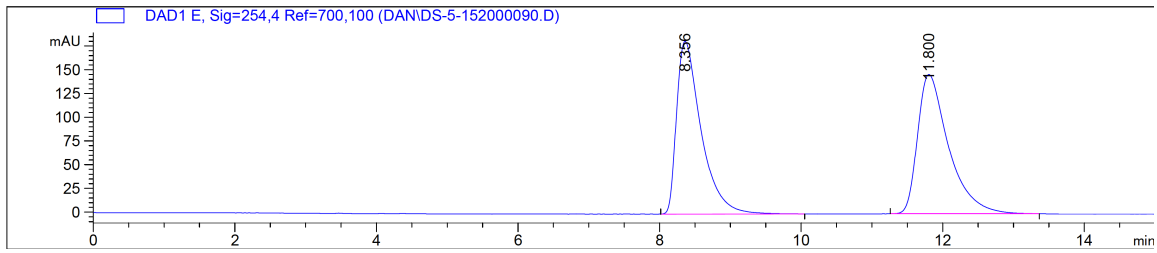
2d

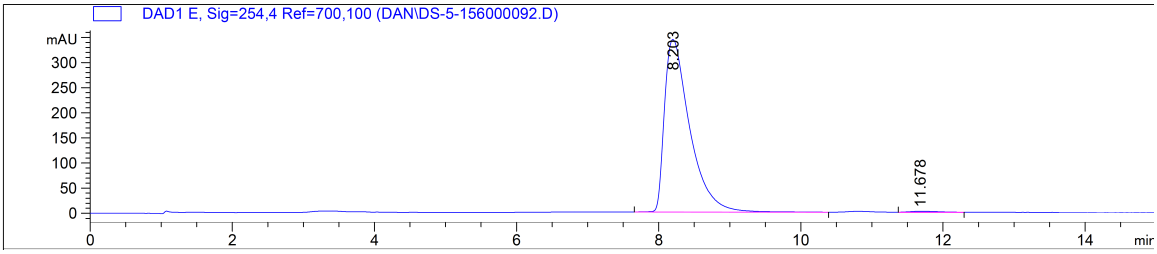

DAD1 E, Sig=254,4 Ref=700,100 (DAN\DS-5-143000080.D)
mAU
3
2
1
0
-1
-2
-3
-4
20.154
22.134
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
min


DAD1 E, Sig=254,4 Ref=700,100 (DAN\DS-5-147000084.D)
mAU
60
40
20
0
20.386
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
min



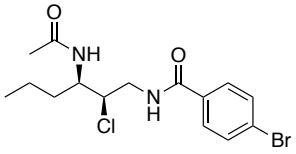
2e



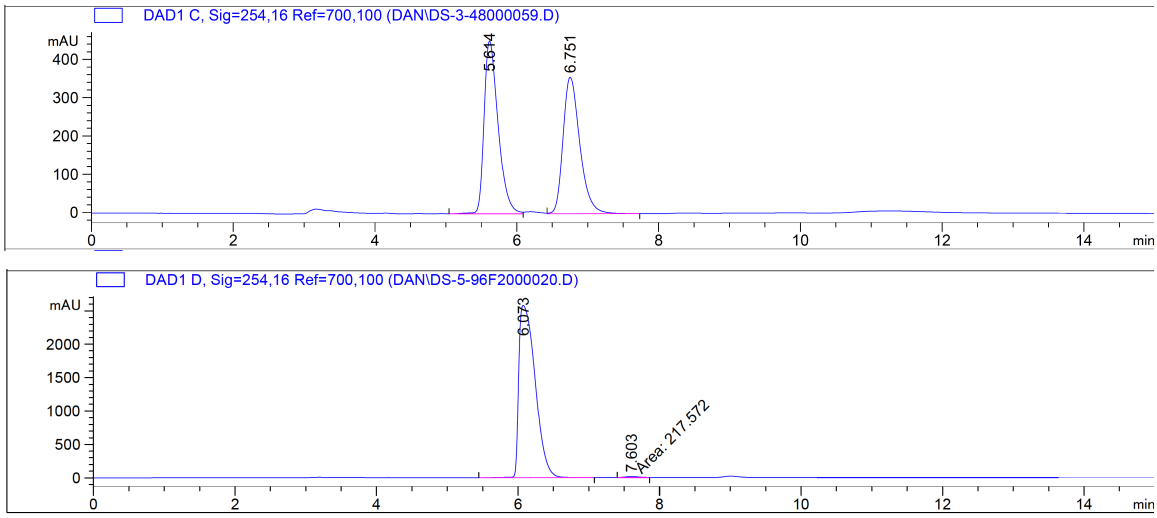


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.203	BB	0.3696	8463.86426	343.38287	99.4164
2	11.678	BB	0.3346	49.68662	1.78556	0.5836

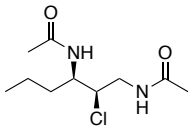


2f

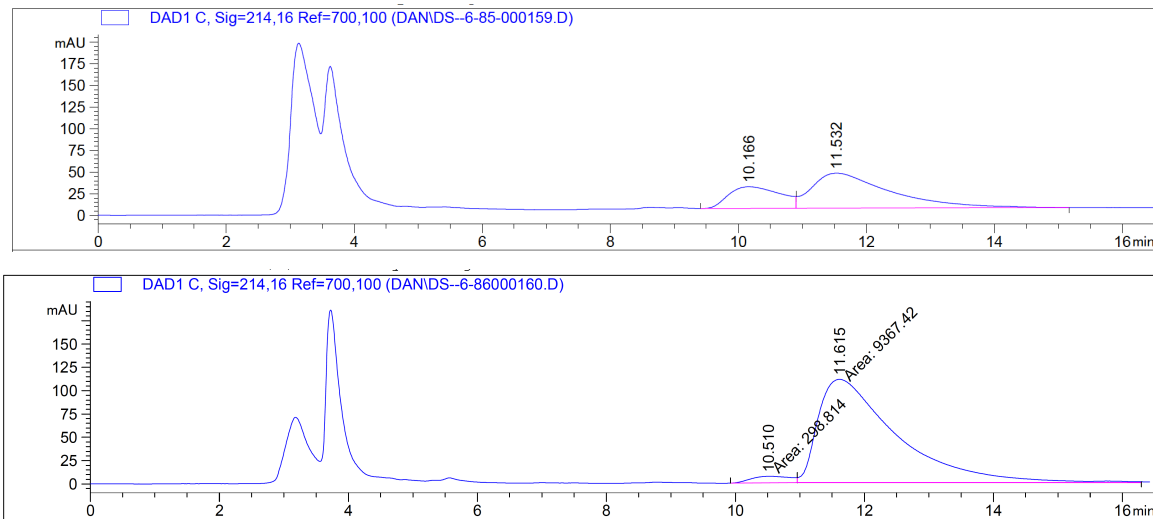


Signal 4: DAD1 D, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.073	BB	0.2587	4.12460e4	2578.03955	99.4753
2	7.603	MM	0.2260	217.57217	16.04398	0.5247



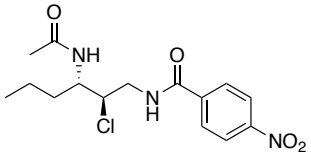
2g



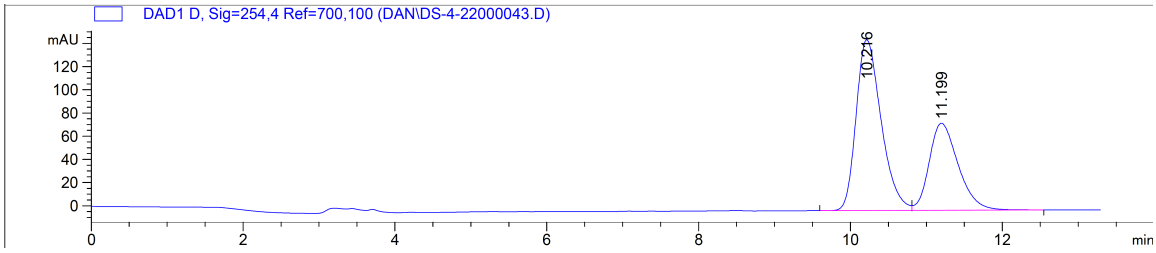

```
Signal 1: DAD1 C, Sig=214,16 Ref=700,100

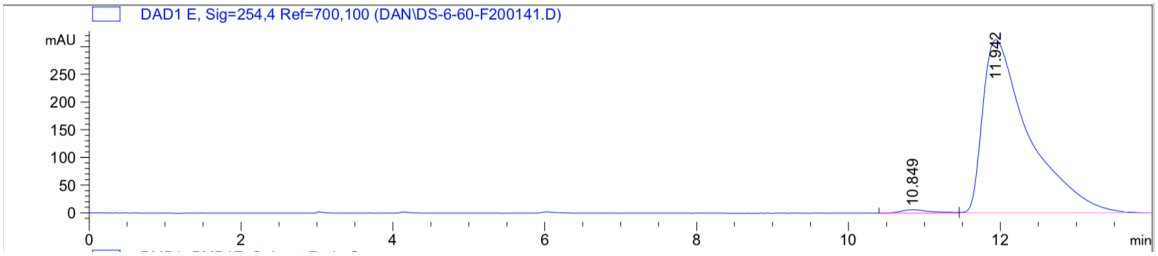
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.510 MM    0.7057  298.81448    7.05724   3.0913
   2  11.615 MM    1.4080 9367.41797  110.88100  96.9087

Totals :                  9666.23245  117.93824
```



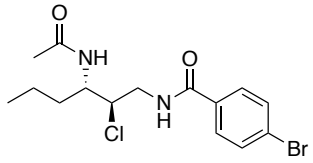
2h



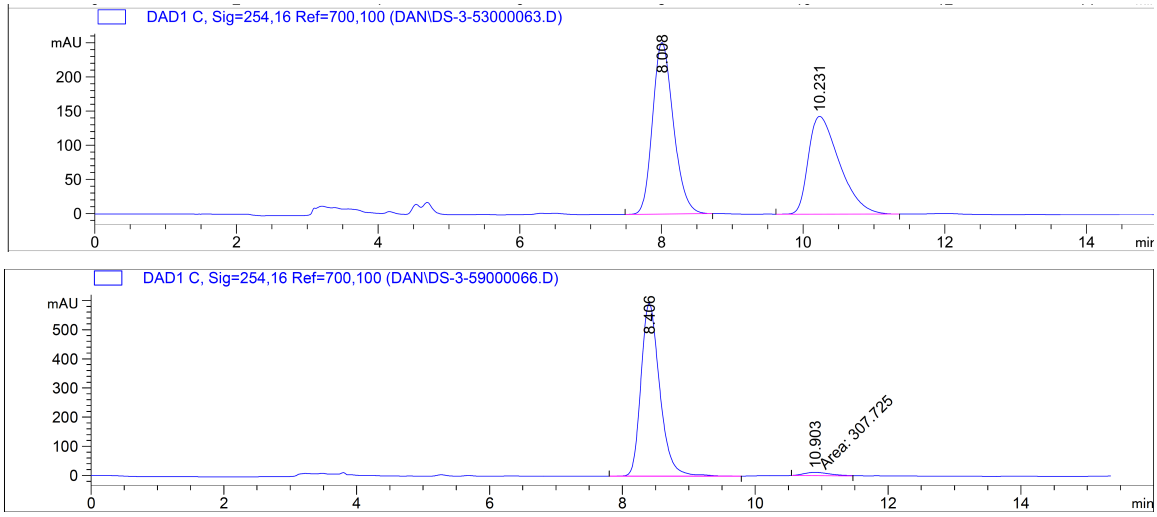


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.849	BV	0.3999	180.29829	6.26180	1.3404
2	11.942	VB	0.6172	1.32704e4	312.66104	98.6596

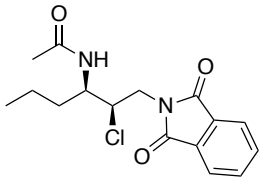


2i

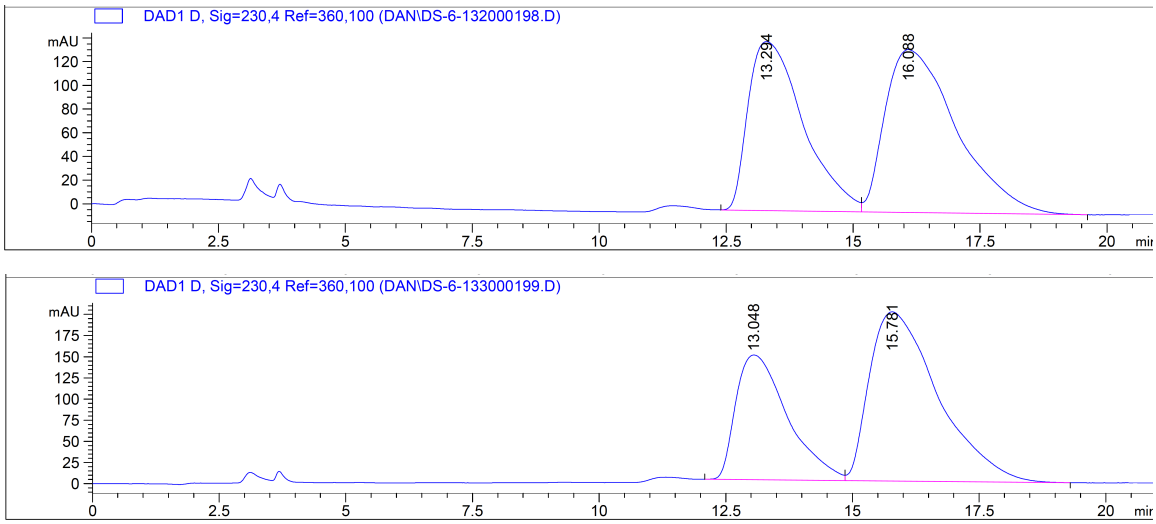


Signal 3: DAD1 C, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.406	BB	0.3031	1.16218e4	591.71783	97.4205
2	10.903	MM	0.4577	307.72479	11.20608	2.5795
Totals :				1.19295e4	602.92391	

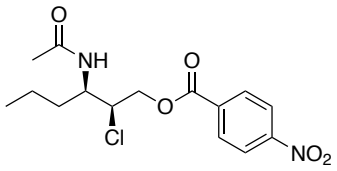


2j

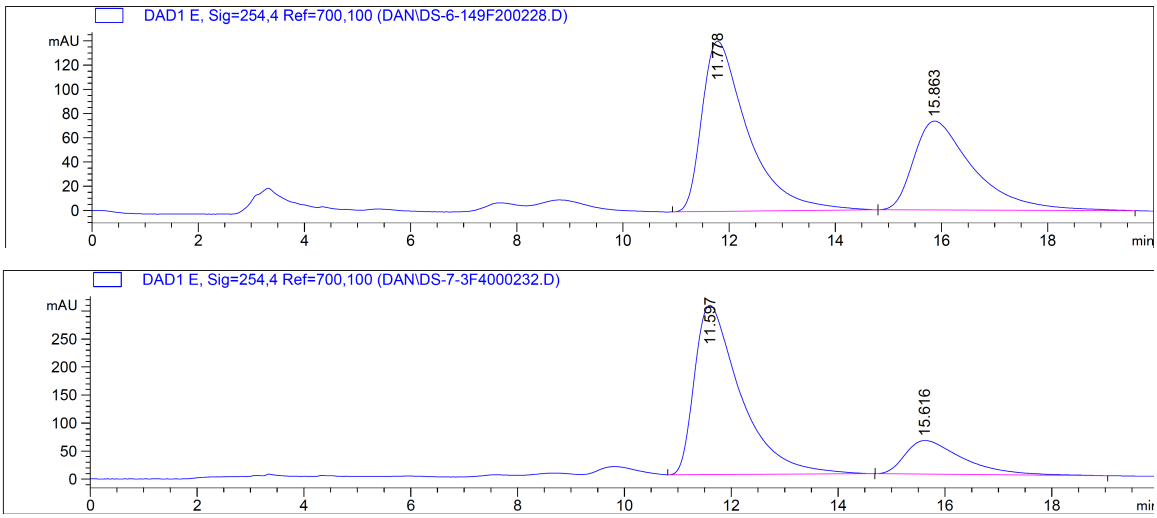


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.048	BV	1.0481	1.04244e4	147.21996	35.6476
2	15.781	VB	1.3527	1.88186e4	199.83273	64.3524
Totals :				2.92430e4	347.05269	

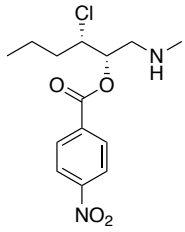


2k

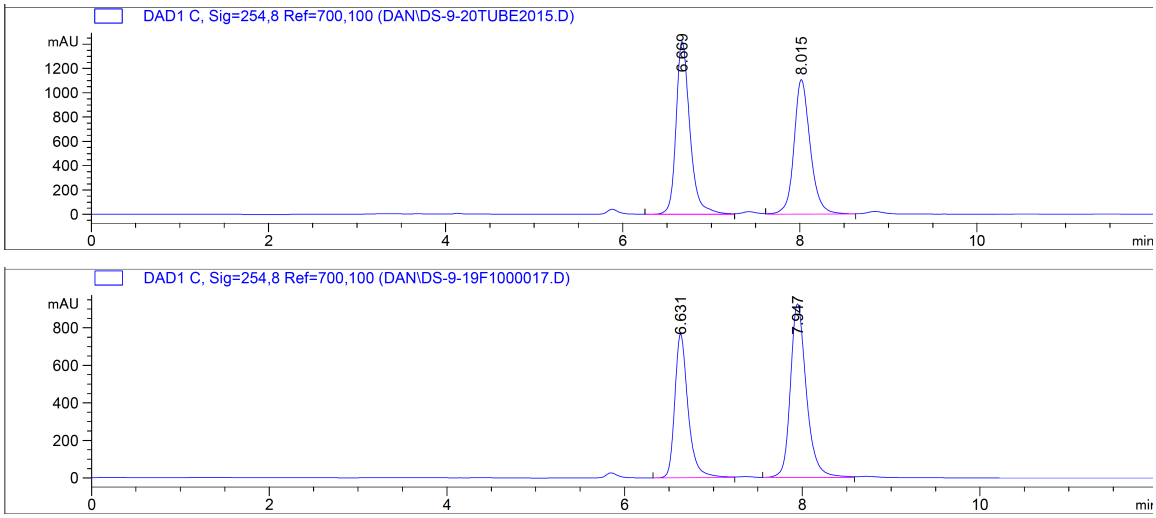


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.597	BB	0.8794	1.81429e4	301.76712	80.1808
2	15.616	BB	0.9744	4484.58203	60.11290	19.8192

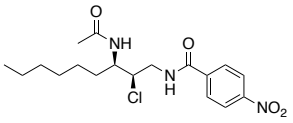


2l”

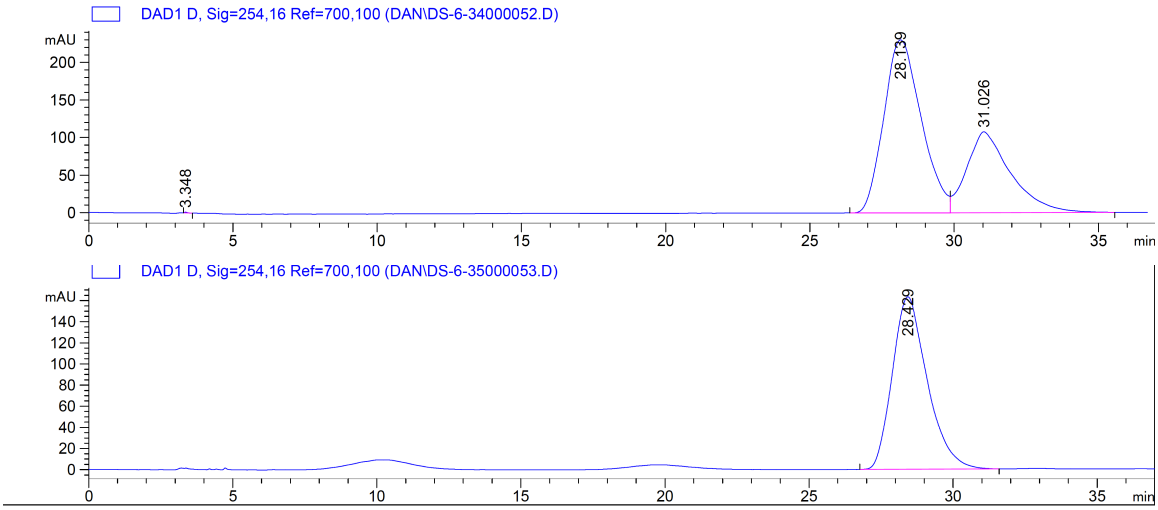


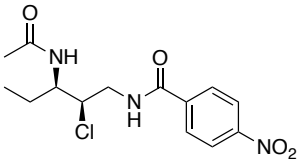
Signal 3: DAD1 C, Sig=254,8 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.631	BV	0.1572	7959.15527	766.04663	40.7930
2	7.947	BV	0.1897	1.15519e4	925.20074	59.2070

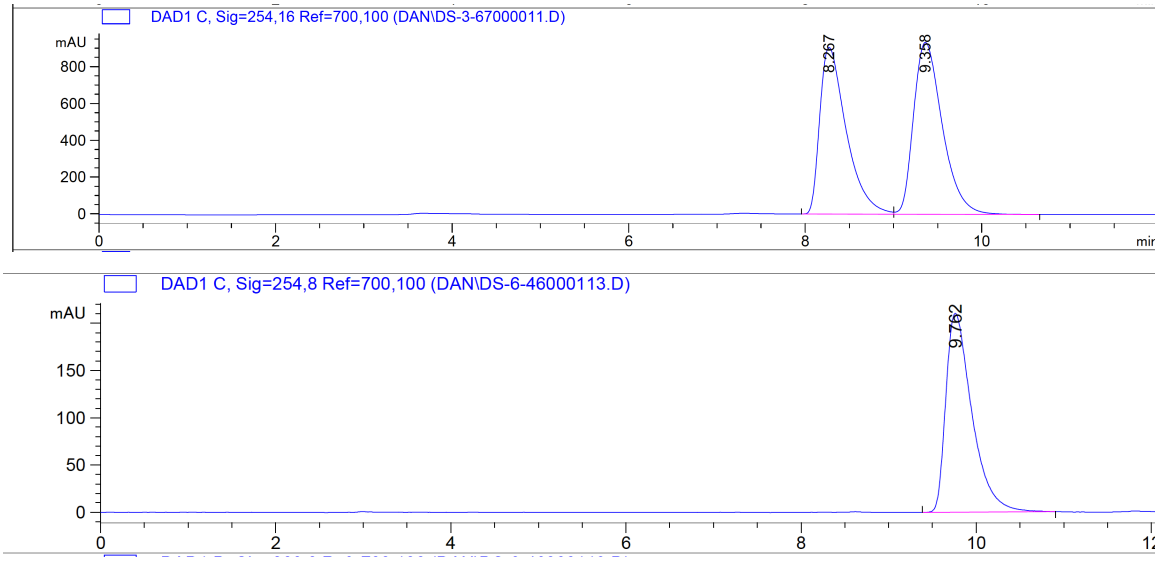


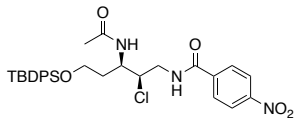
2m


DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-6-34000052.D)
mAU
28.139
31.026
3.348
min
DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-6-35000053.D)
mAU
28.429
min

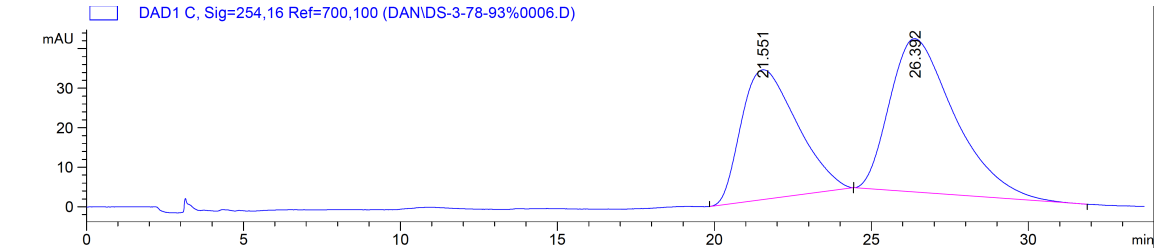


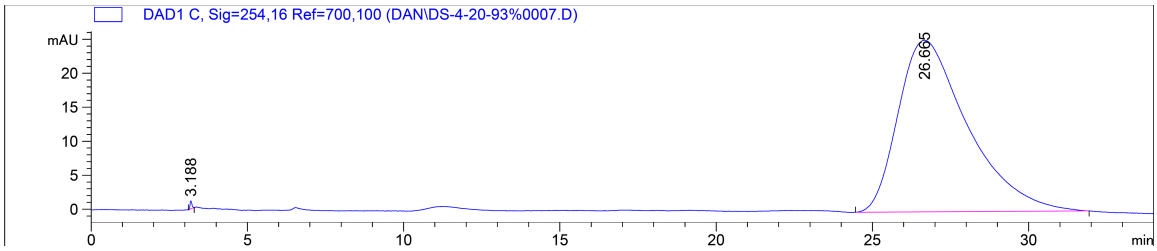
2n

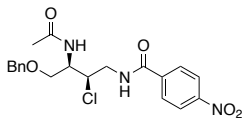

DAD1 C, Sig=254,16 Ref=700,100 (DAN\DS-3-67000011.D)
mAU
8.267
9.358
min
DAD1 C, Sig=254,8 Ref=700,100 (DAN\DS-6-46000113.D)
mAU
9.762

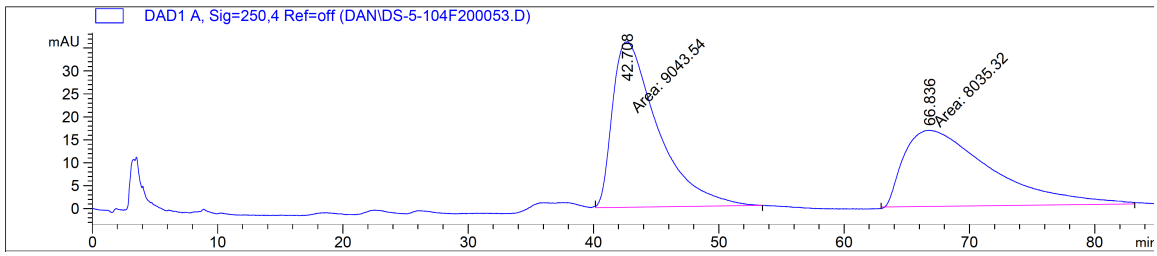

O
NH
O
TBDPSO
N
H
Cl
NO2

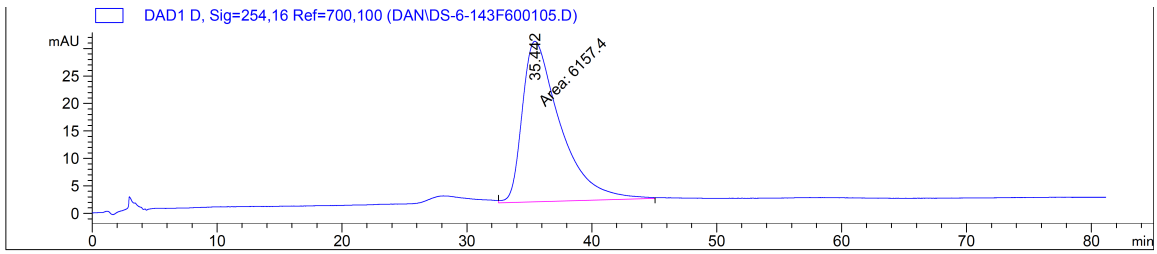
2o

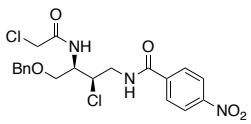

DAD1 C, Sig=254,16 Ref=700,100 (DAN\DS-3-78-93%0006.D)
mAU
21.551
26.392
min

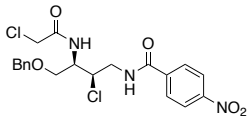

DAD1 C, Sig=254,16 Ref=700,100 (DAN\DS-4-20-93%0007.D)
mAU
3.188
26.665
min


O
NH
O
BnO
N
H
Cl
NO2

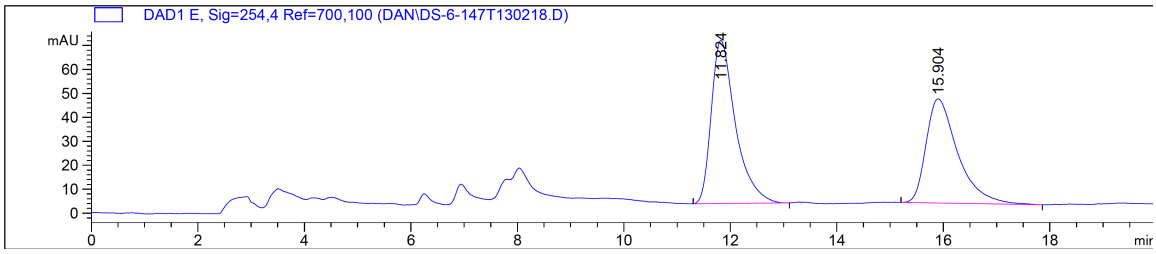

DAD1 A, Sig=250,4 Ref=off (DAN\DS-5-104F200053.D)
mAU
42.708
Area: 9043.54
66.836
Area: 8035.32
min

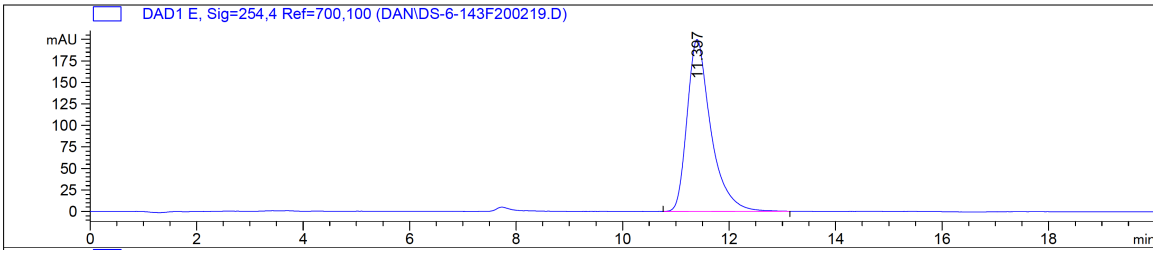

DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-6-143F600105.D)
mAU
35.442
Area: 6157.4
min

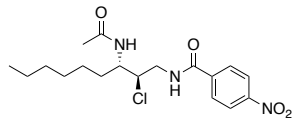

O
Cl
NH
O
BnO
N
H
Cl
NO2



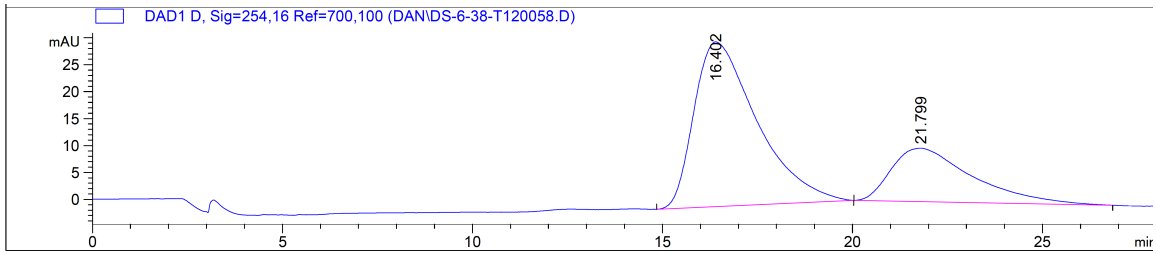
2p’

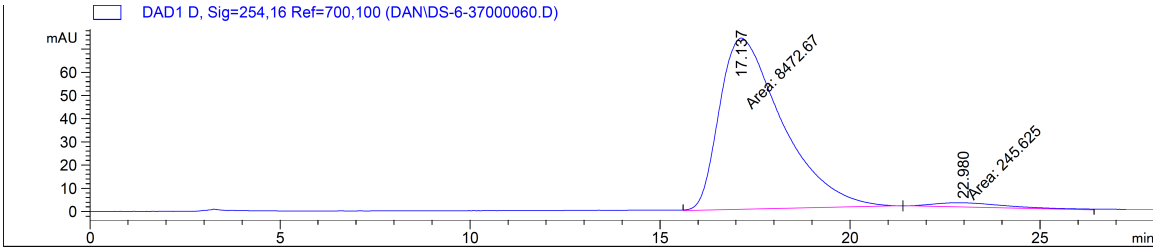






2q



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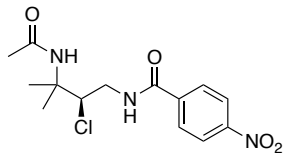
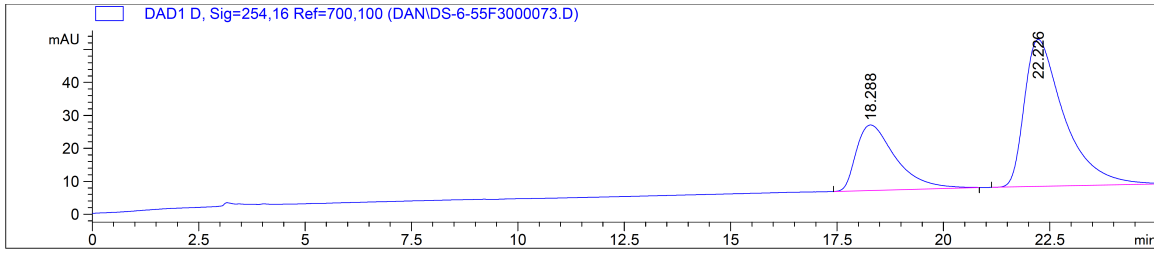
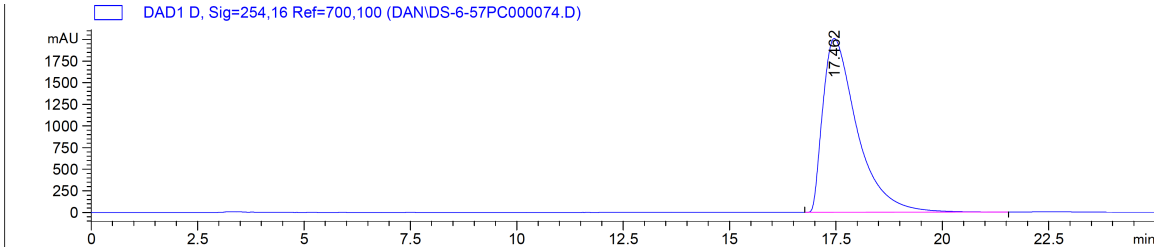
Signal 4: DAD1 D, Sig=254,16 Ref=700,100

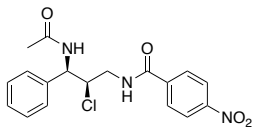
Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.137 MM    1.9136 8472.66602   73.79383  97.1827
   2  22.980 MM    2.2774  245.62465    1.79753   2.8173
```



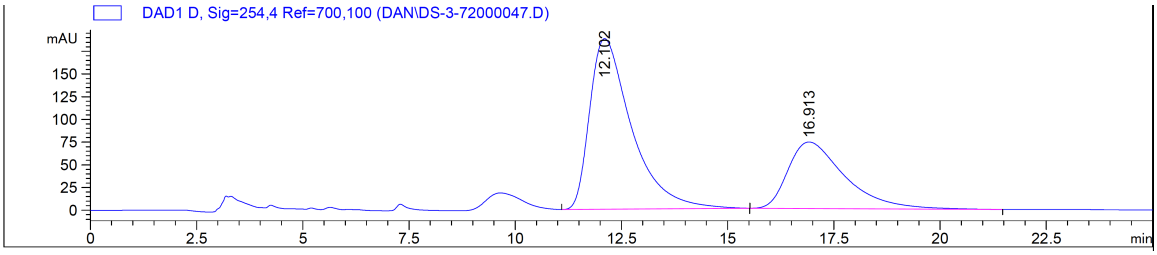
2r

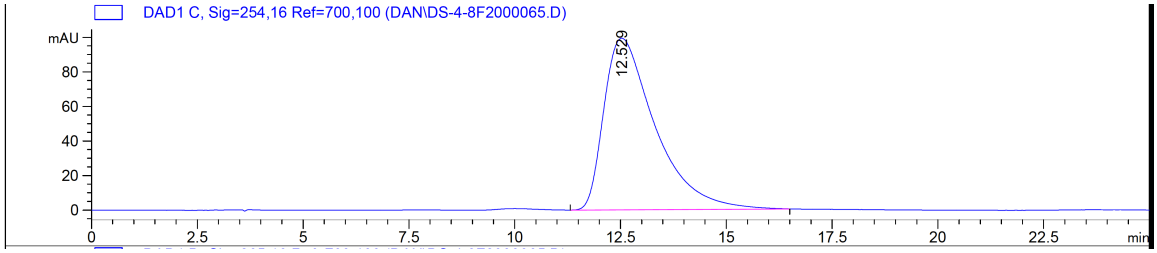

DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-6-55F3000073.D)
mAU
18.288
22.226
min

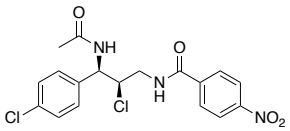

DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-6-57PC000074.D)
mAU
17.482
min



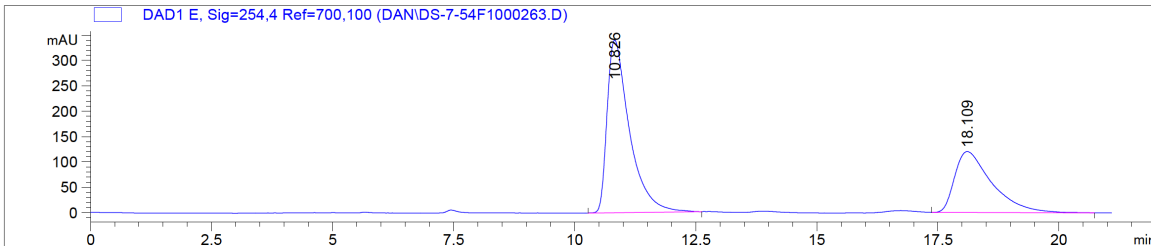
2s


DAD1 D, Sig=254,4 Ref=700,100 (DAN\DS-3-72000047.D)
mAU
12.102
16.913
min


DAD1 C, Sig=254,16 Ref=700,100 (DAN\DS-4-8F2000065.D)
mAU
12.529
min

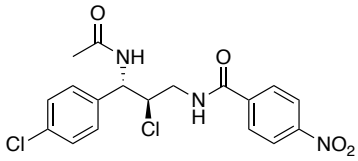


2t

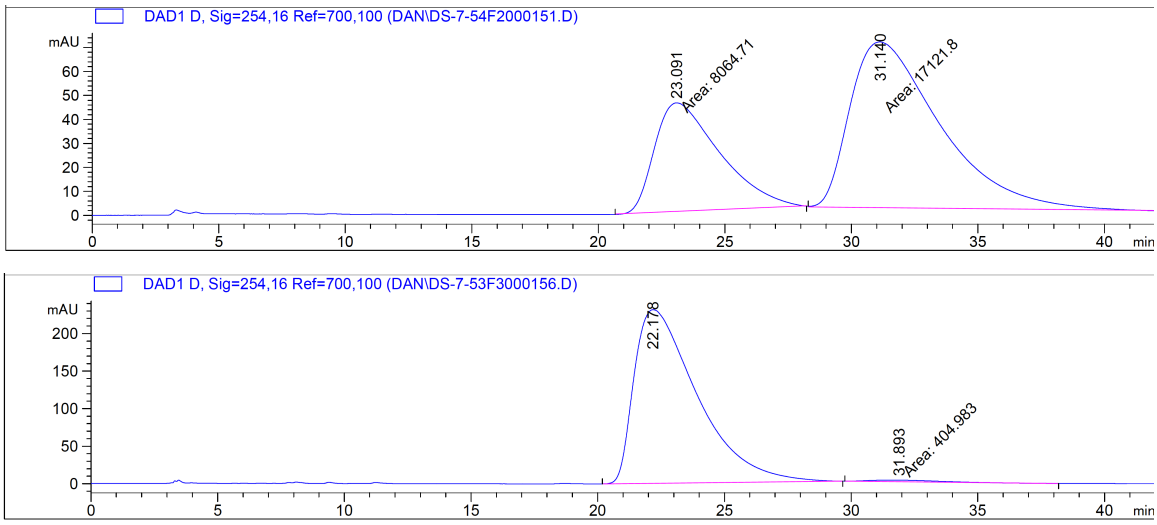


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.822	MM	0.4891	181.56491	6.18745	1.4050
2	17.612	MM	0.8567	1.27413e4	247.88031	98.5950

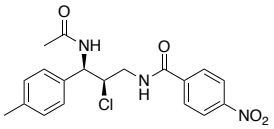


2t-D

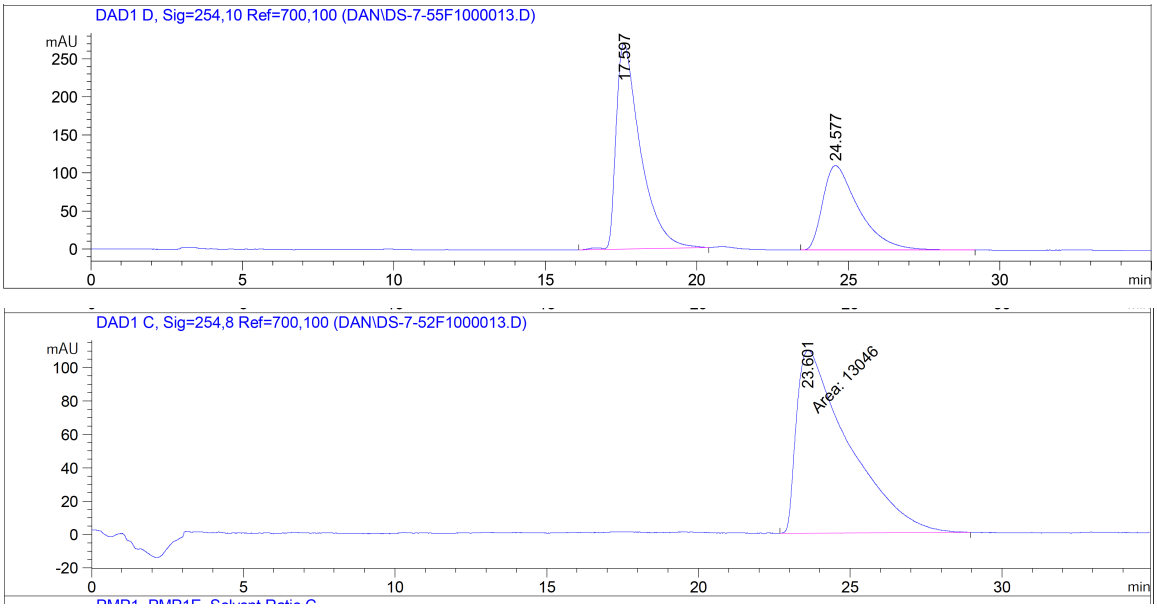


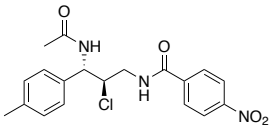
Signal 4: DAD1 D, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.178	BB	2.3715	4.00380e4	231.06677	98.9986
2	31.893	MM	3.1338	404.98325	2.15385	1.0014

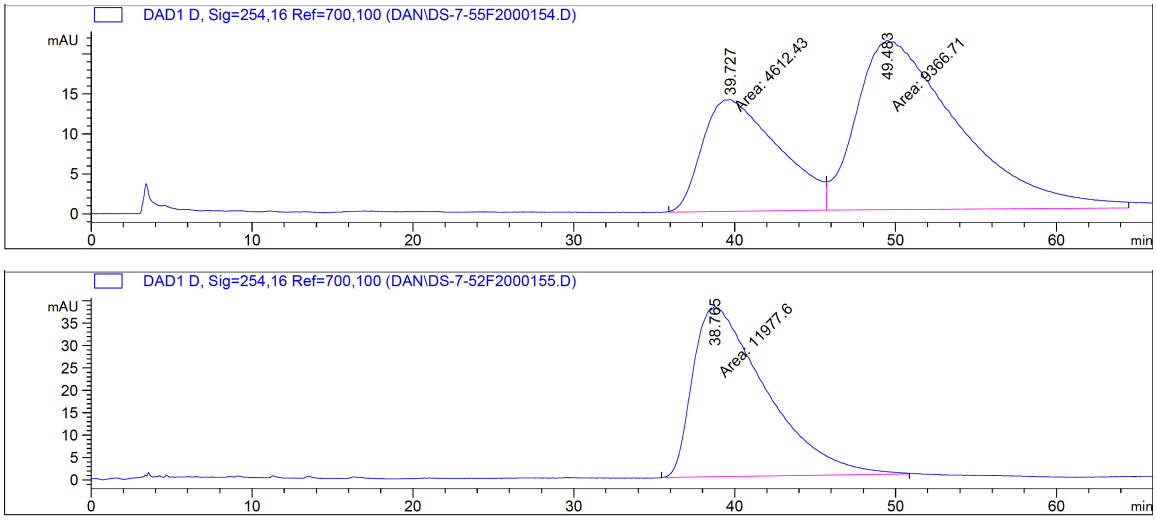


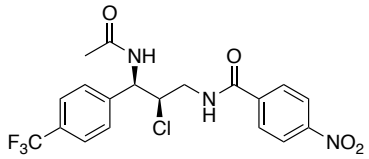
2u



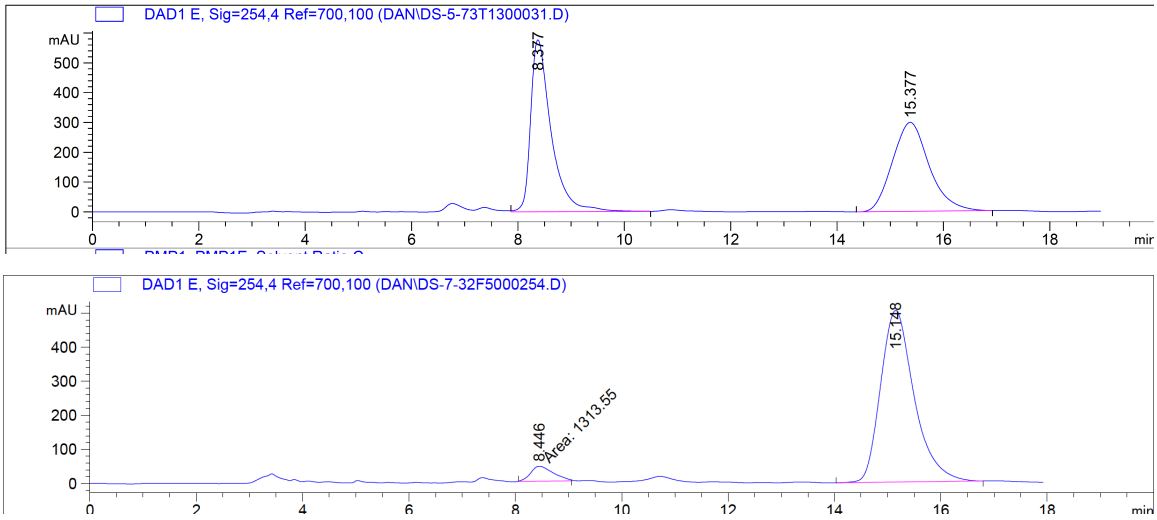

O
NH
O
N
H
Cl
NO2

2u-D


DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-7-55F2000154.D)
mAU
39.727
Area: 4612.43
49.483
Area: 9366.71
min
DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-7-52F2000155.D)
mAU
38.785
Area: 11977.6
min

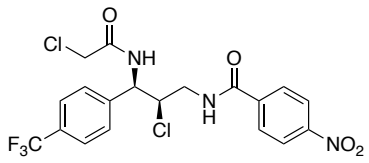


2v

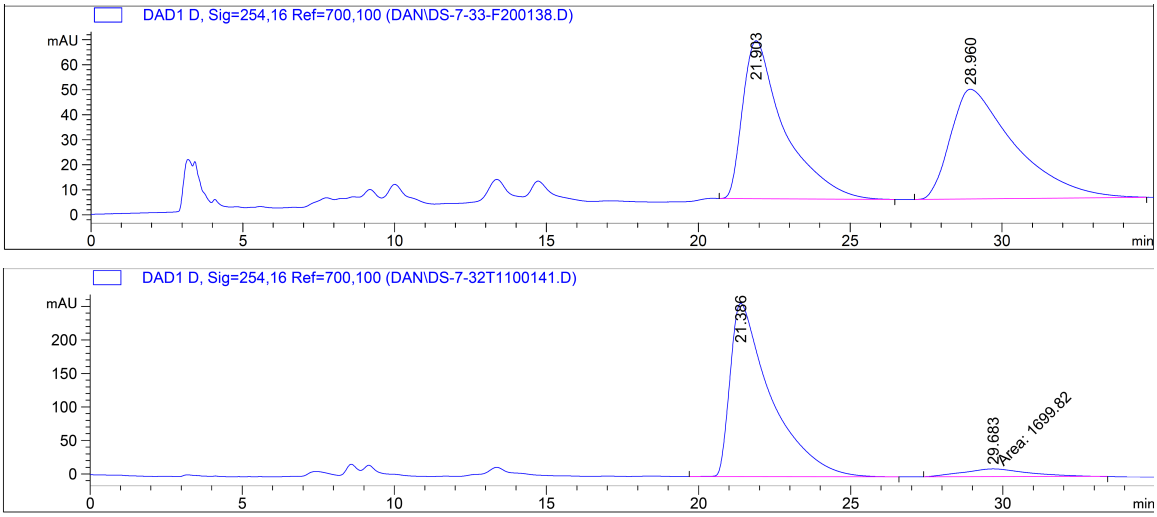


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.446	MM	0.4936	1313.55164	44.34906	5.6139
2	15.148	BB	0.6652	2.20845e4	504.02090	94.3861

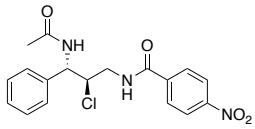


2v'

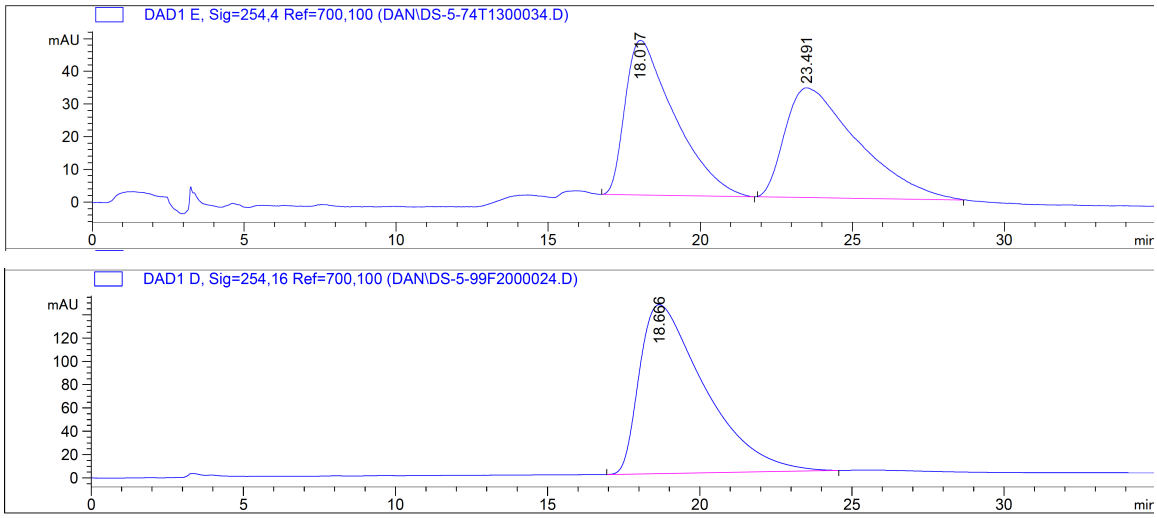


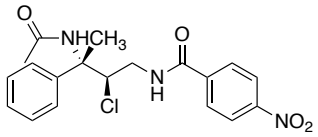
Signal 4: DAD1 D, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.386	BB	1.3222	2.41083e4	258.47577	93.4136
2	29.683	MM	2.4475	1699.81824	11.57501	6.5864

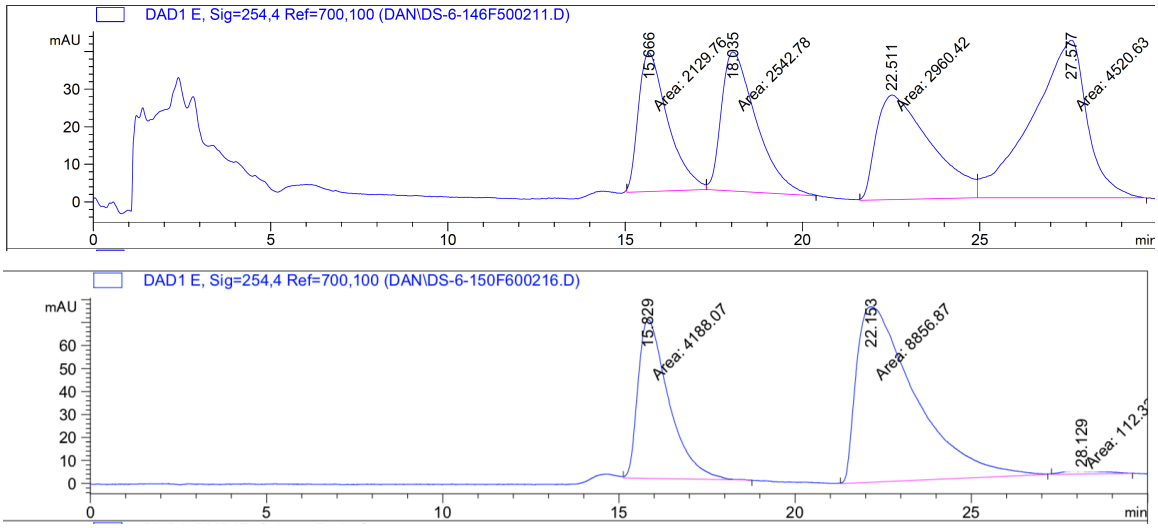


2w


DAD1 E, Sig=254,4 Ref=700,100 (DAN\DS-5-74T1300034.D)
mAU
18.017
23.491
min
DAD1 D, Sig=254,16 Ref=700,100 (DAN\DS-5-99F2000024.D)
mAU
18.666
min

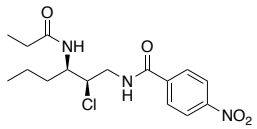


2x

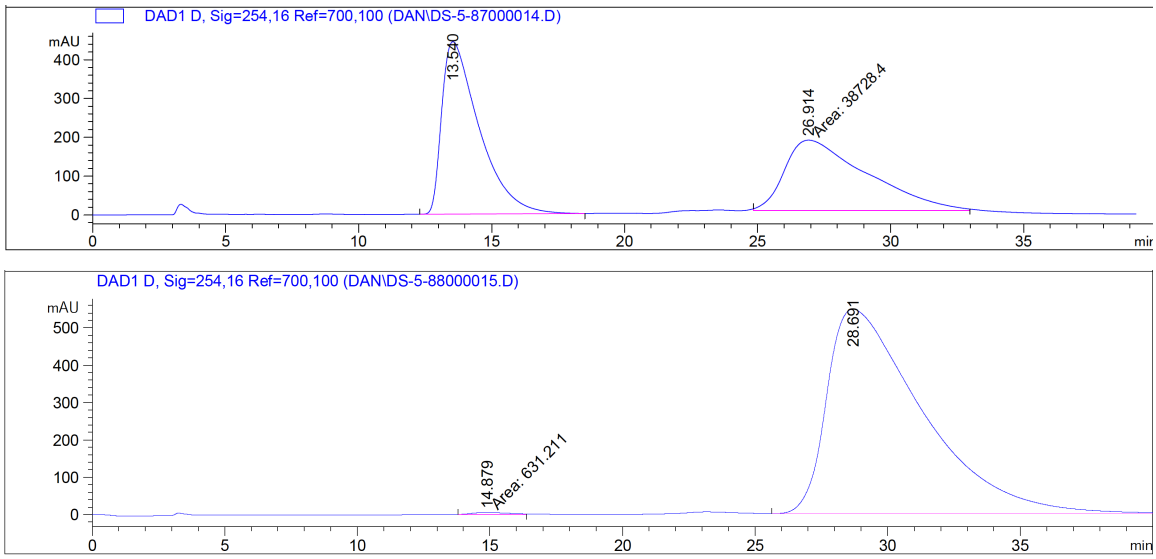


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.829	MM	1.0107	4188.06689	69.06340	31.8309
2	22.153	MM	1.9335	8856.86719	76.34757	67.3155
3	28.129	MM	1.5342	112.32303	1.22023	0.8537

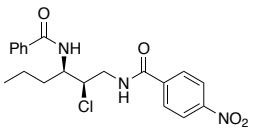


2aa

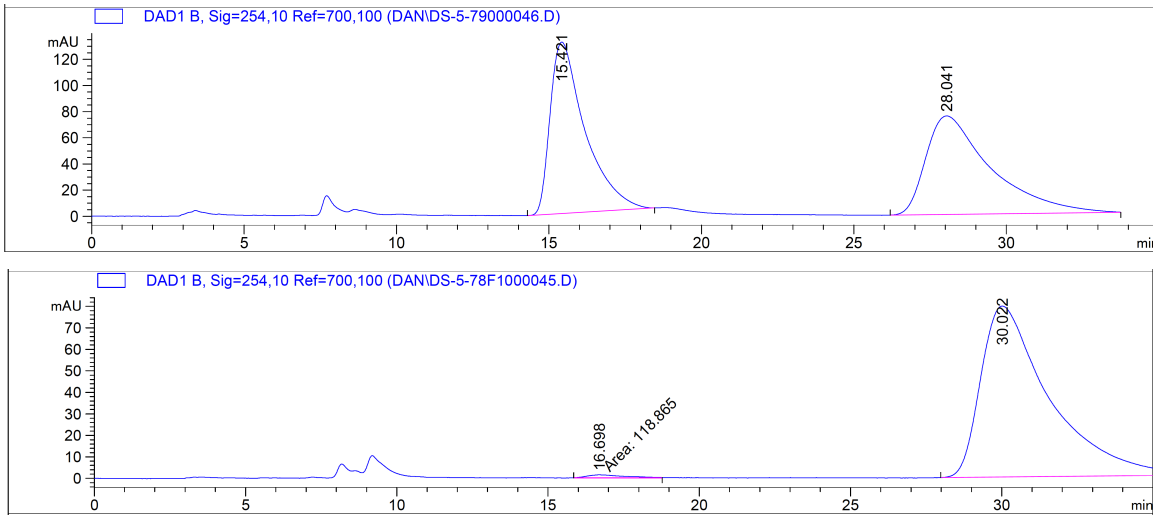


Signal 4: DAD1 D, Sig=254,16 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.879	MM	1.7033	631.21051	6.17631	0.4586
2	28.691	BB	3.3370	1.36998e5	547.56433	99.5414

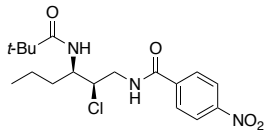


2ab

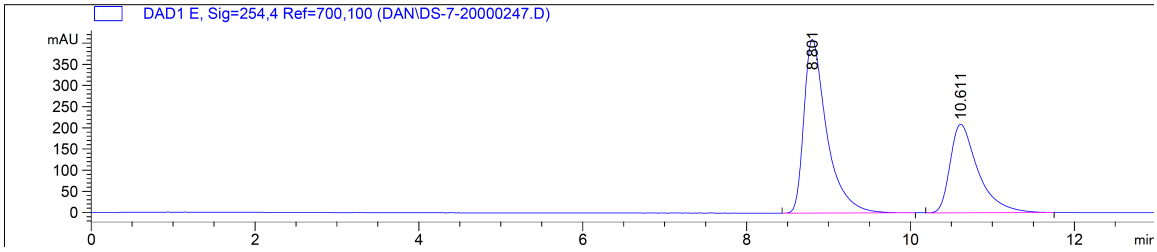


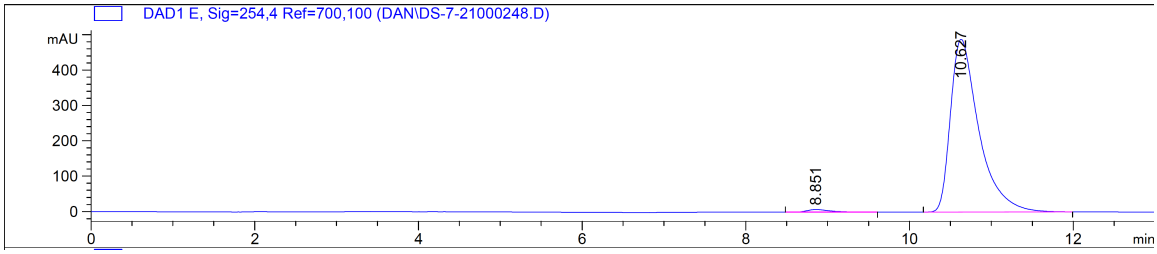
Signal 2: DAD1 B, Sig=254,10 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.698	MM	1.4209	118.86465	1.39422	0.9342
2	30.022	BB	1.8681	1.26046e4	79.48485	99.0658



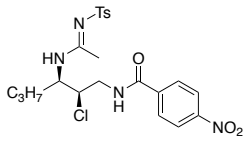
2ac



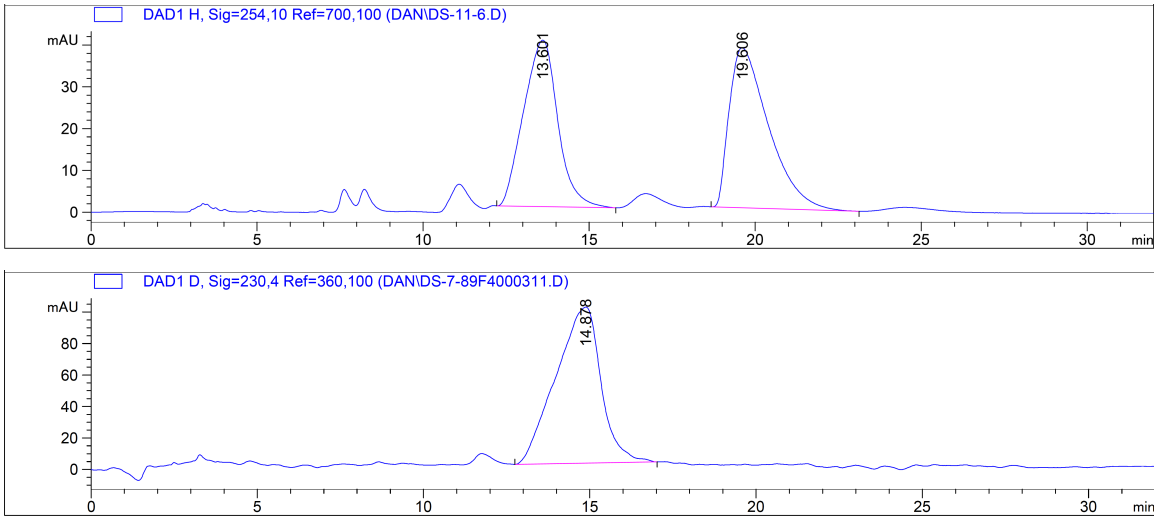


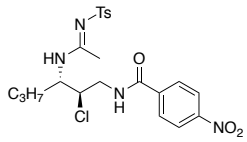
Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.851	BB	0.2829	146.71075	7.41419	1.2334
2	10.627	BB	0.3605	1.17484e4	488.62601	98.7666

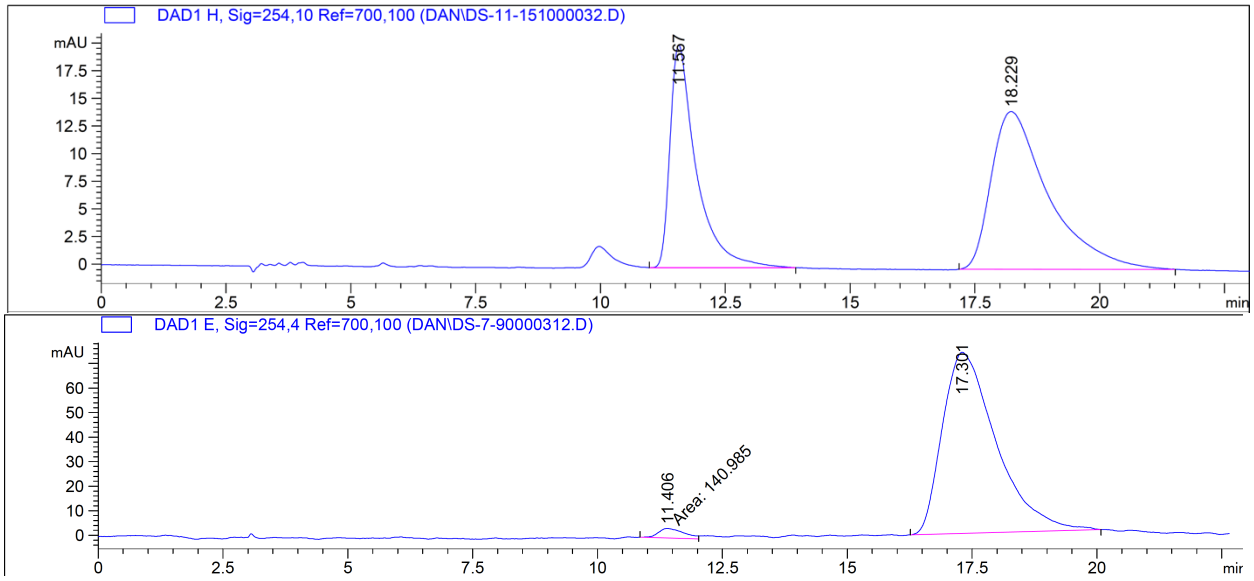

Ts
N
HN
O
C3H7
N
H
Cl
NO2

3a


DAD1 H, Sig=254,10 Ref=700,100 (DAN\DS-11-6.D)
mAU
13.601
19.606
min
DAD1 D, Sig=230,4 Ref=360,100 (DAN\DS-7-89F4000311.D)
mAU
14.878
min

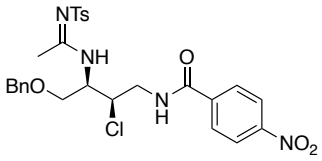


3h

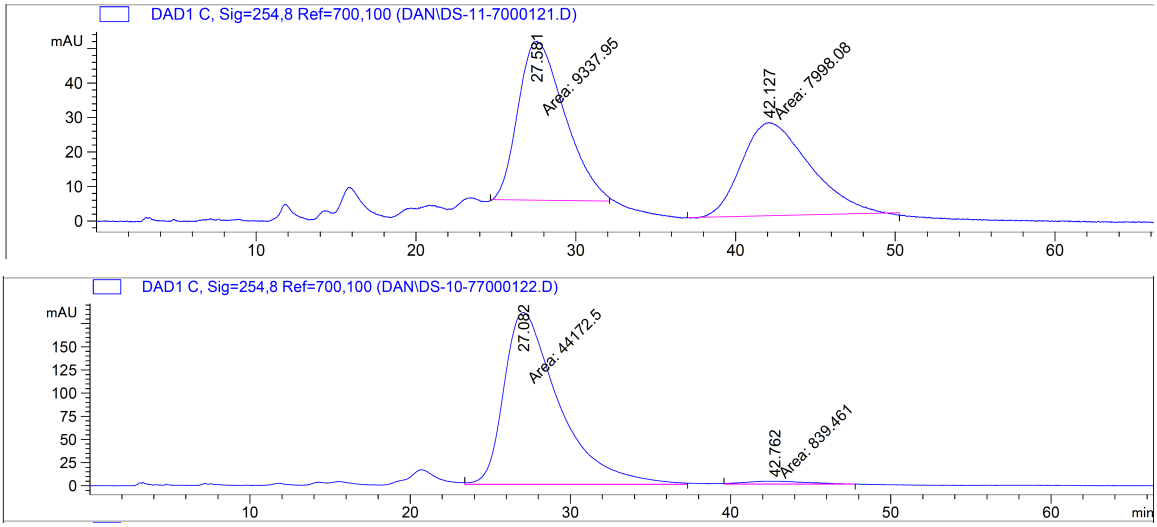


Signal 5: DAD1 E, Sig=254,4 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.406	MM	0.6049	140.98515	3.88441	2.4857
2	17.301	BB	0.9759	5530.86084	73.84030	97.5143

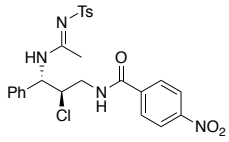


3p

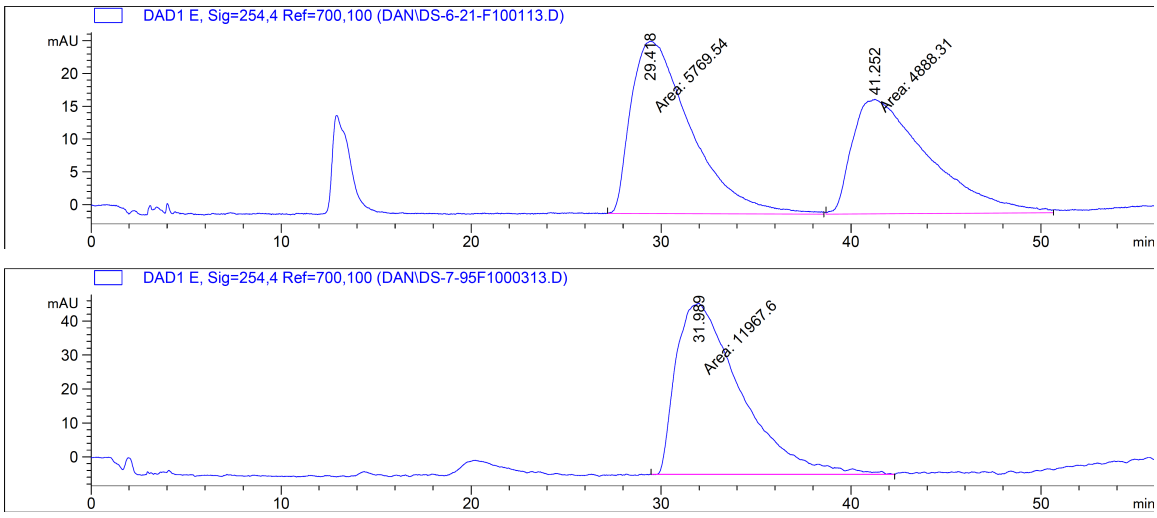


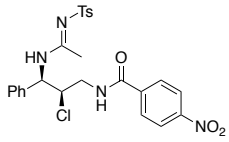
Signal 3: DAD1 C, Sig=254,8 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.082	MM	3.9727	4.41725e4	185.31581	98.1350
2	42.762	MM	4.4539	839.46094	3.14126	1.8650
Totals :				4.50119e4	188.45707	

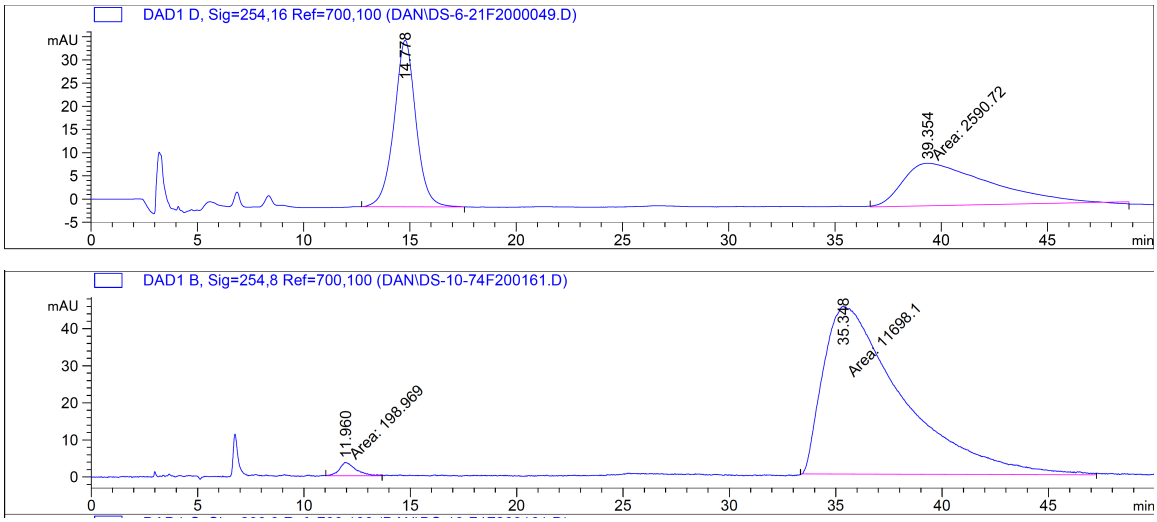


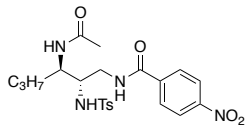
3s



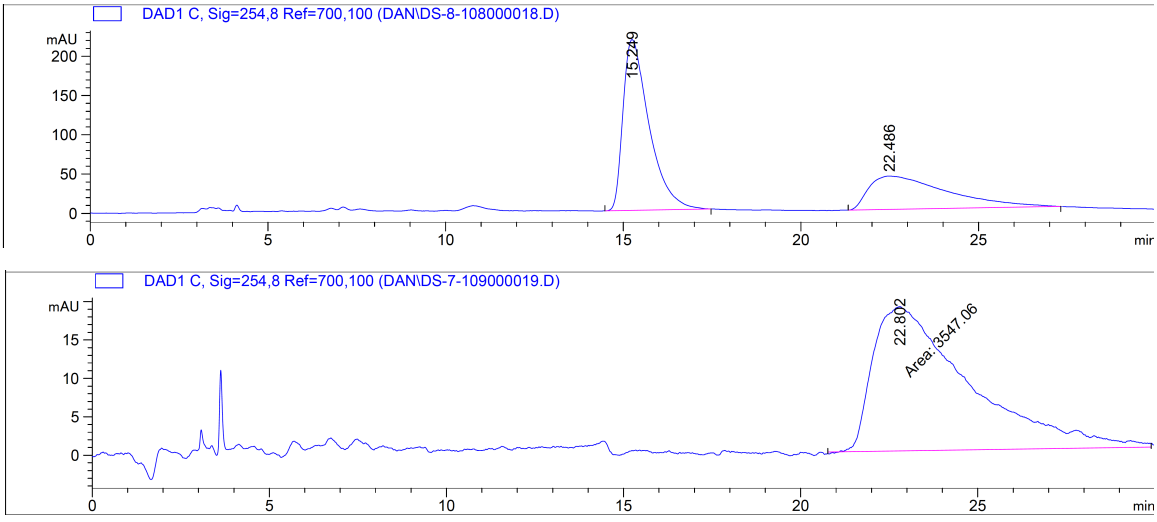


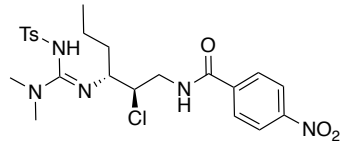
3s-diastereomer



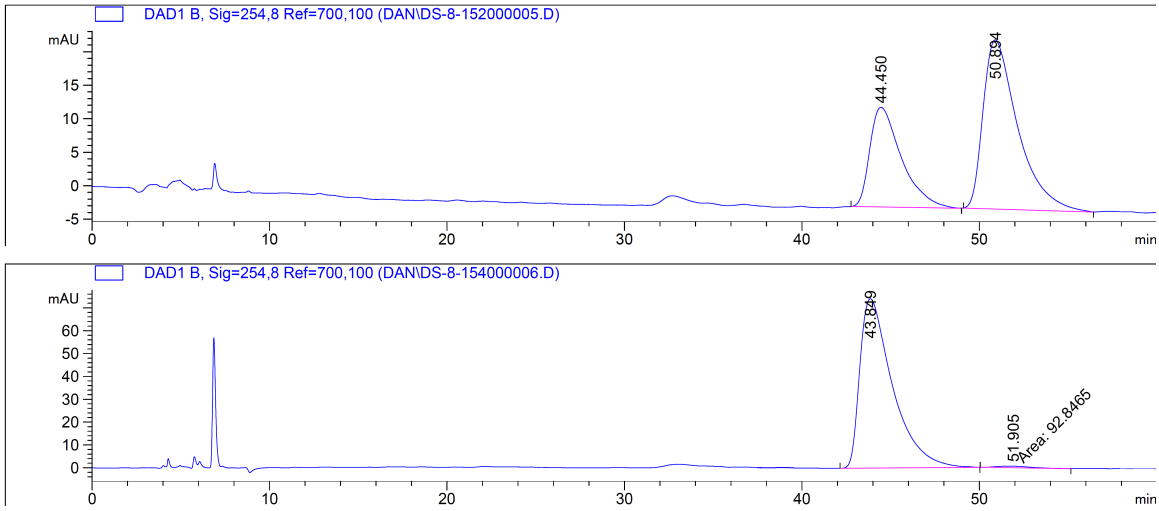


6a





7a



Signal 1: DAD1 B, Sig=254,8 Ref=700,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.849	BB	1.7508	9477.57227	74.16925	99.0299
2	51.905	MM	2.1032	92.84650	7.35769e-1	0.9701

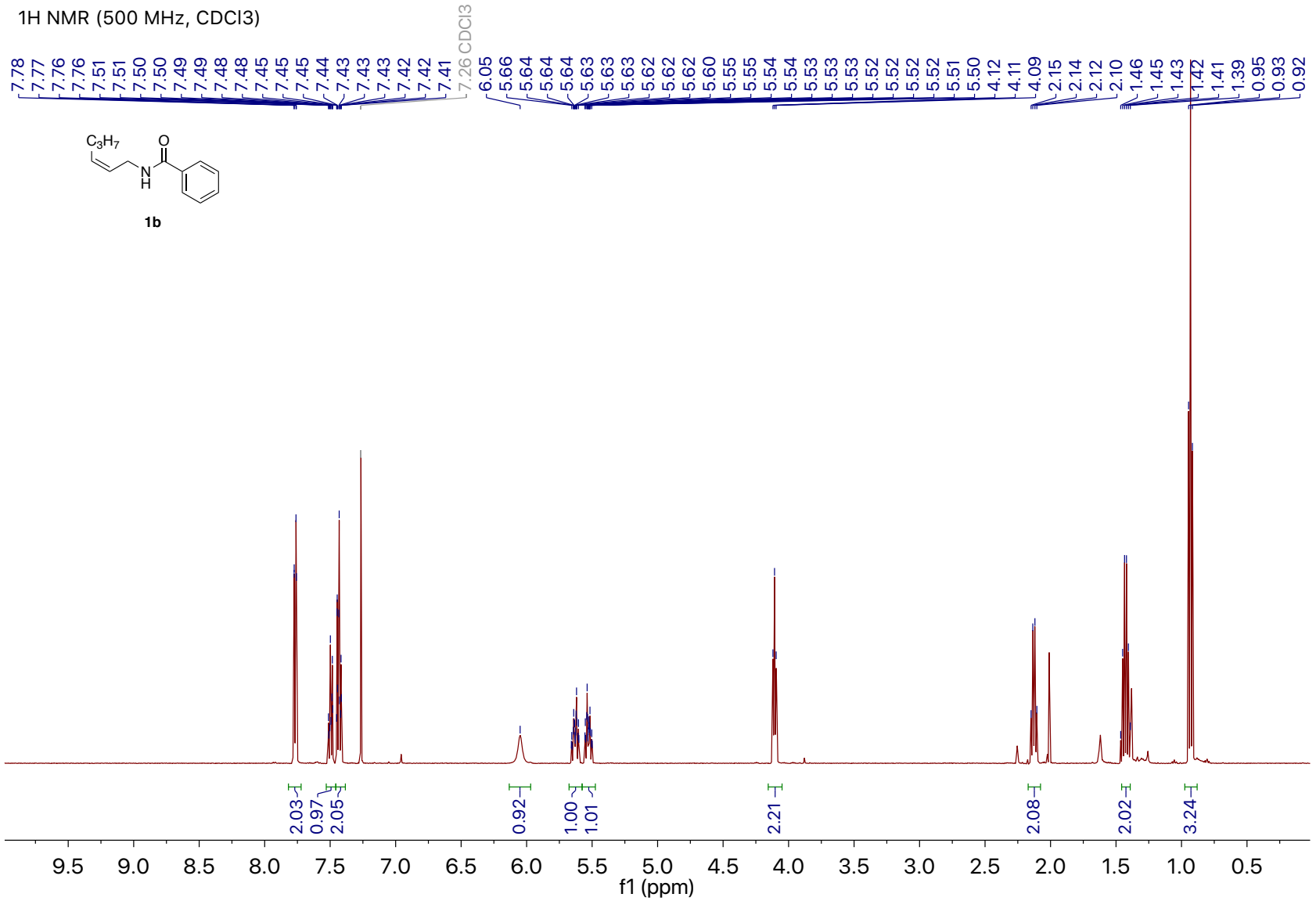
XI References:

(1) Soltanzadeh, B.; Jaganathan, A.; Staples, R. J.; Borhan, B. Highly Stereoselective Intermolecular Haloetherification and Haloesterification of Allyl Amides. *Angew. Chem. Int. Ed.* **2015**, *54*, 9517.

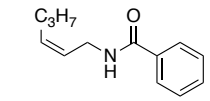
(2) Gadwood, R. C.; Kamdar, B. V.; Dubray, L. A.; Wolfe, M. L.; Smith, M. P.; Watt, W.; Mizsak, S. A.; Groppi, V. E. Synthesis and biological activity of spirocyclic benzopyran imidazolone potassium channel openers. *J. Med. Chem.* **1993**, *36*, 1480.

(3) Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B. An Organocatalytic Asymmetric Chlorolactonization. *J. Am. Chem. Soc.* **2010**, *132*, 3298.

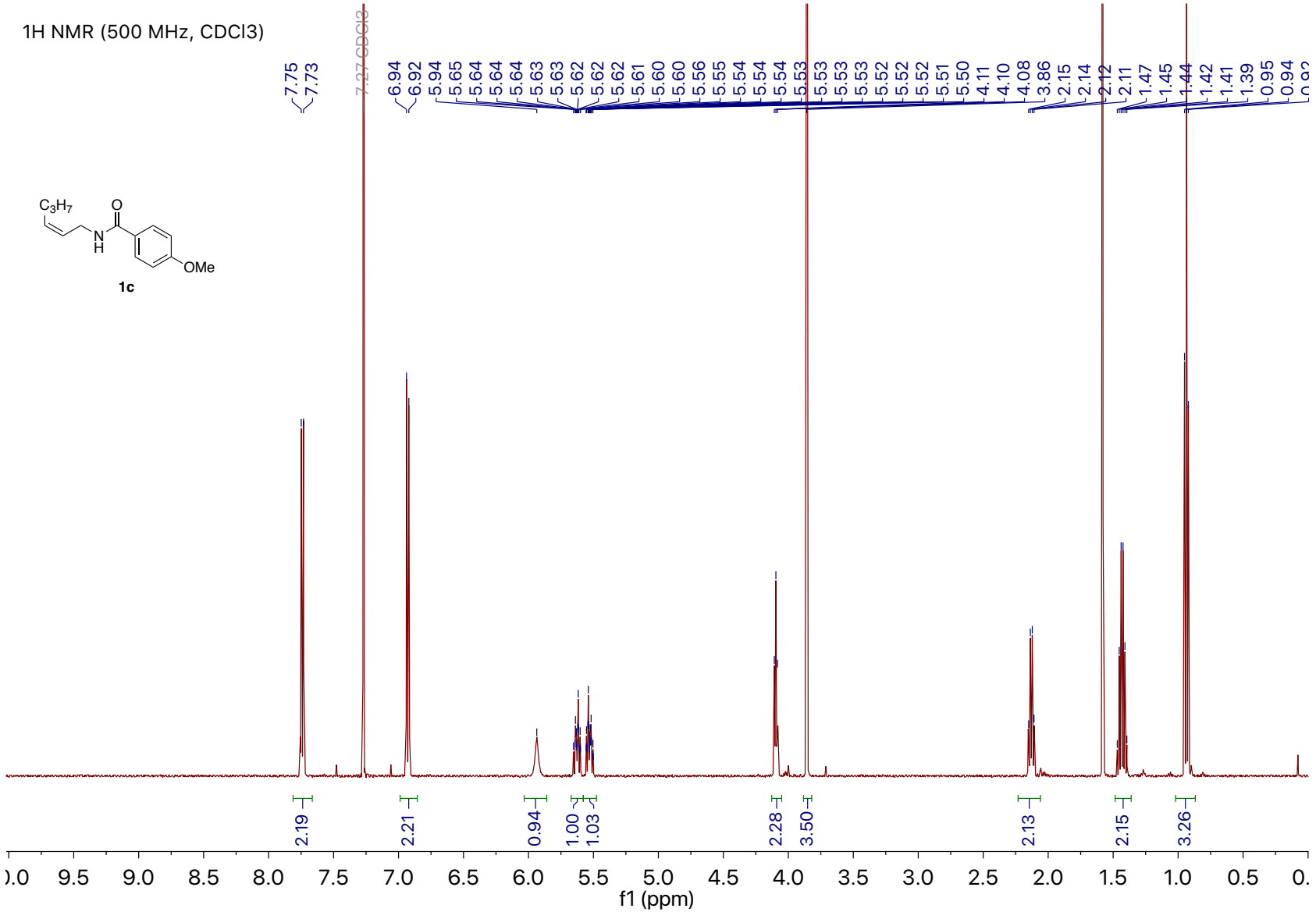
XII NMR Spectra:

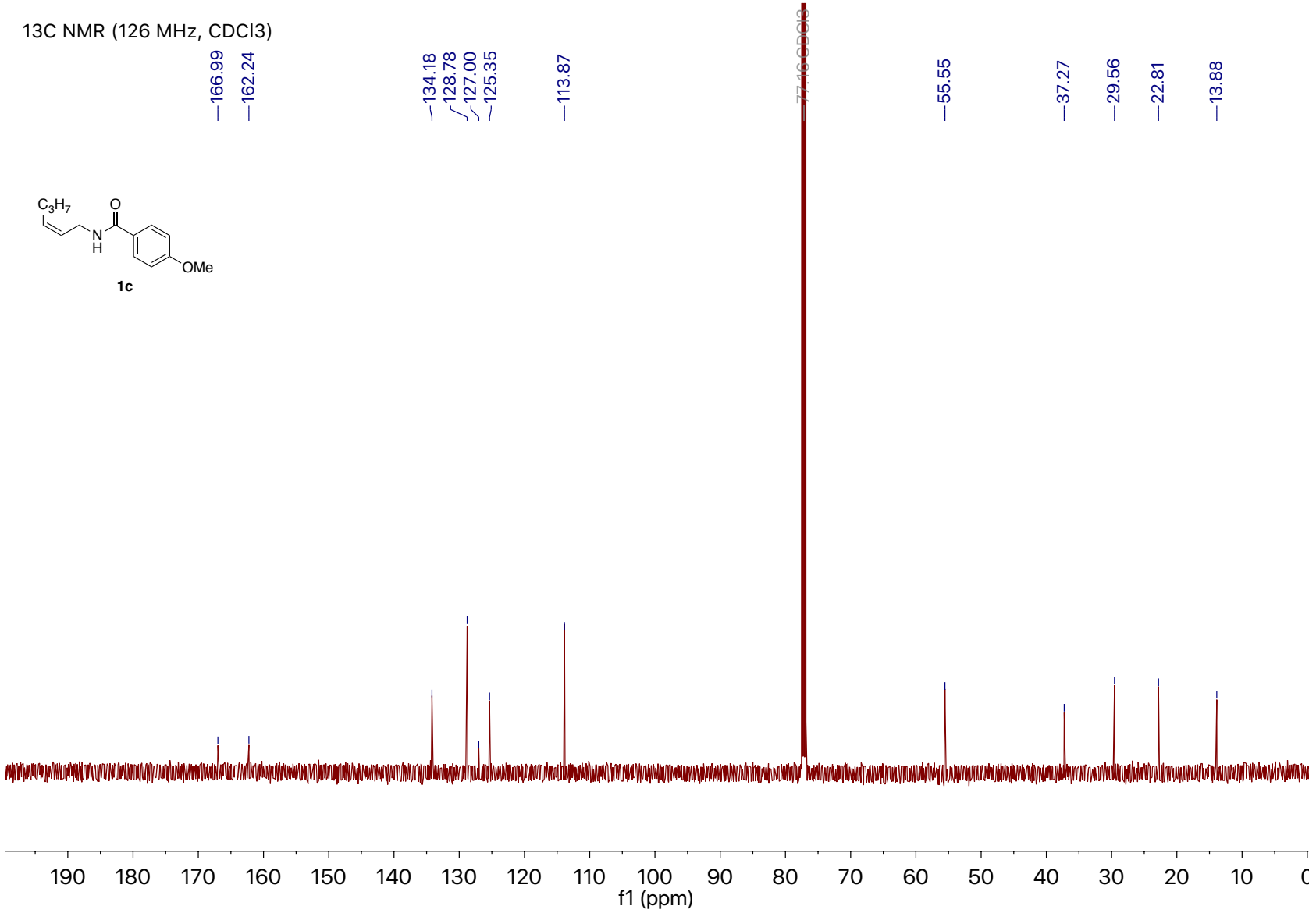

1H NMR (500 MHz, CDCl3)
7.78 7.77 7.76 7.76 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.45 7.45 7.45 7.44 7.43 7.43 7.43 7.42 7.42 7.41
7.26 CDCl3
6.05 5.66 5.64 5.64 5.64 5.63 5.63 5.63 5.62 5.62 5.62 5.60 5.55 5.55 5.54 5.54 5.53 5.53 5.53 5.52 5.52 5.52 5.52 5.51 5.50 4.12 4.11 4.09 2.15 2.14 2.12 2.10 1.46 1.45 1.43 1.42 1.41 1.39 0.95 0.93 0.92
C3H7
O
N
H
1b
2.03
0.97
2.05
0.92
1.00
1.01
2.21
2.08
2.02
3.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

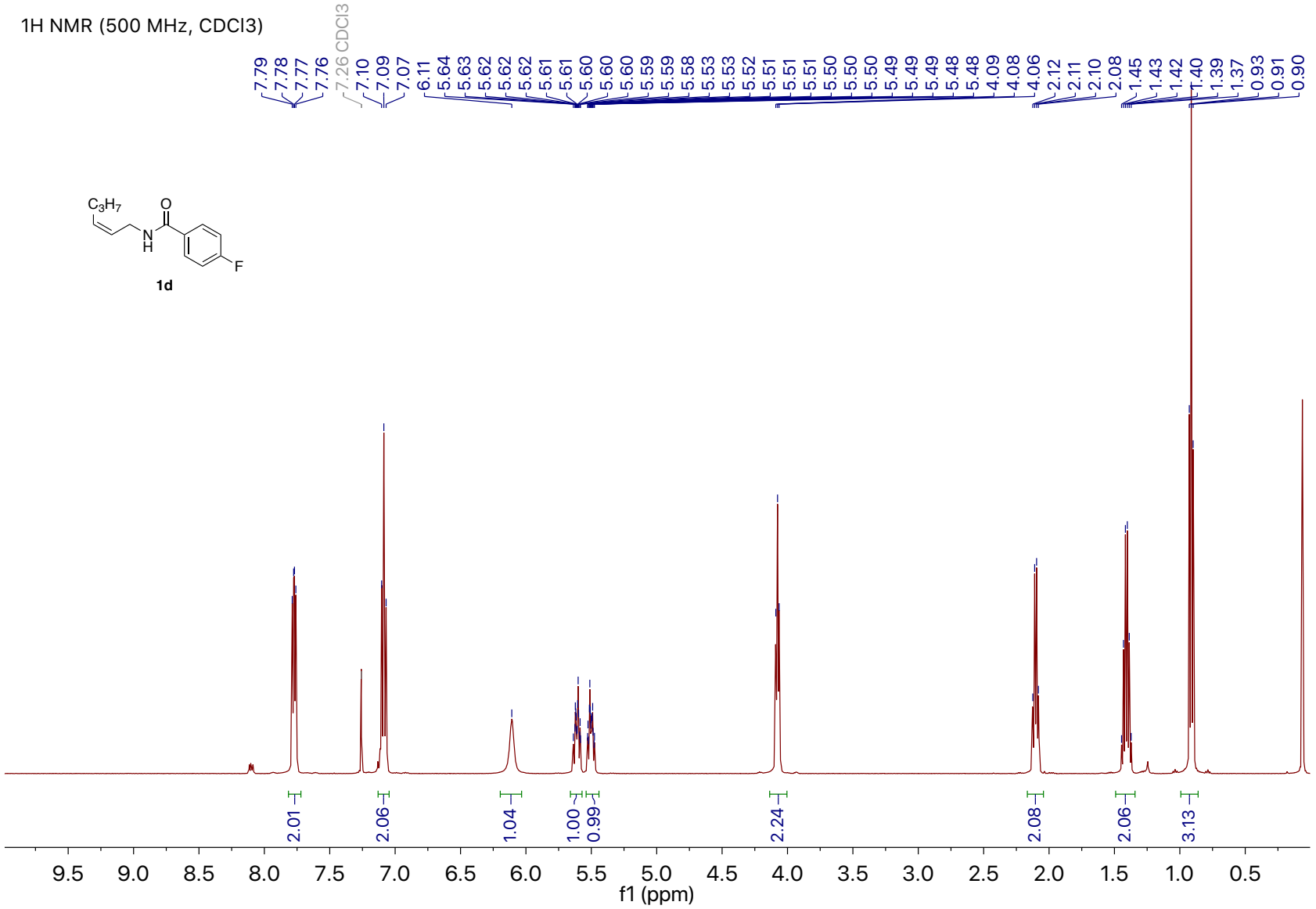
13C NMR (126 MHz, CDCl3)



1b

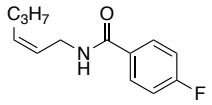

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
f1 (ppm)
1c


13C NMR (126 MHz, CDCl3)
166.99
162.24
134.18
128.78
127.00
125.35
113.87
77.16 CDCl3
55.55
37.27
29.56
22.81
13.88
C3H7
O
N
H
OMe
1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

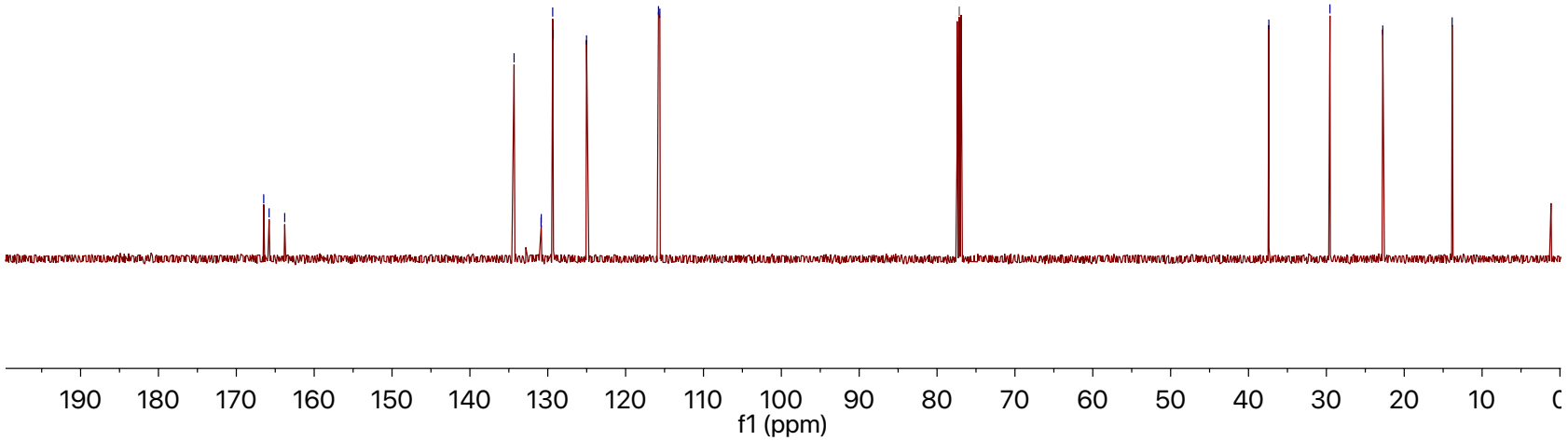

1H NMR (500 MHz, CDCl3)
7.79
7.78
7.77
7.76
7.26 CDCl3
7.10
7.09
7.07
6.11
5.64
5.63
5.62
5.62
5.62
5.61
5.61
5.60
5.60
5.60
5.60
5.59
5.59
5.58
5.53
5.53
5.52
5.51
5.51
5.51
5.50
5.50
5.50
5.49
5.49
5.48
5.48
4.09
4.08
4.06
2.12
2.11
2.10
2.08
1.45
1.43
1.42
1.40
1.39
1.37
0.93
0.91
0.90
C3H7
O
N
H
F
1d
2.01
2.06
1.04
1.00
0.99
2.24
2.08
2.06
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

13C NMR (126 MHz, CDCl3)

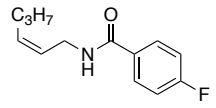
166.48
165.79
163.79
134.33
130.86
130.84
129.37
129.30
125.02
115.78
115.60
77.16 CDCl3
37.39
29.54
22.76
13.85



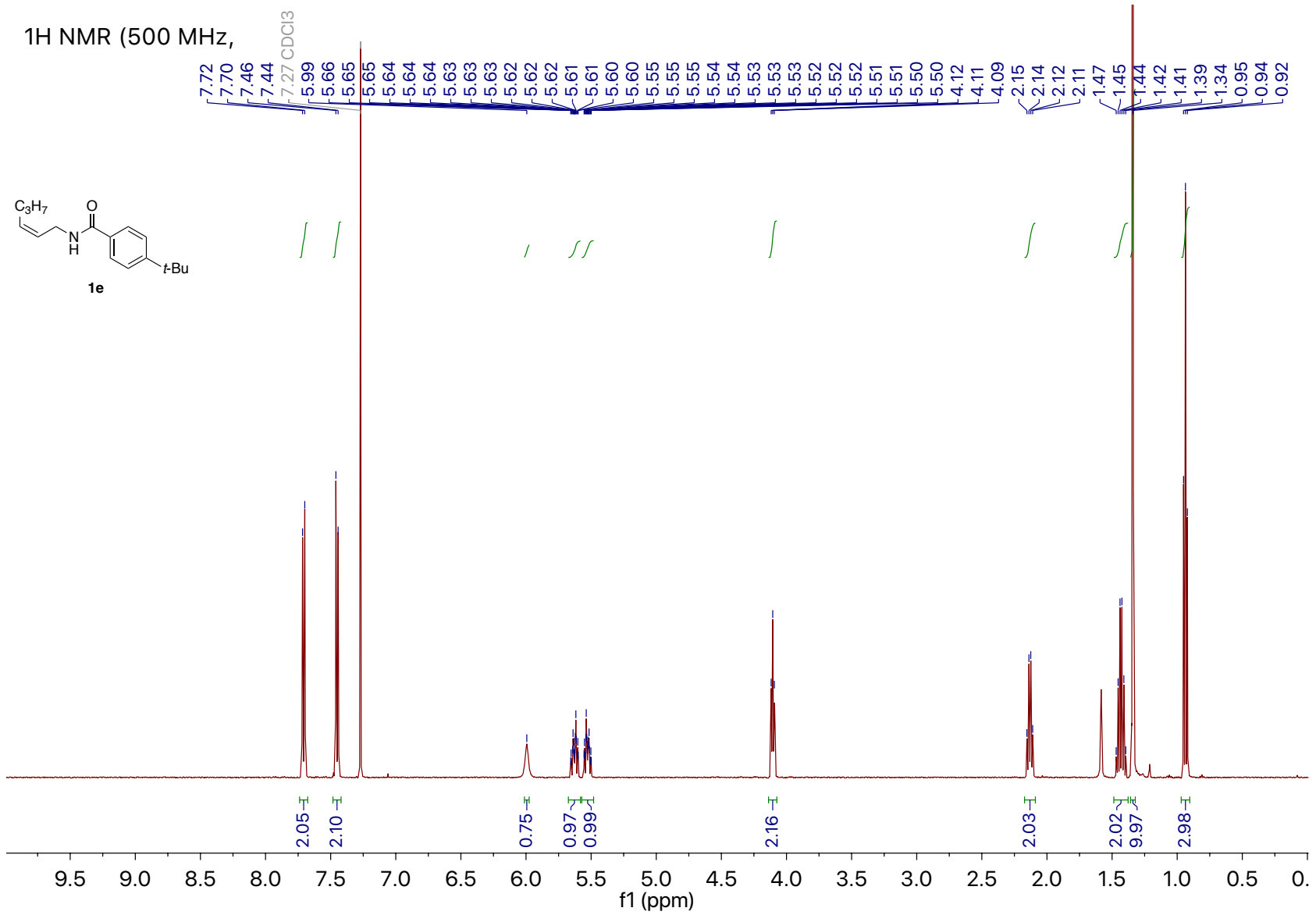
1d



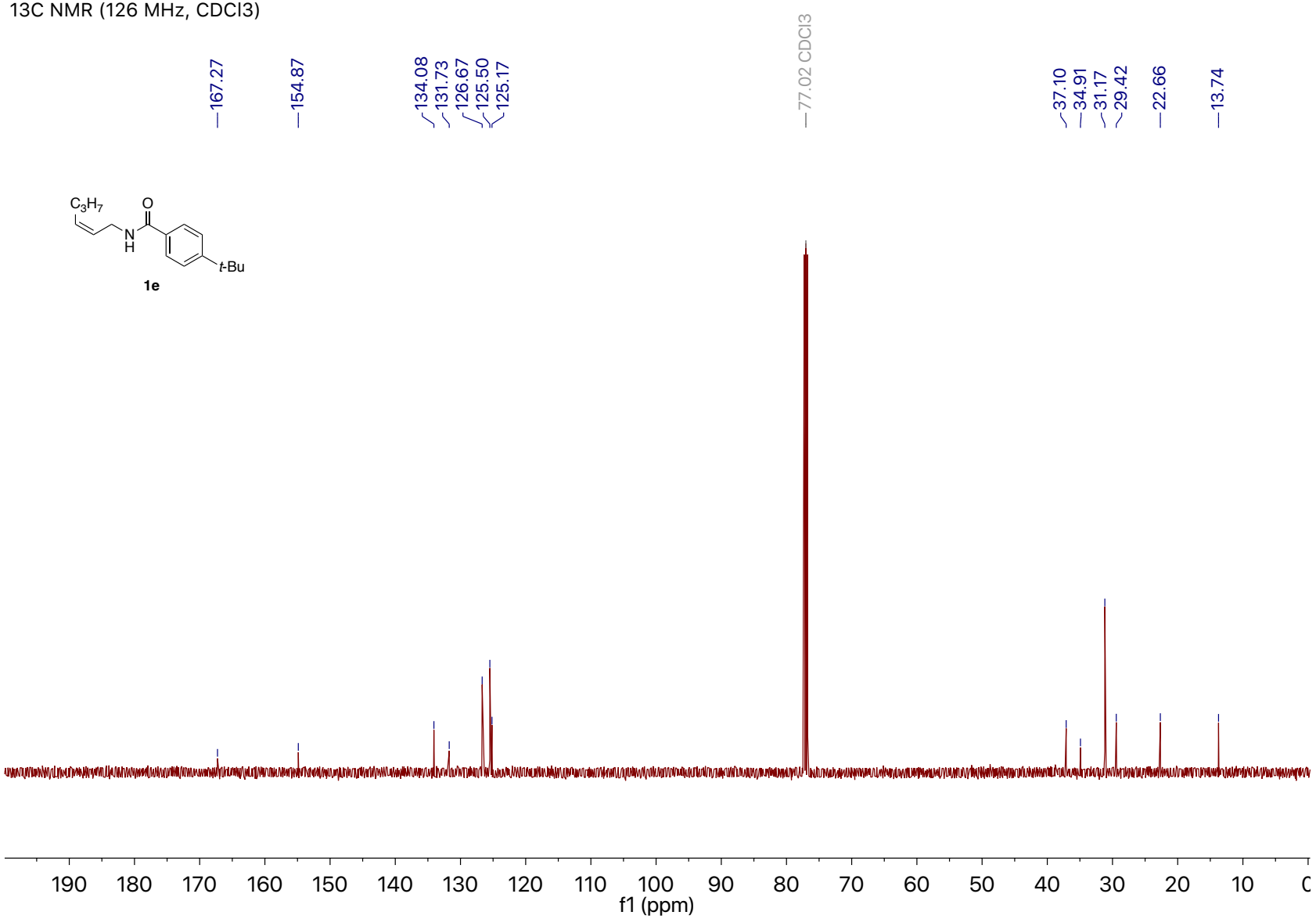
19F NMR (470 MHz, CDCl3)

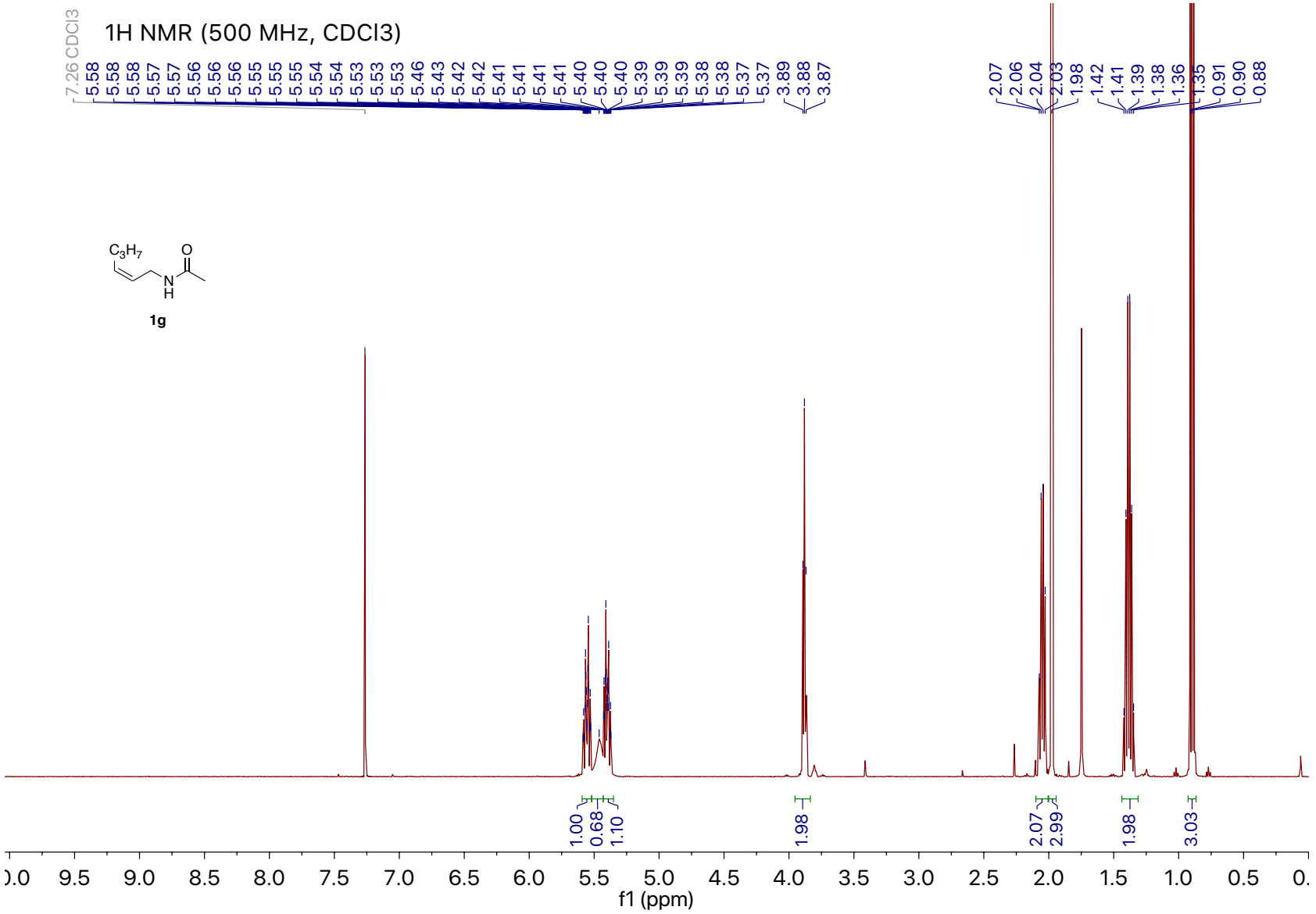


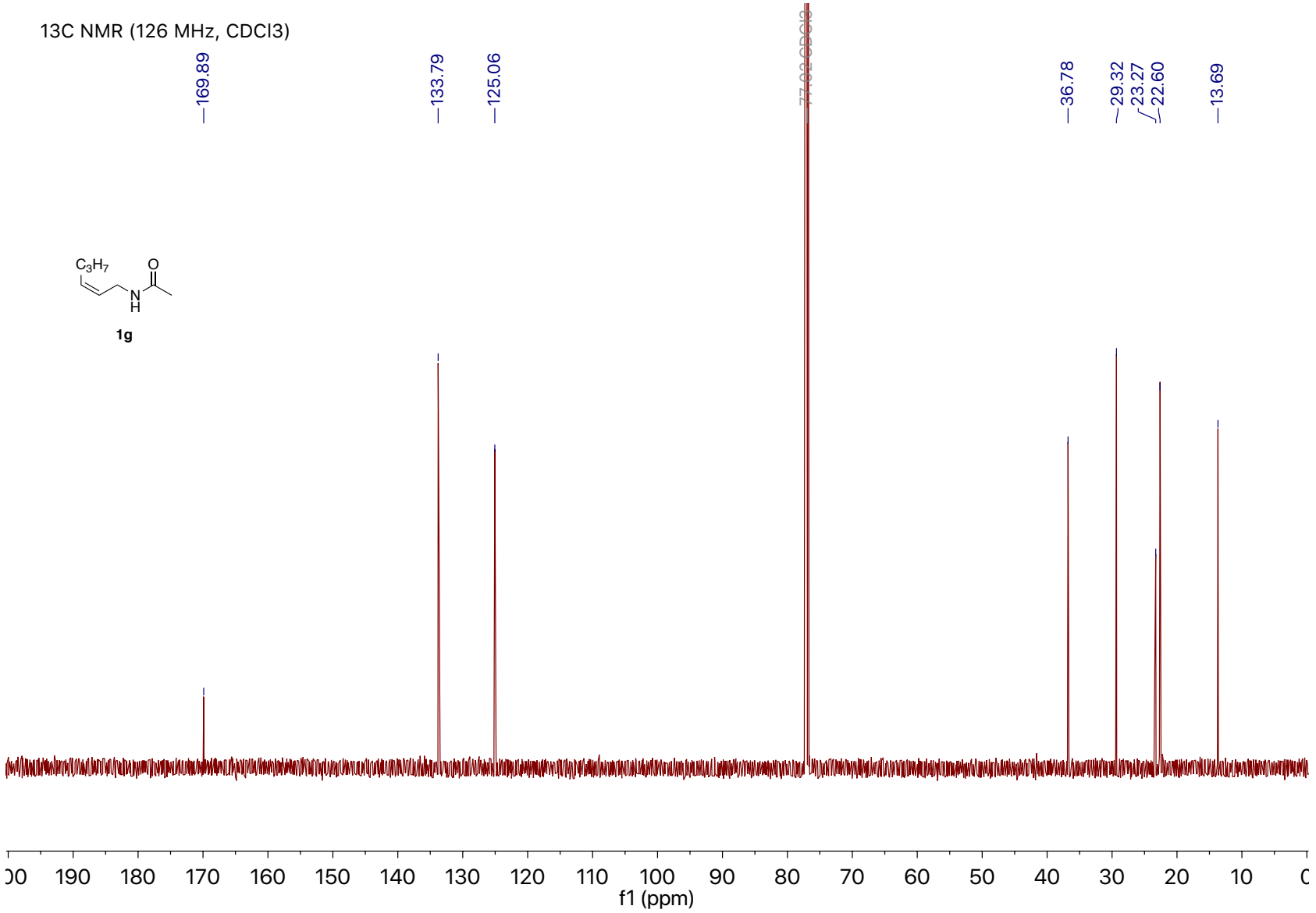
1d

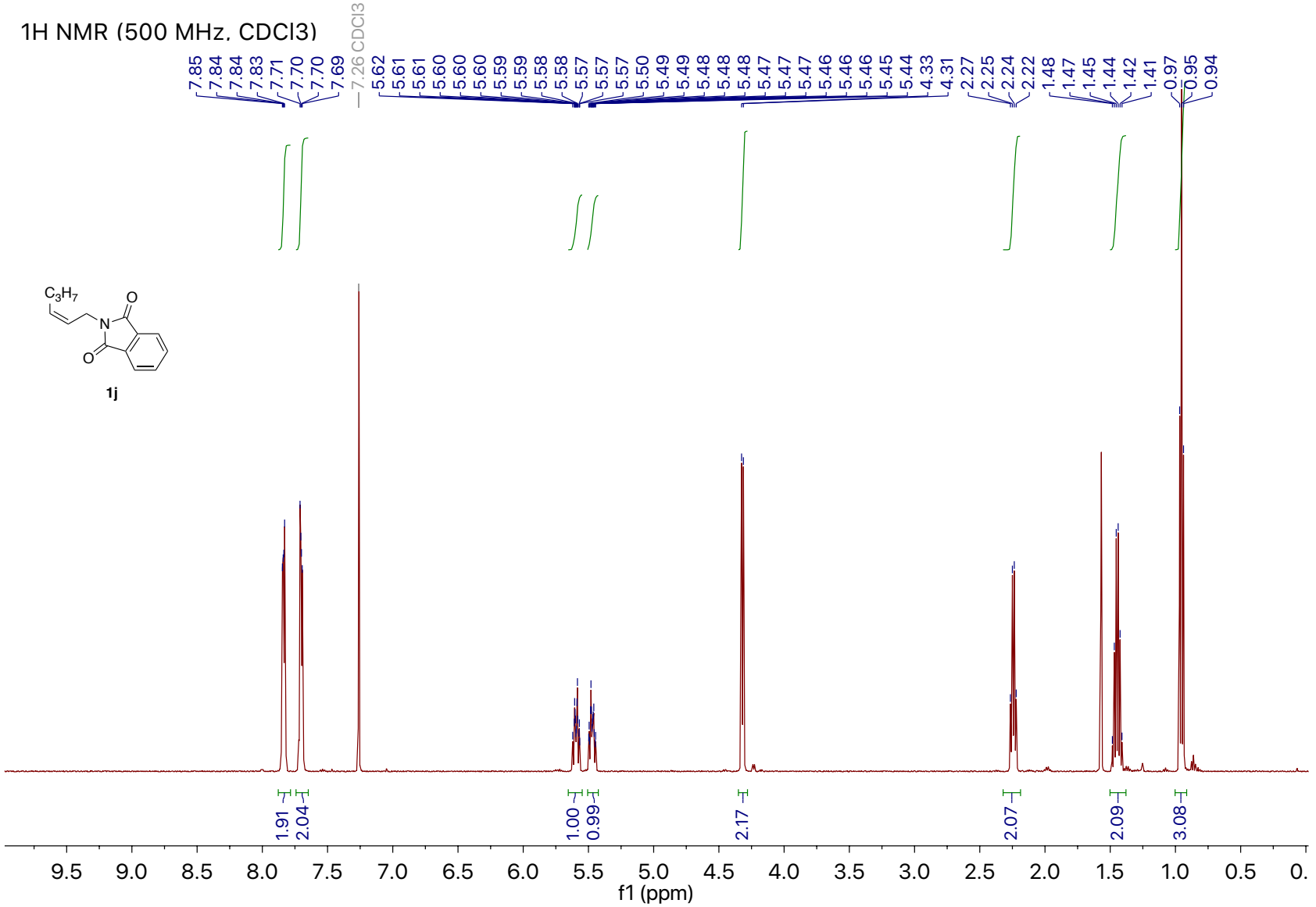

1H NMR (500 MHz,
7.27 CDCl3
7.72 7.70 7.46 7.44 5.99 5.66 5.65 5.65 5.64 5.64 5.64 5.63 5.63 5.63 5.62 5.62 5.62 5.61 5.61 5.60 5.60 5.55 5.55 5.55 5.54 5.54 5.53 5.53 5.53 5.52 5.52 5.52 5.51 5.51 5.50 5.50 4.12 4.11 4.09 2.15 2.14 2.12 2.11 1.47 1.45 1.44 1.42 1.41 1.39 1.34 0.95 0.94 0.92
C3H7
O
N
H
t-Bu
1e
2.05
2.10
0.75
0.97
0.99
2.16
2.03
2.02
9.97
2.98
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.
f1 (ppm)

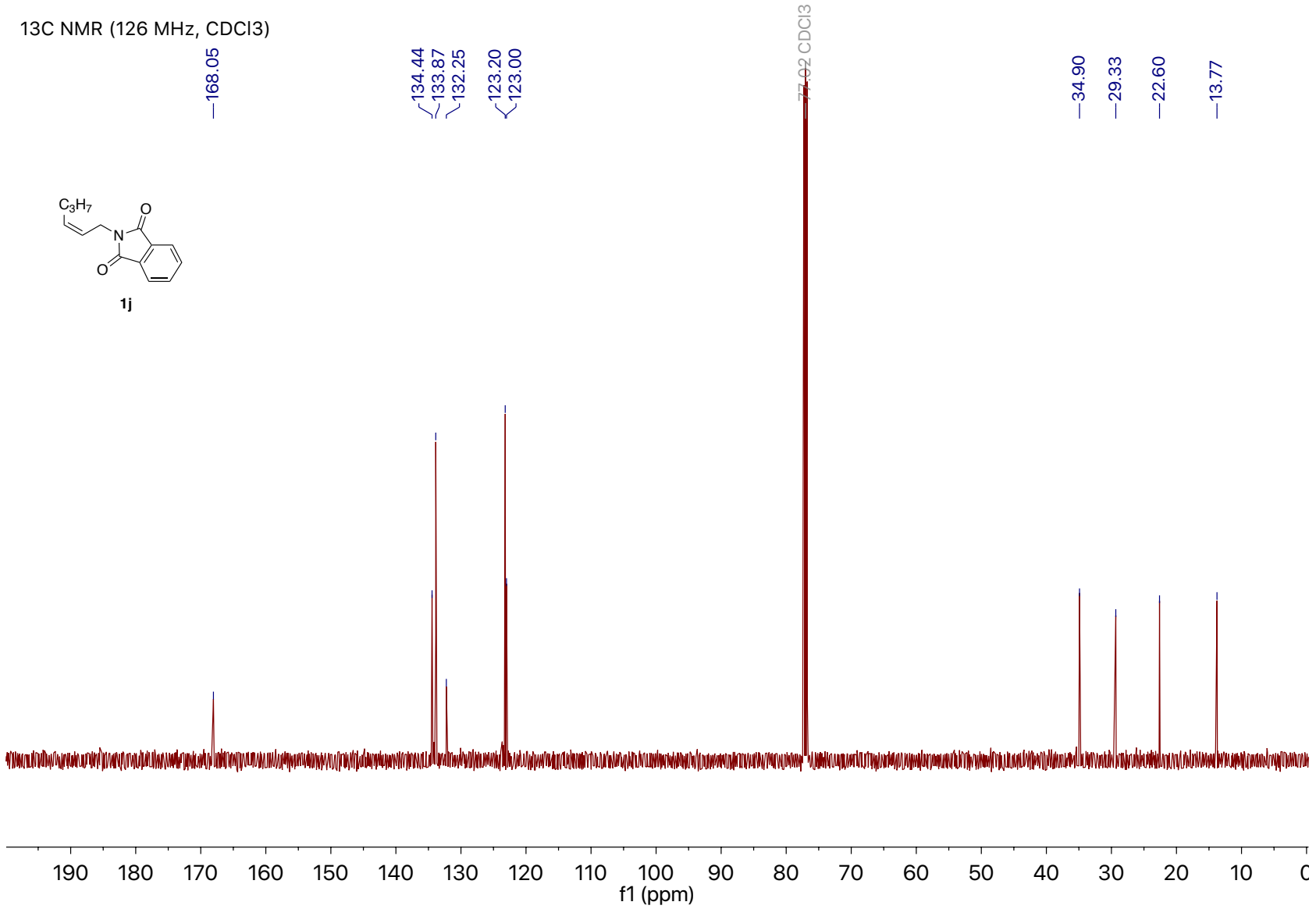
13C NMR (126 MHz, CDCl3)



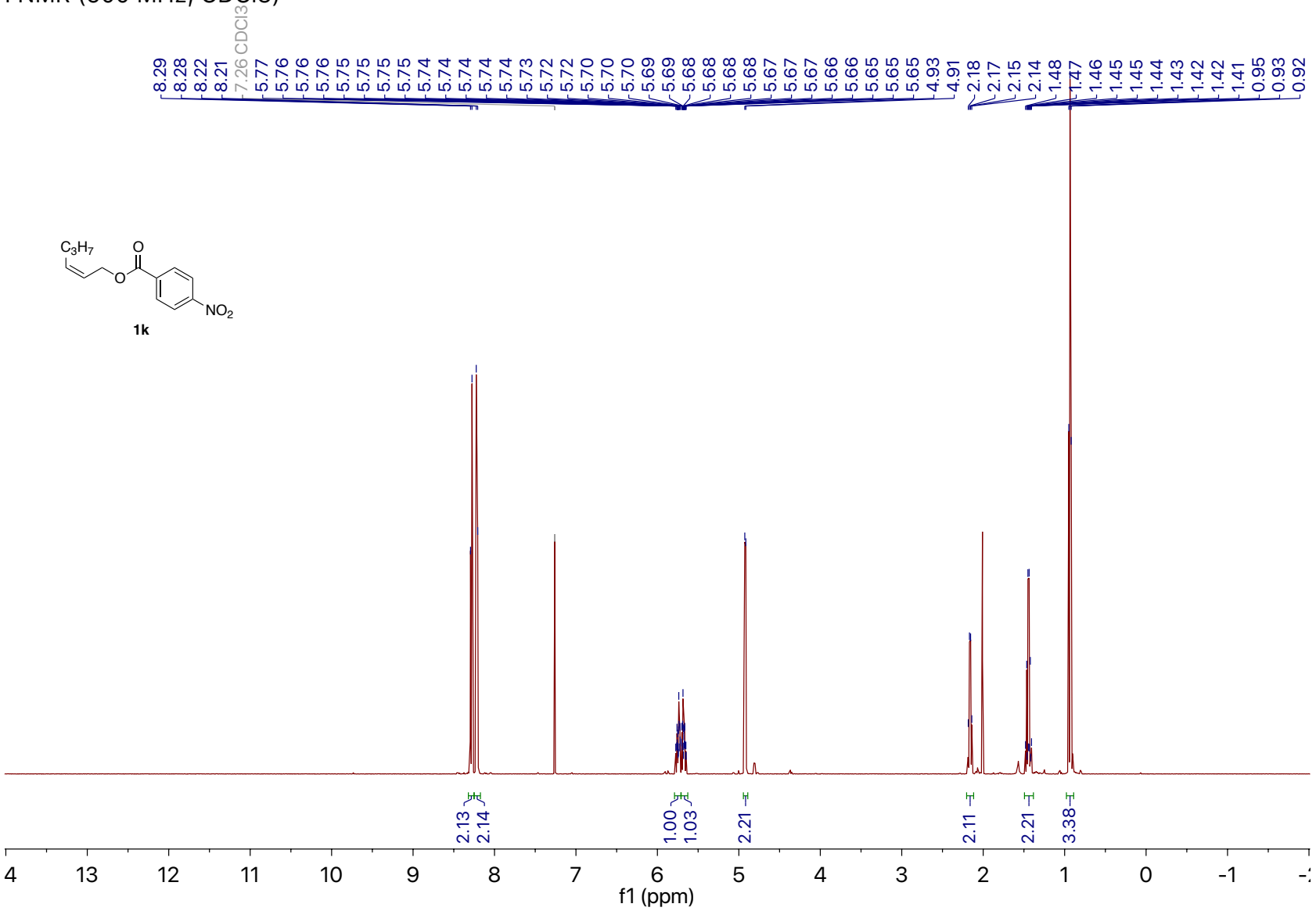

1H NMR (500 MHz, CDCl3)
7.26 CDCl3
5.58 5.58 5.58 5.57 5.57 5.56 5.56 5.56 5.55 5.55 5.55 5.54 5.54 5.53 5.53 5.53 5.46 5.43 5.42 5.42 5.41 5.41 5.41 5.40 5.40 5.40 5.39 5.39 5.39 5.38 5.38 5.37 5.37
3.89 3.88 3.87
2.07 2.06 2.04 2.03 1.98 1.42 1.41 1.39 1.38 1.36 1.35 0.91 0.90 0.88
C3H7
O
N
H
1g
1.00 0.68 1.10 1.98 2.07 2.99 1.98 3.03
f1 (ppm)

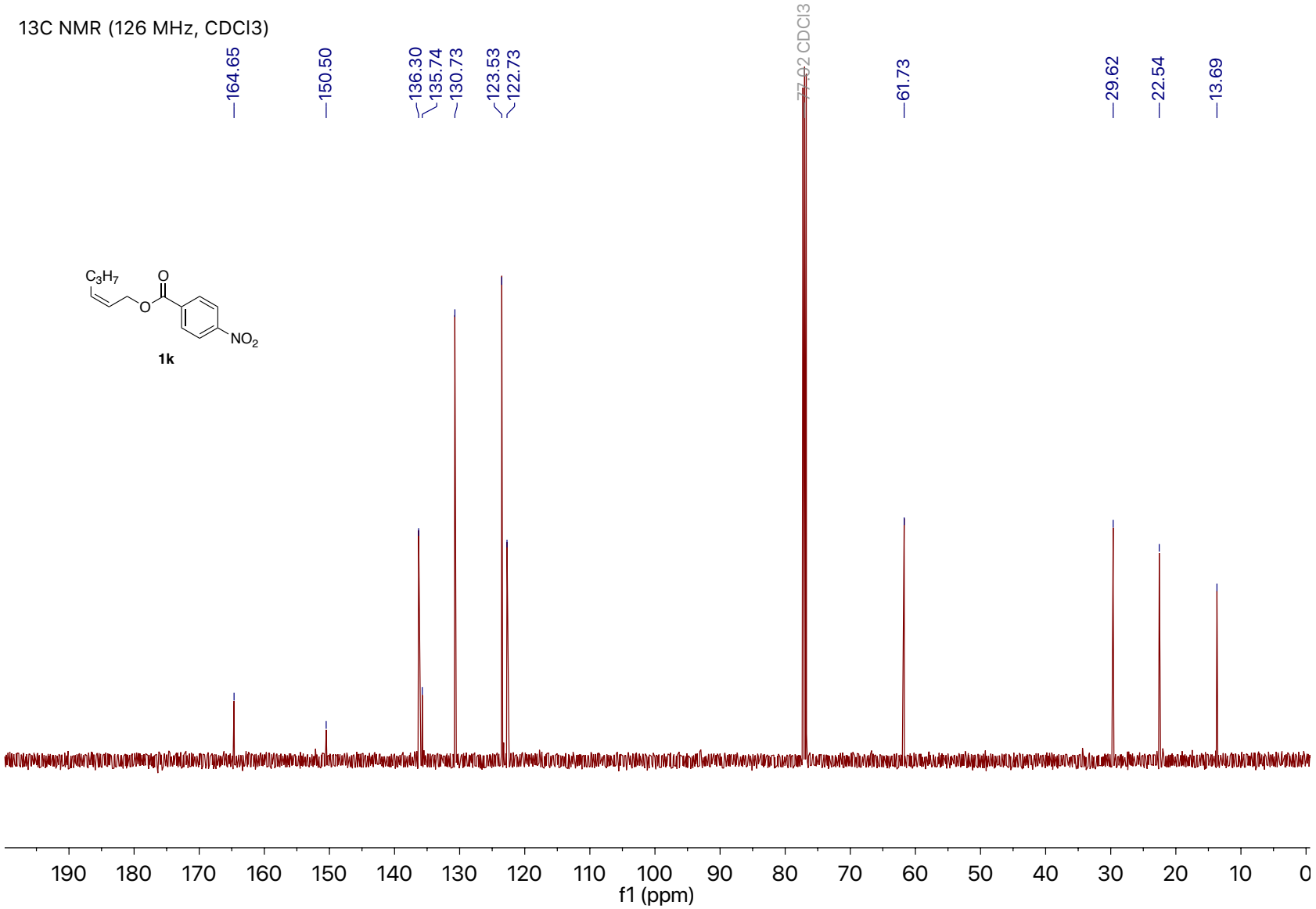

13C NMR (126 MHz, CDCl3)
169.89
133.79
125.06
77.02
36.78
29.32
23.27
22.60
13.69
C3H7
O
N
H
1g
f1 (ppm)

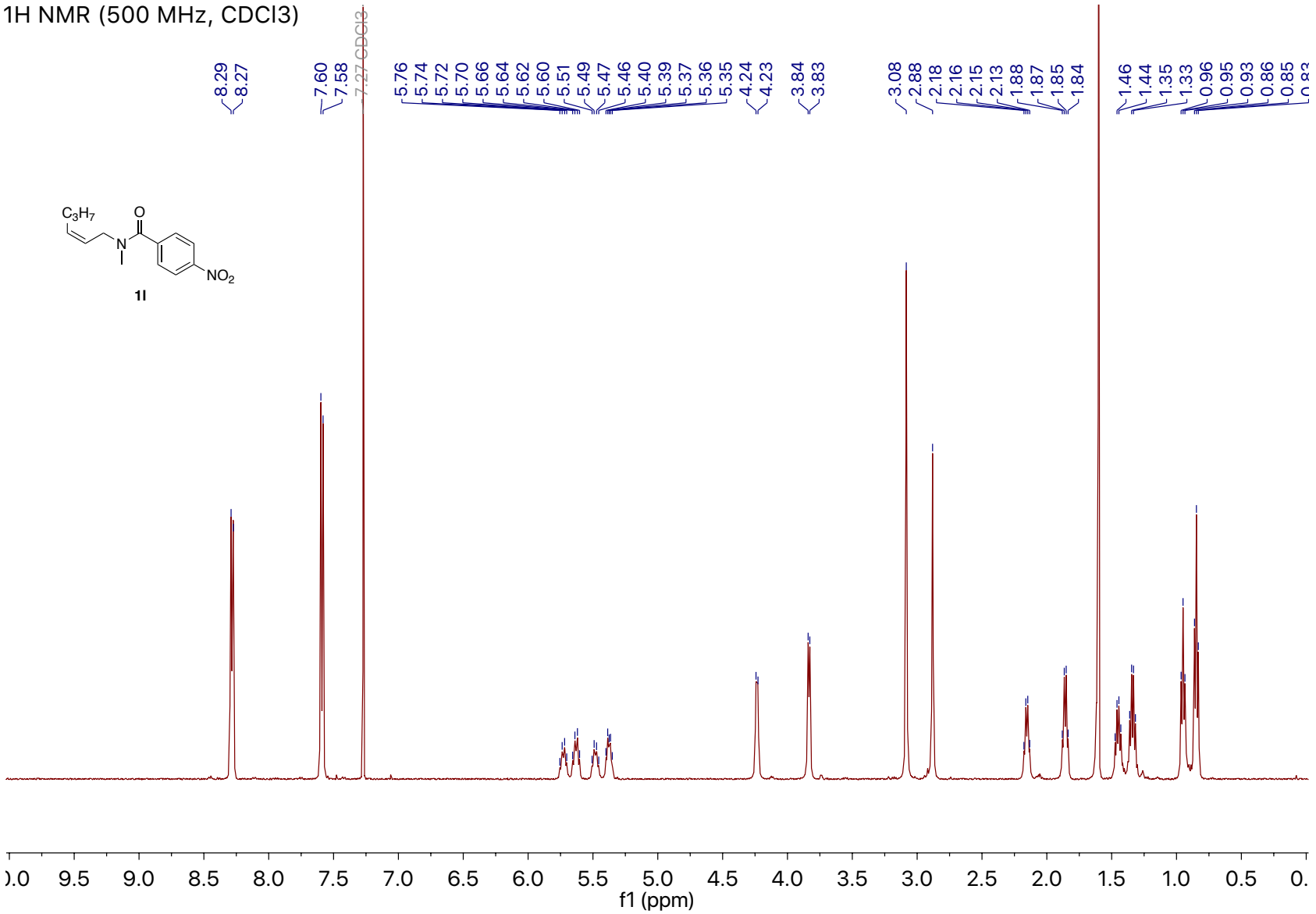

1H NMR (500 MHz, CDCl3)
7.85 7.84 7.84 7.83 7.71 7.70 7.70 7.69
7.26 CDCl3
5.62 5.61 5.61 5.60 5.60 5.60 5.59 5.59 5.58 5.58 5.57 5.57 5.57 5.50 5.49 5.49 5.48 5.48 5.48 5.47 5.47 5.47 5.46 5.46 5.46 5.45 5.44 4.33 4.31
2.27 2.25 2.24 2.22
1.48 1.47 1.45 1.44 1.42 1.41
0.97 0.95 0.94
C3H7
O
N
O
1j
1.91
2.04
1.00
0.99
2.17
2.07
2.09
3.08
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.
f1 (ppm)

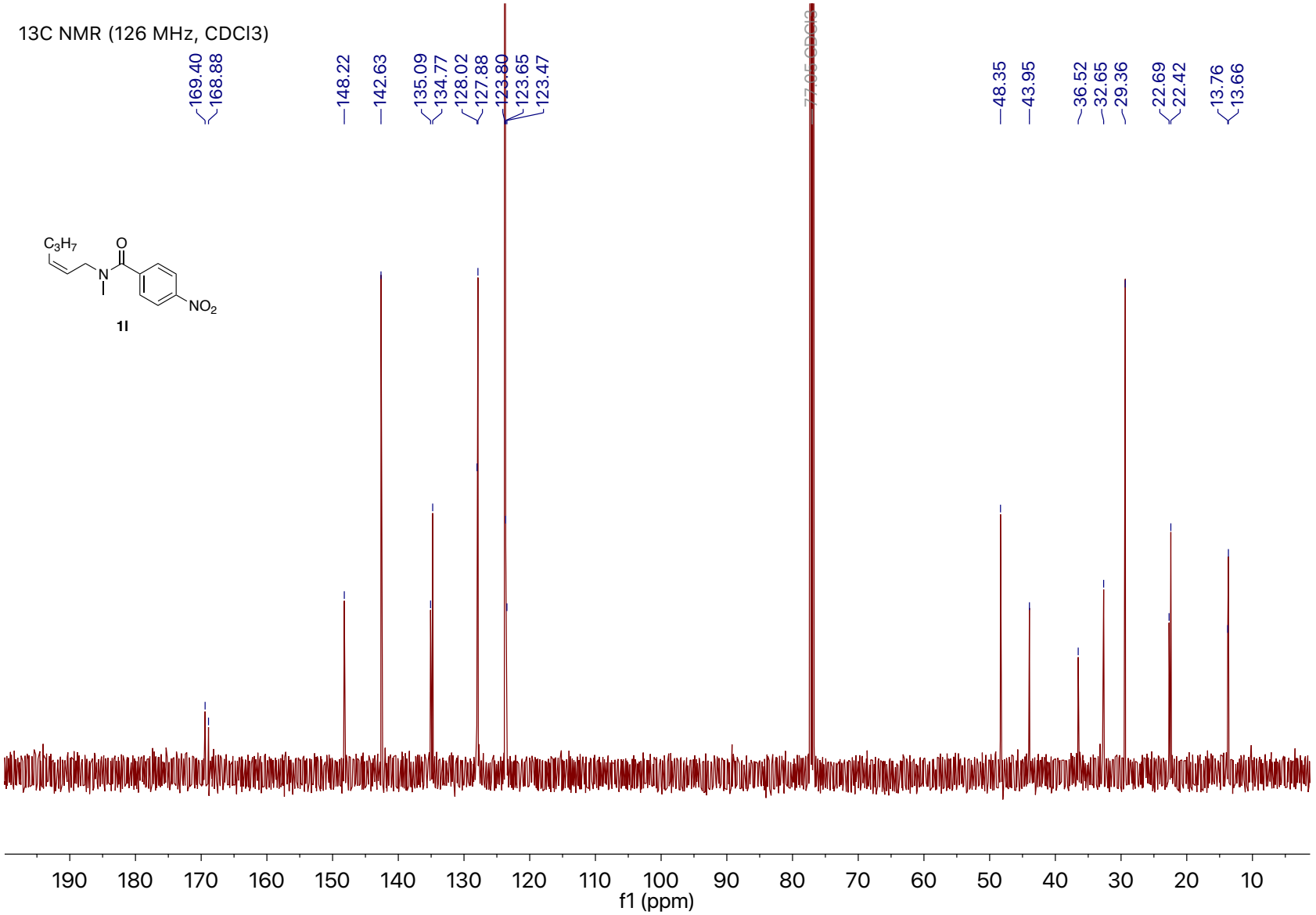

13C NMR (126 MHz, CDCl3)
168.05
134.44
133.87
132.25
123.20
123.00
77.02 CDCl3
34.90
29.33
22.60
13.77
C3H7
N
O
O
1j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1H NMR (500 MHz, CDCl3)

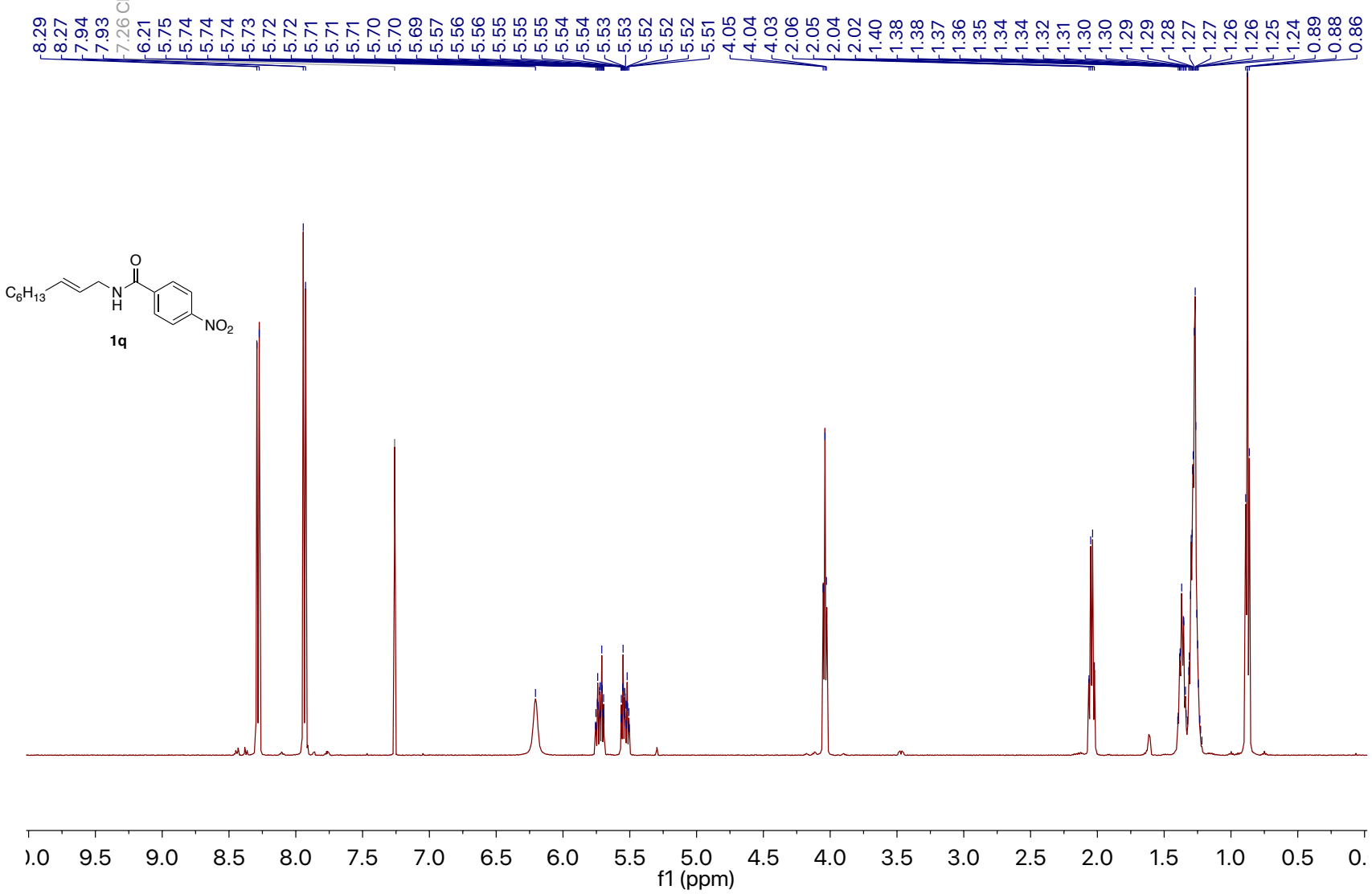



13C NMR (126 MHz, CDCl3)
164.65
150.50
136.30
135.74
130.73
123.53
122.73
77.02 CDCl3
61.73
29.62
22.54
13.69
C3H7
O
O
NO2
1k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

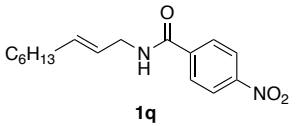

1H NMR (500 MHz, CDCl3)
8.29
8.27
7.60
7.58
7.27 CDCl3
5.76
5.74
5.72
5.70
5.66
5.64
5.62
5.60
5.51
5.49
5.47
5.46
5.40
5.39
5.37
5.36
5.35
4.24
4.23
3.84
3.83
3.08
2.88
2.18
2.16
2.15
2.13
1.88
1.87
1.85
1.84
1.46
1.44
1.35
1.33
0.96
0.95
0.93
0.86
0.85
C3H7
O
N
NO2
1l
f1 (ppm)


13C NMR (126 MHz, CDCl3)
169.40
168.88
148.22
142.63
135.09
134.77
128.02
127.88
123.80
123.65
123.47
77.05 CDCl3
48.35
43.95
36.52
32.65
29.36
22.69
22.42
13.76
13.66
C3H7
O
N
NO2
1l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

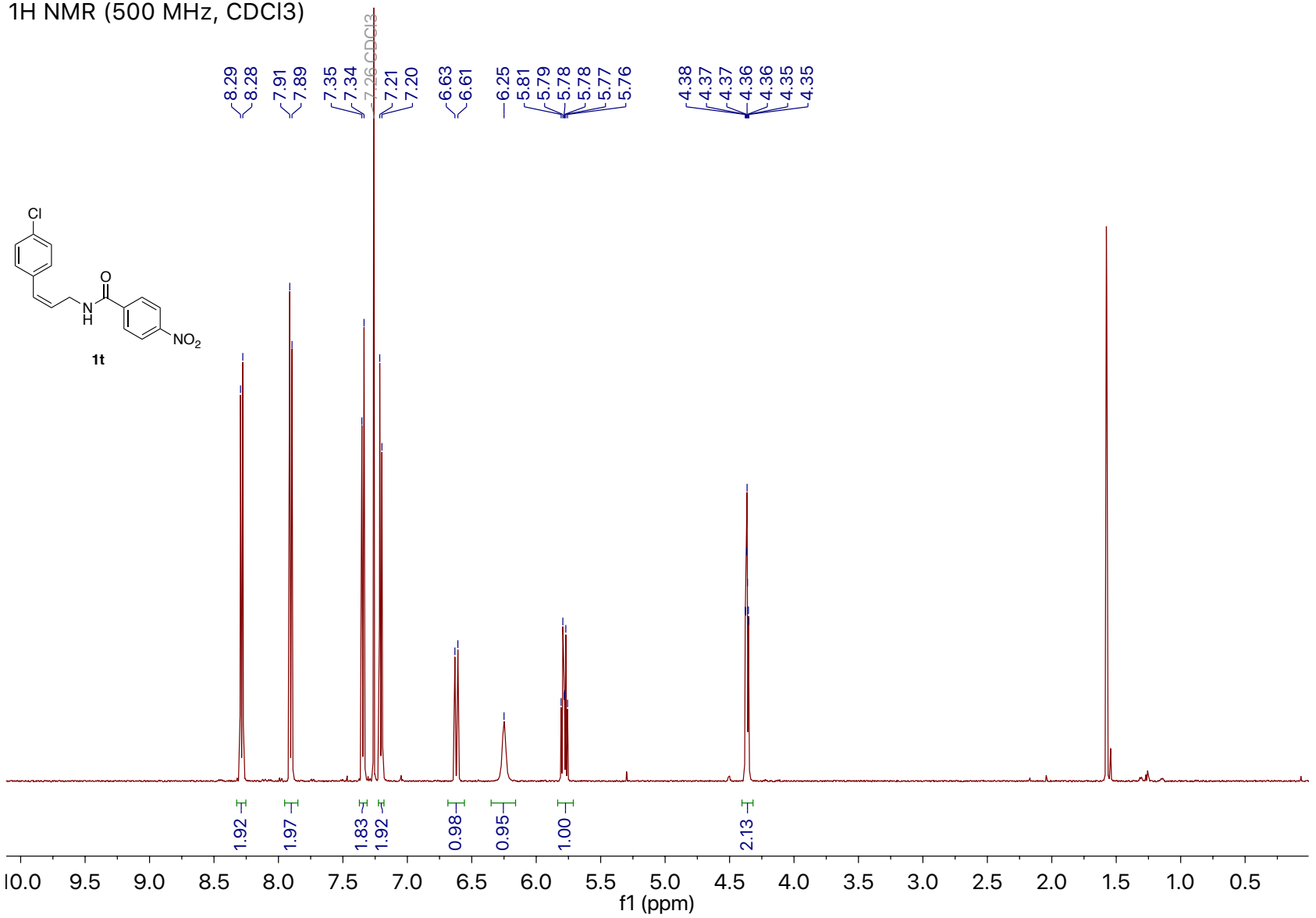
1H NMR (500 MHz, CDCl3)

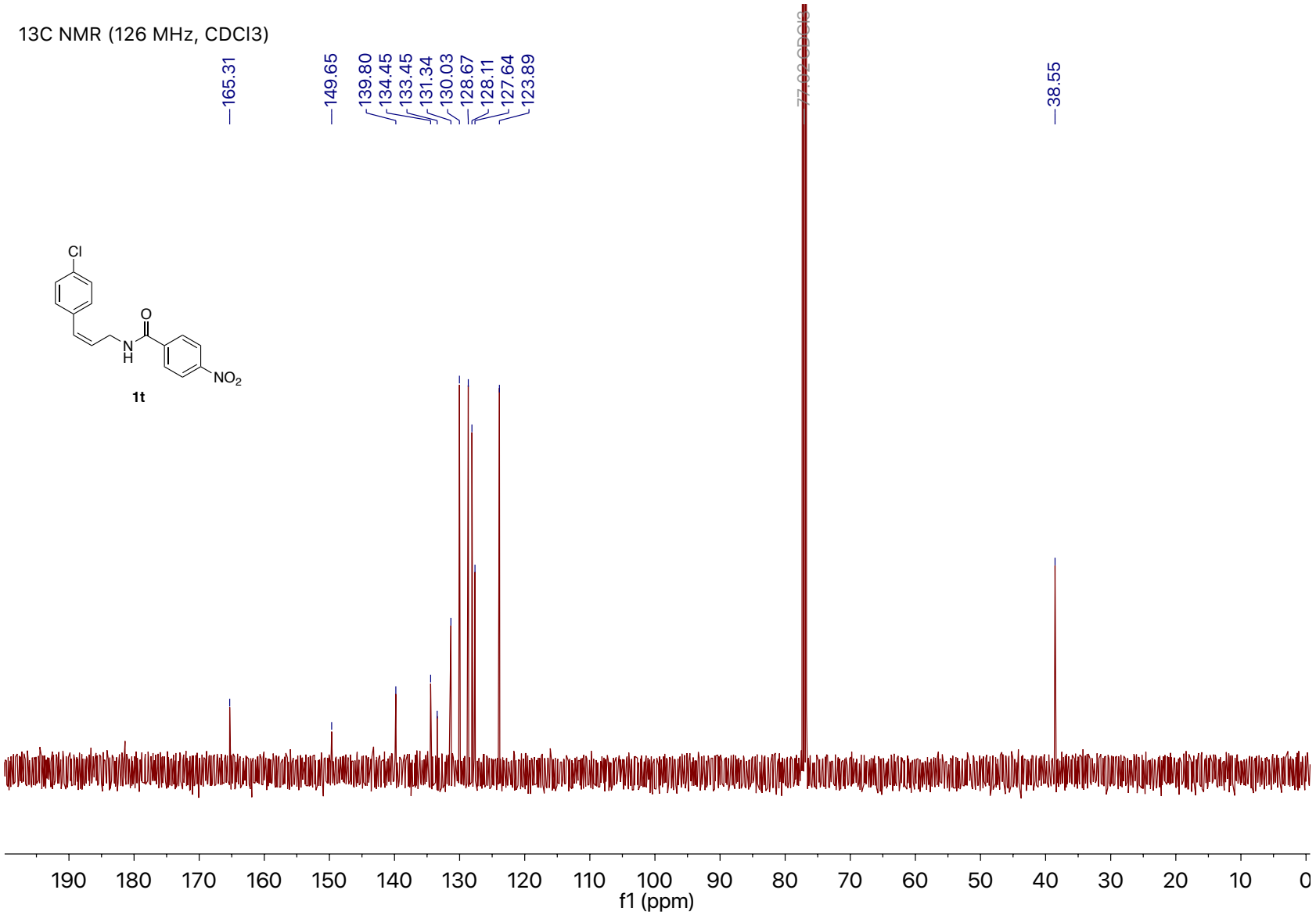


13C NMR (126 MHz, CDCl3)

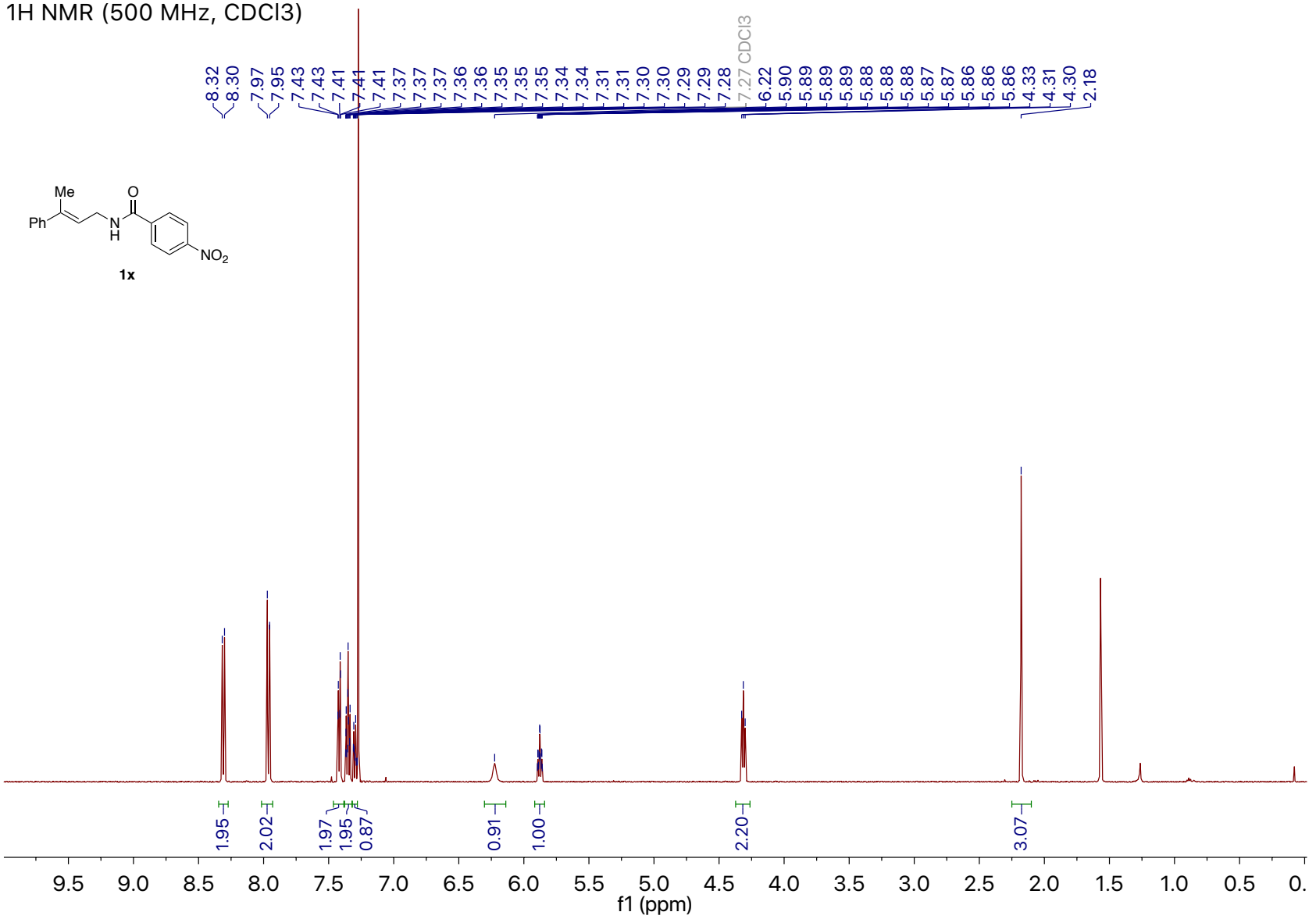


1q

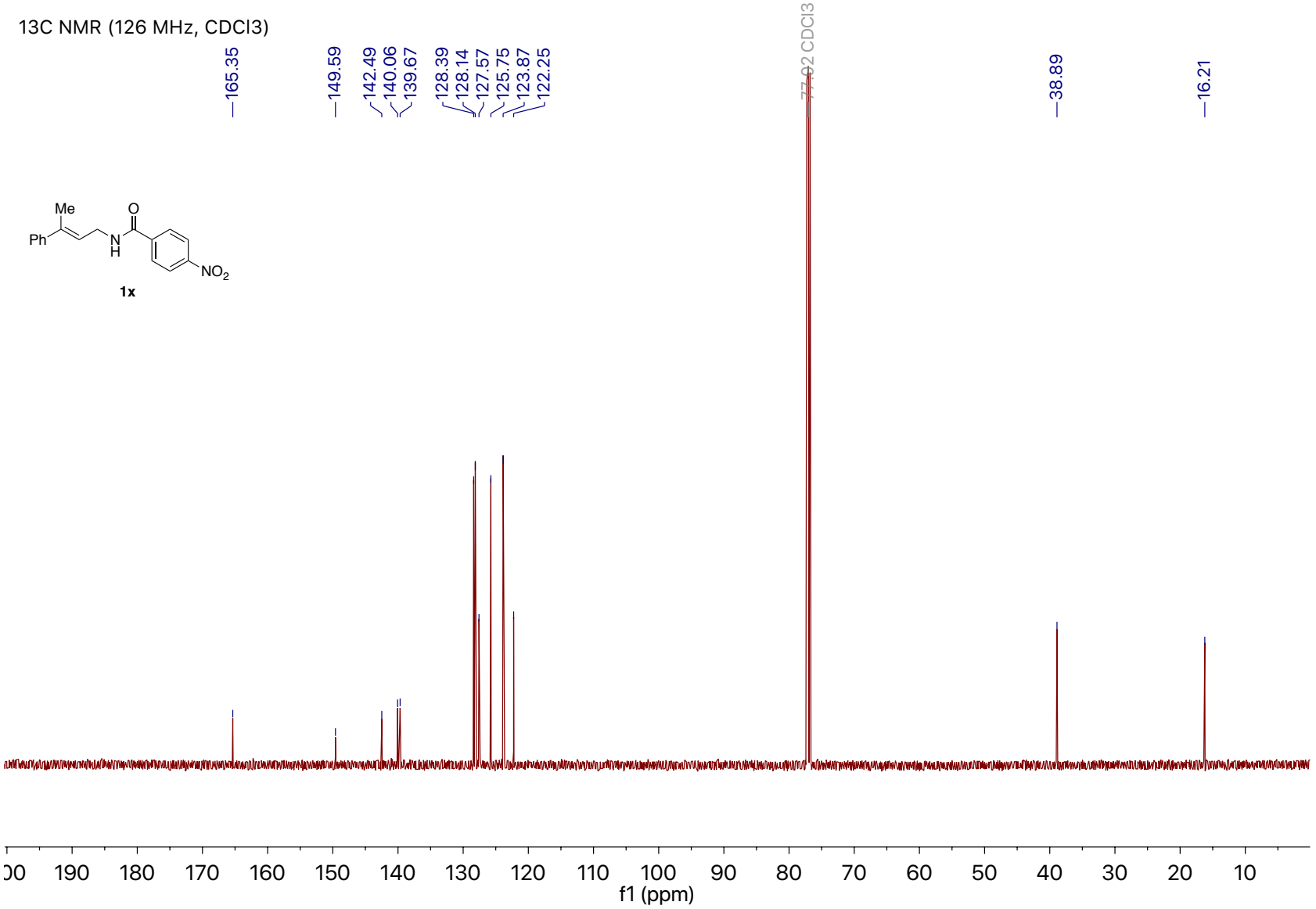

1H NMR (500 MHz, CDCl3)
8.29
8.28
7.91
7.89
7.35
7.34
7.26 CDCl3
7.21
7.20
6.63
6.61
6.25
5.81
5.79
5.78
5.78
5.77
5.76
4.38
4.37
4.37
4.36
4.36
4.35
4.35
Cl
O
N
H
NO2
1t
1.92
1.97
1.83
1.92
0.98
0.95
1.00
2.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


13C NMR (126 MHz, CDCl3)
165.31
149.65
139.80
134.45
133.45
131.34
130.03
128.67
128.11
127.64
123.89
77.02
38.55
Cl
O
N
H
NO2
1t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

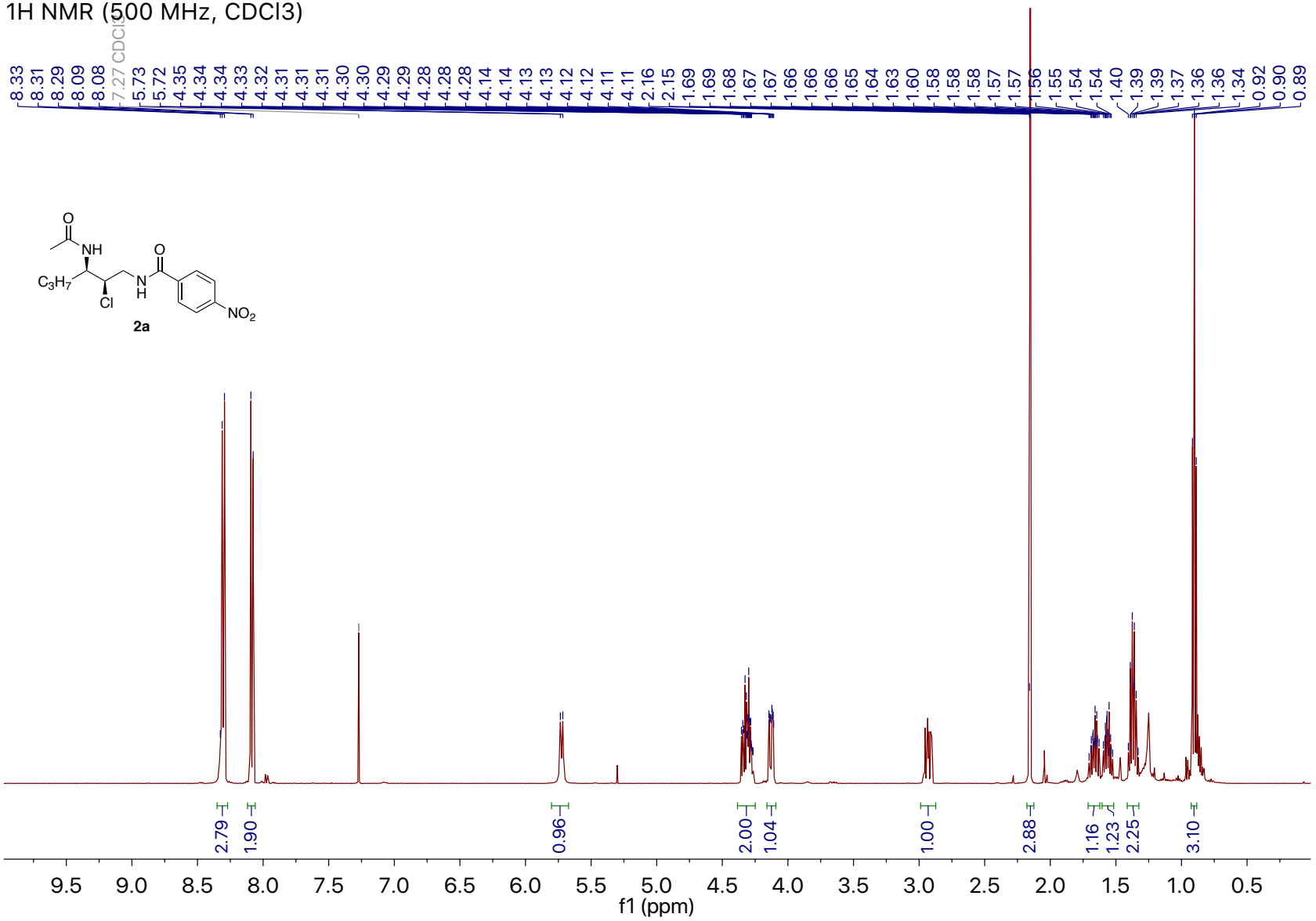
1H NMR (500 MHz, CDCl3)



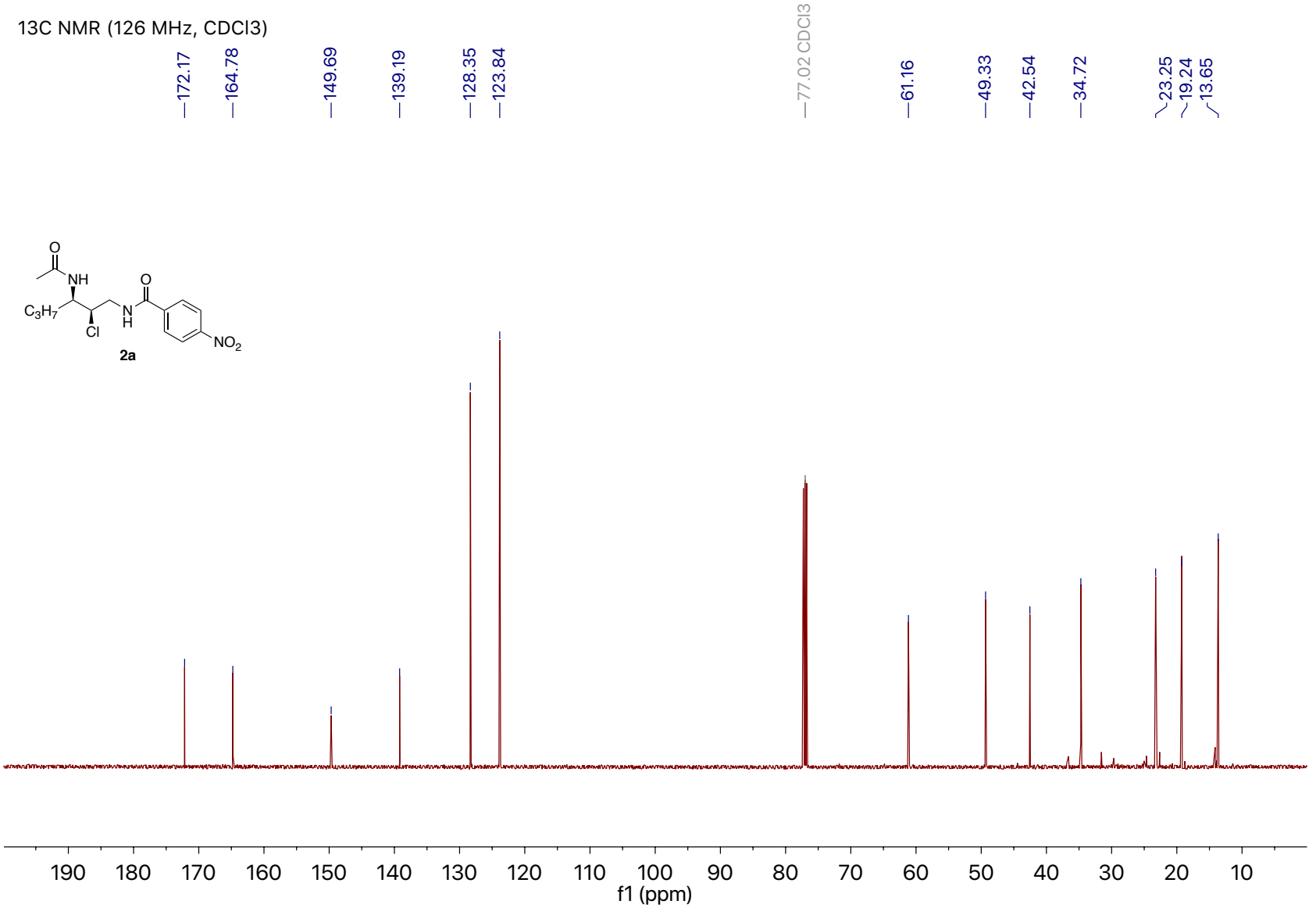
13C NMR (126 MHz, CDCl3)

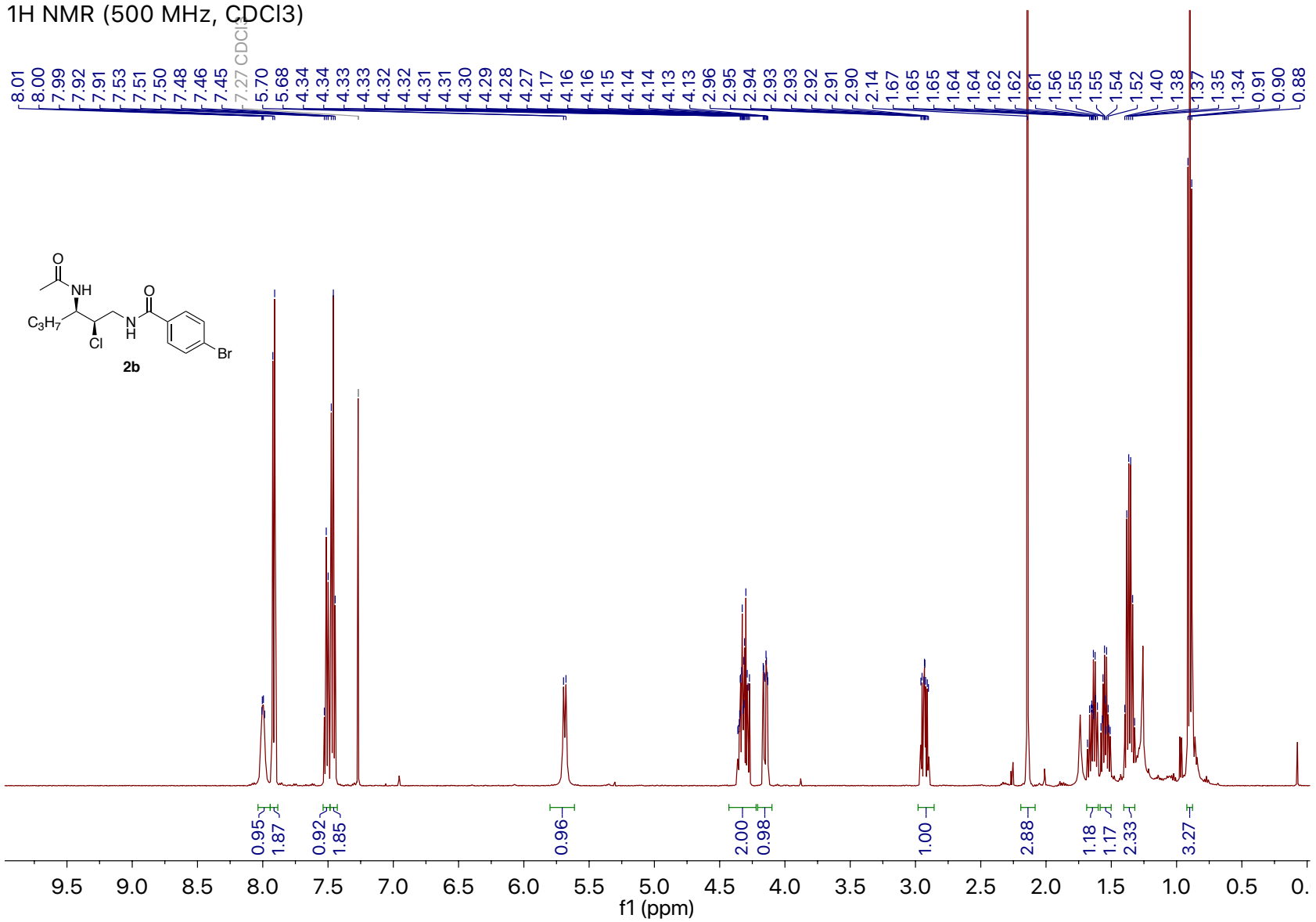


1H NMR (500 MHz, CDCl3)

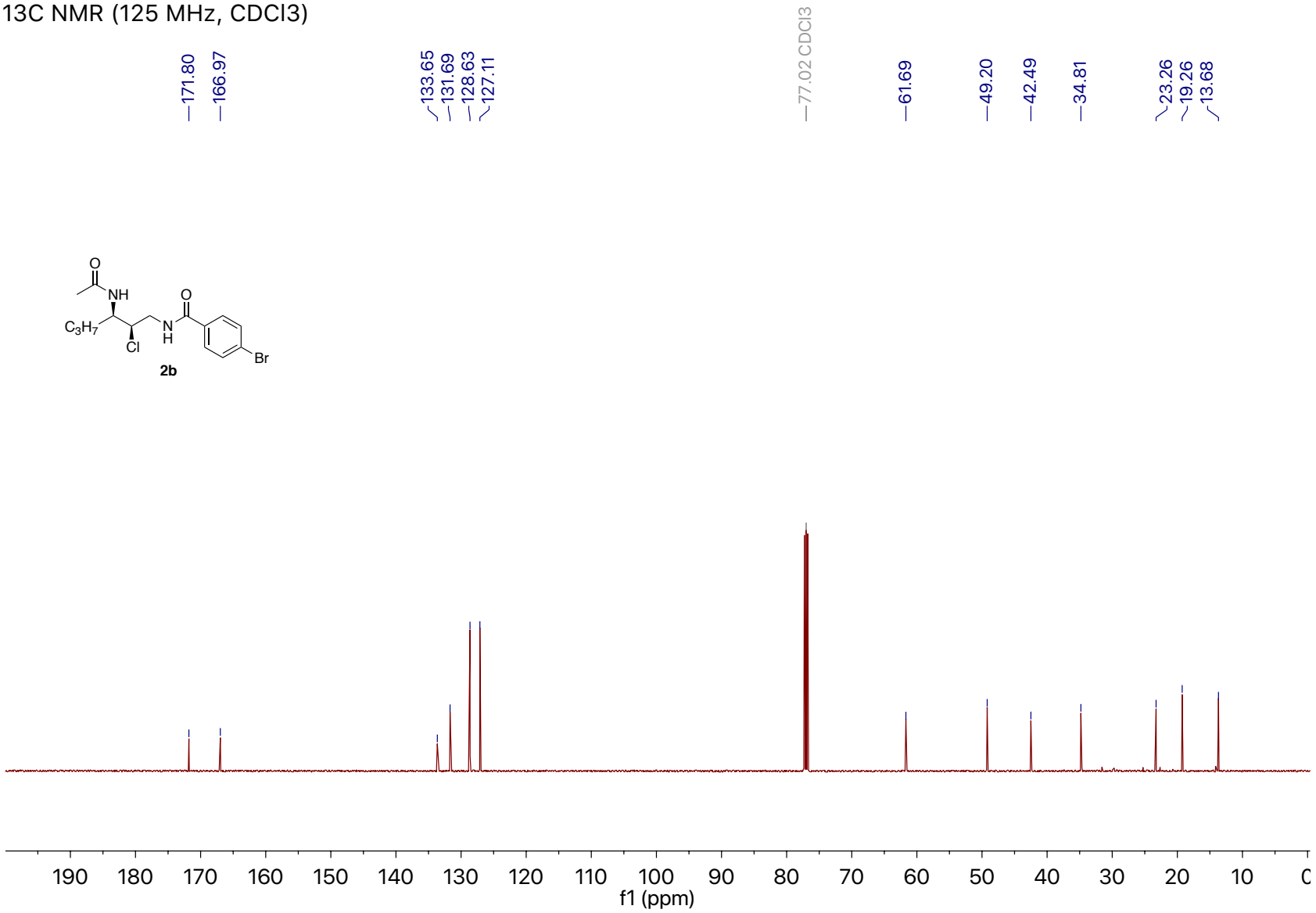


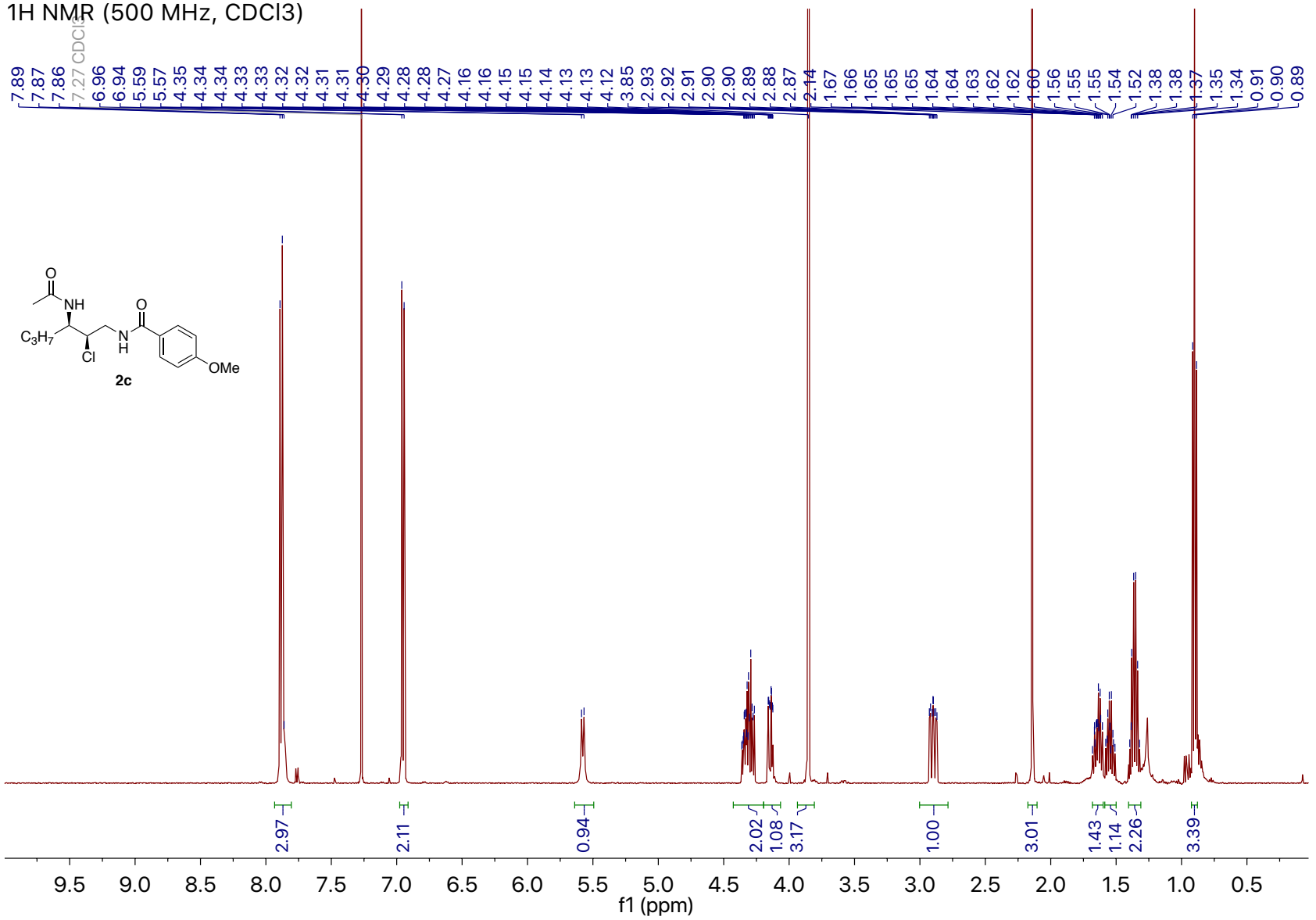
13C NMR (126 MHz, CDCl3)



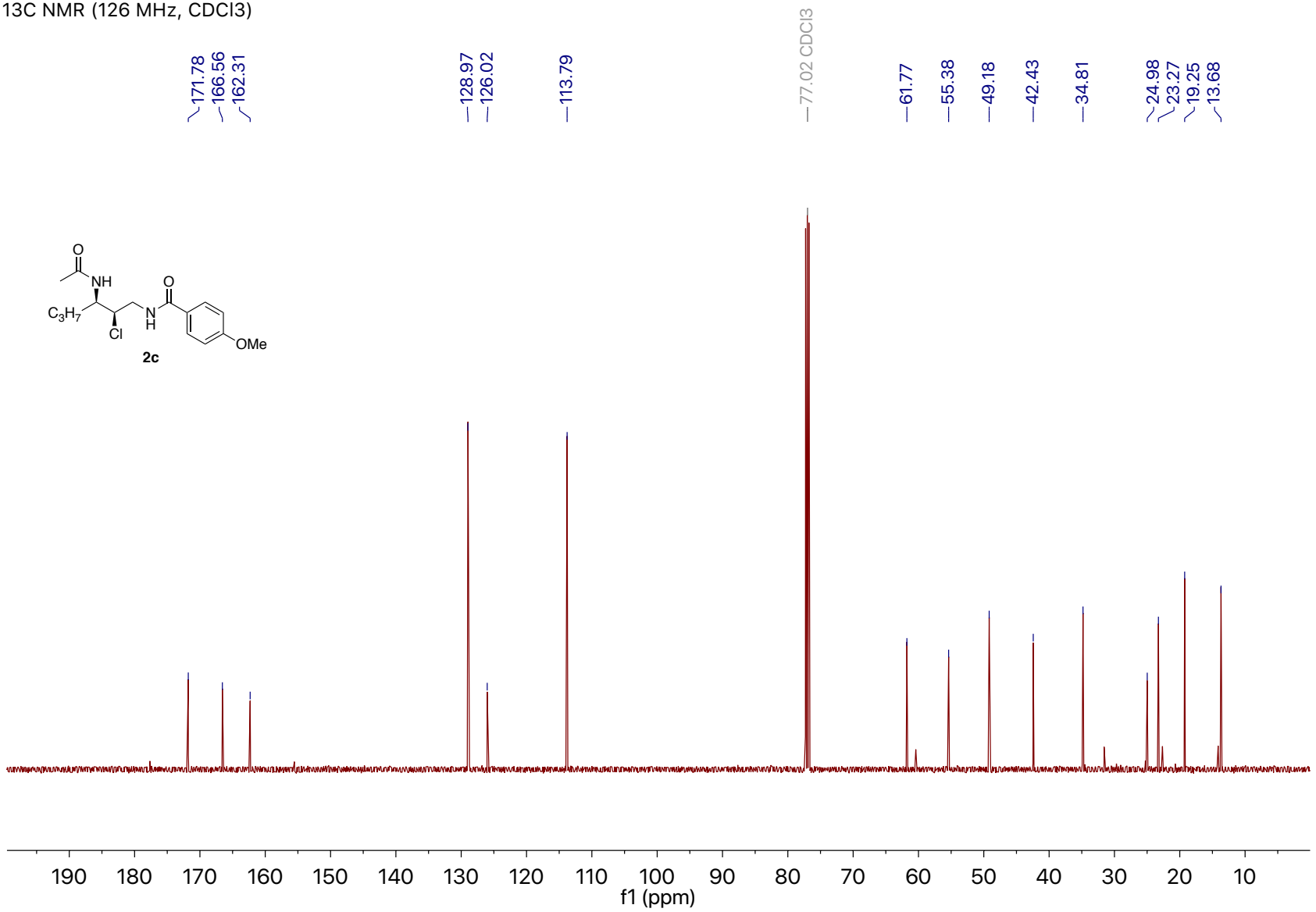

1H NMR (500 MHz, CDCl3)
8.01 8.00 7.99 7.92 7.91 7.53 7.51 7.50 7.48 7.46 7.45 7.27 CDCl3 5.70 5.68 4.34 4.34 4.33 4.33 4.32 4.32 4.31 4.31 4.30 4.29 4.28 4.27 4.17 4.16 4.16 4.15 4.14 4.14 4.13 4.13 2.96 2.95 2.94 2.93 2.93 2.92 2.91 2.90 2.14 1.67 1.65 1.65 1.64 1.64 1.62 1.62 1.61 1.56 1.55 1.55 1.54 1.52 1.40 1.38 1.37 1.35 1.34 0.91 0.90 0.88
O
NH
O
C3H7
N
H
Cl
Br
2b
0.95 1.87 0.92 1.85 0.96 2.00 0.98 1.00 2.88 1.18 1.17 2.33 3.27
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.
f1 (ppm)

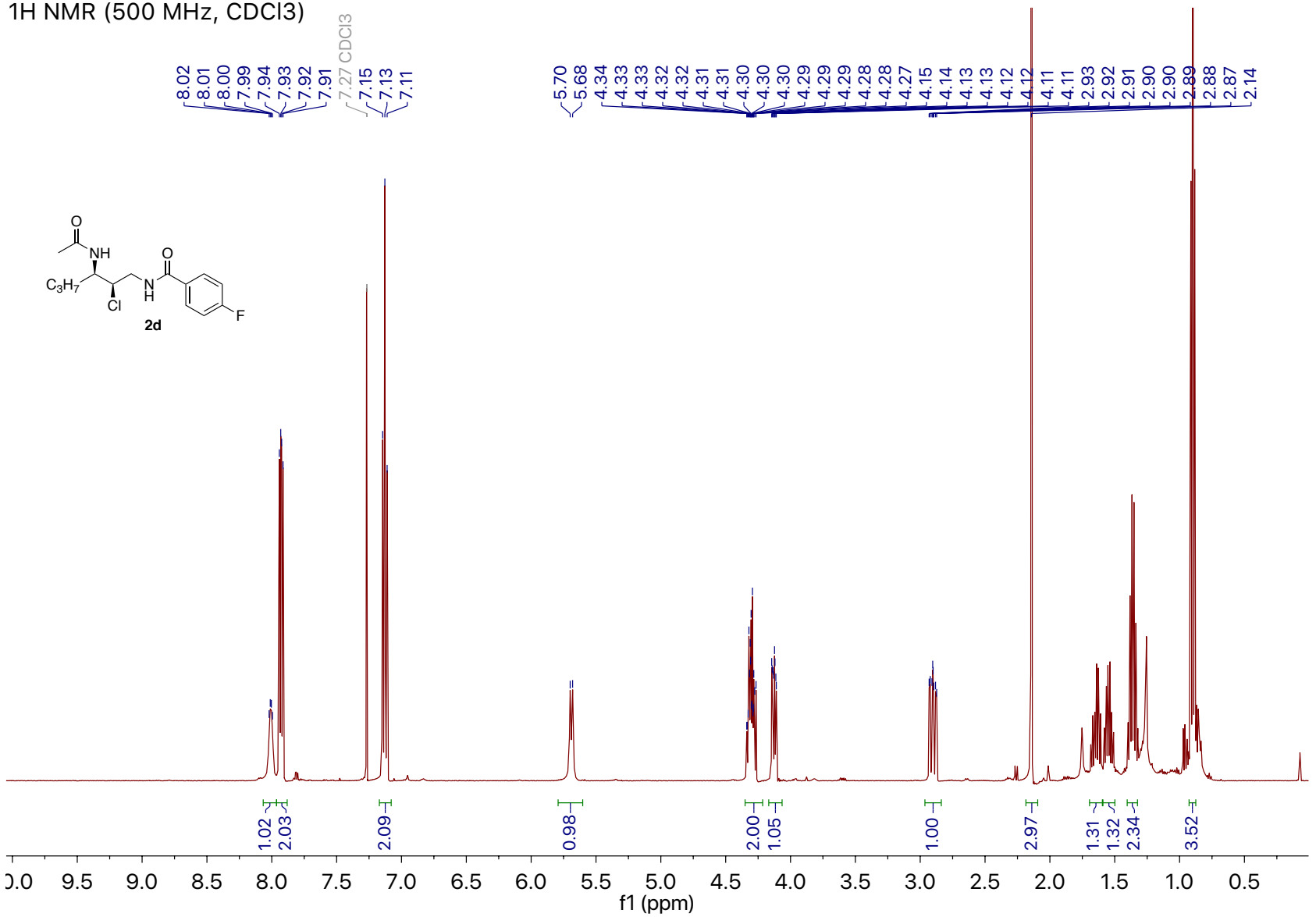
13C NMR (125 MHz, CDCl3)



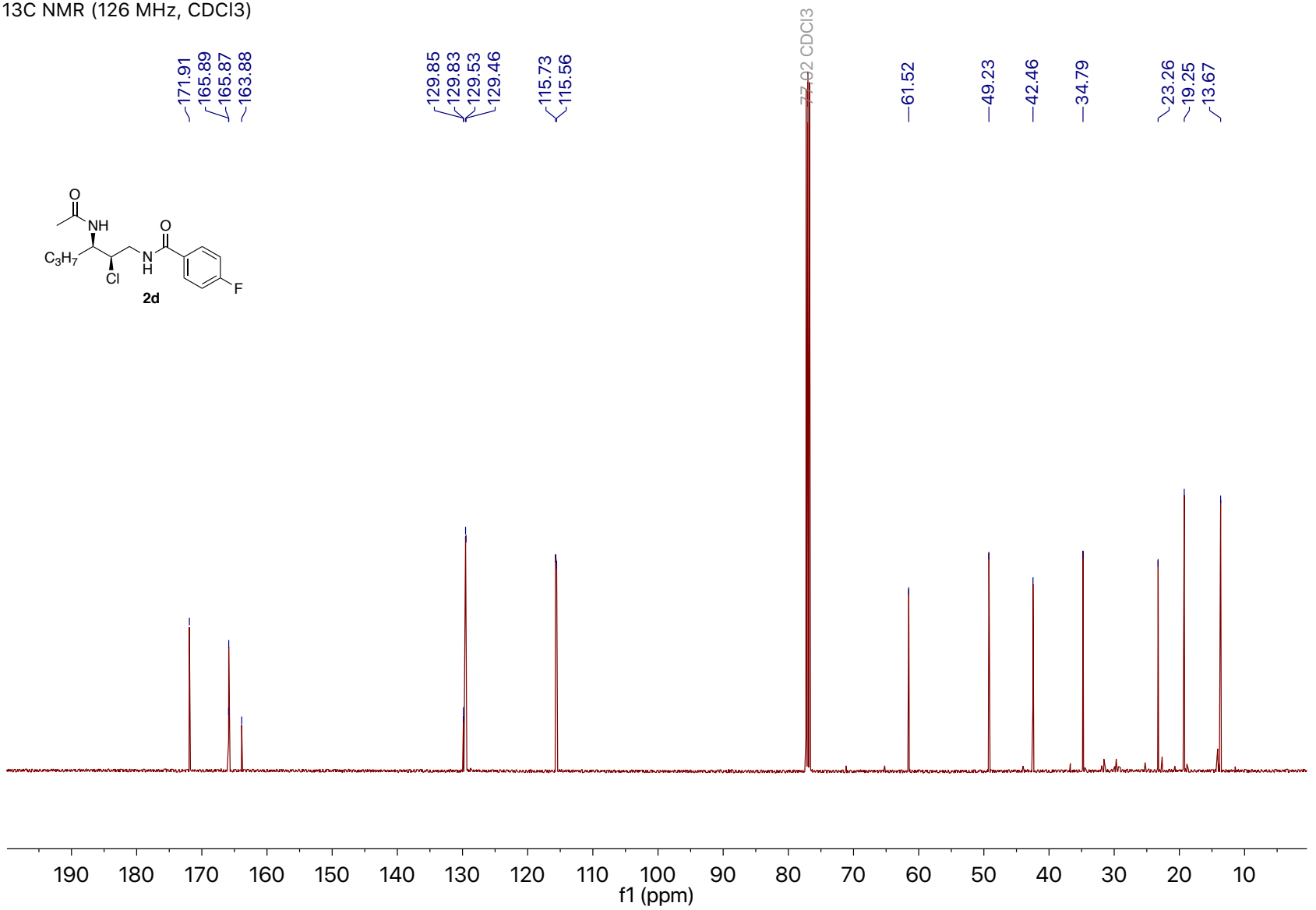

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
7.89
7.87
7.86
6.96
6.94
5.59
5.57
4.35
4.34
4.34
4.33
4.33
4.32
4.32
4.31
4.31
4.30
4.29
4.28
4.28
4.27
4.16
4.16
4.15
4.15
4.14
4.13
4.13
4.12
3.85
2.93
2.92
2.91
2.90
2.90
2.89
2.88
2.87
2.14
1.67
1.66
1.65
1.65
1.65
1.64
1.64
1.63
1.62
1.62
1.60
1.56
1.55
1.55
1.54
1.52
1.38
1.38
1.37
1.35
1.34
0.91
0.90
0.89
O
NH
O
C3H7
N
H
Cl
OMe
2c
2.97
2.11
0.94
2.02
1.08
3.17
1.00
3.01
1.43
1.14
2.26
3.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

13C NMR (126 MHz, CDCl3)

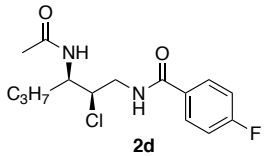



1H NMR (500 MHz, CDCl3)
8.02
8.01
8.00
7.99
7.94
7.93
7.92
7.91
7.27 CDCl3
7.15
7.13
7.11
5.70
5.68
4.34
4.33
4.33
4.32
4.32
4.31
4.31
4.30
4.30
4.30
4.29
4.29
4.28
4.28
4.27
4.15
4.14
4.13
4.13
4.12
4.12
4.11
4.11
2.93
2.92
2.91
2.90
2.90
2.89
2.88
2.87
2.14
O
NH
O
C3H7
N
H
Cl
F
2d
1.02
2.03
2.09
0.98
2.00
1.05
1.00
2.97
1.31
1.32
2.34
3.52
f1 (ppm)

13C NMR (126 MHz, CDCl3)

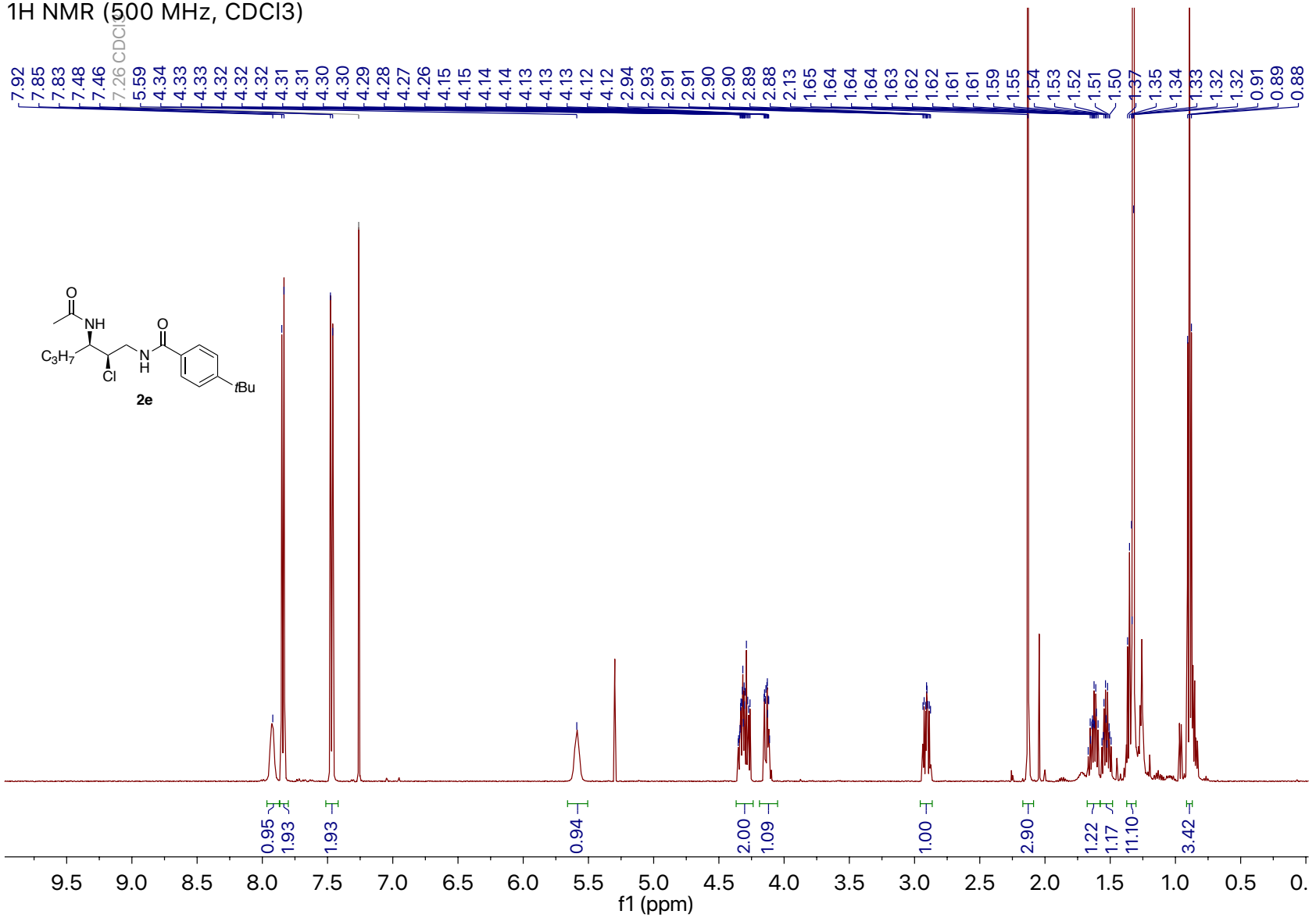


19F NMR (470 MHz, CDCl3)

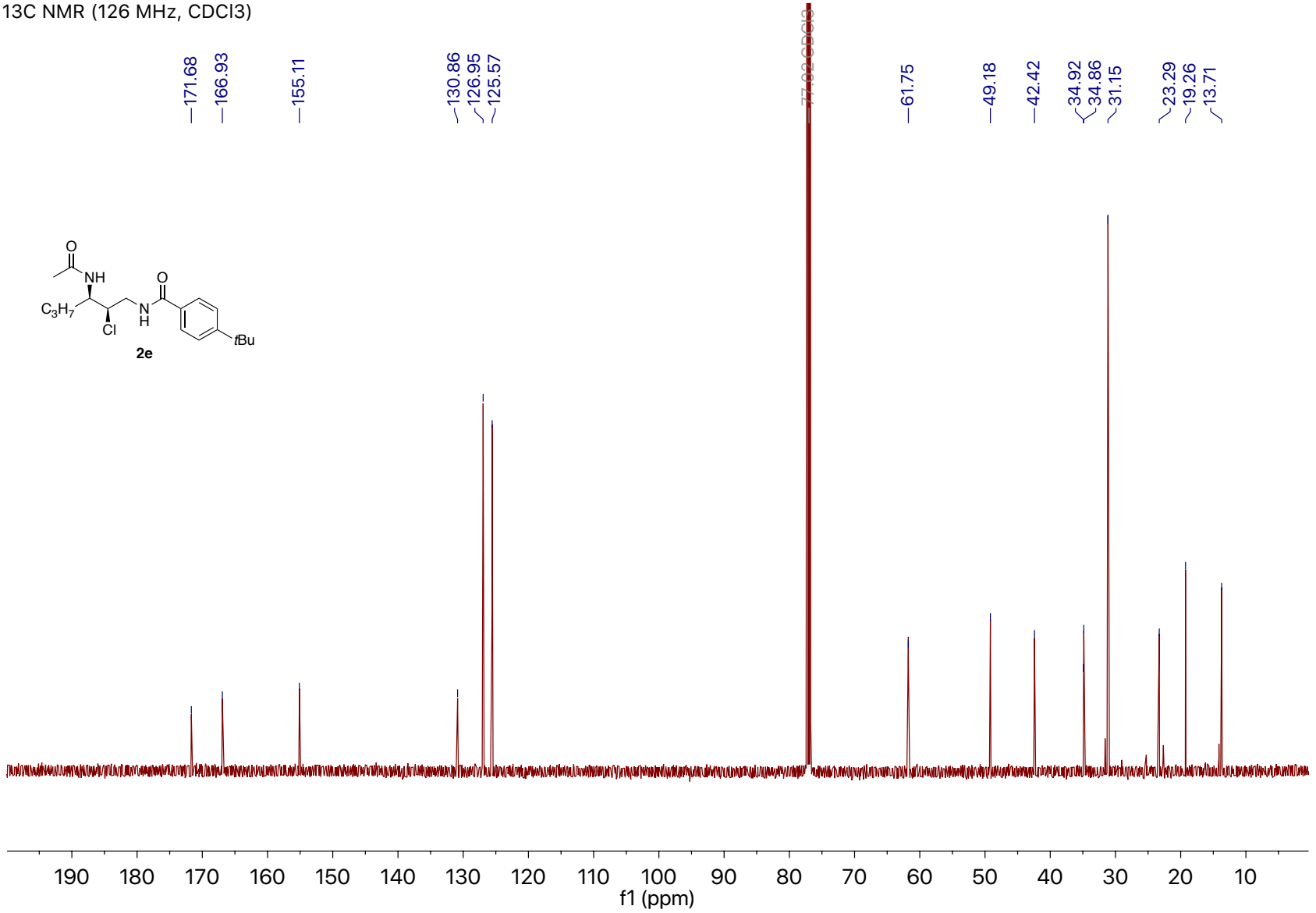


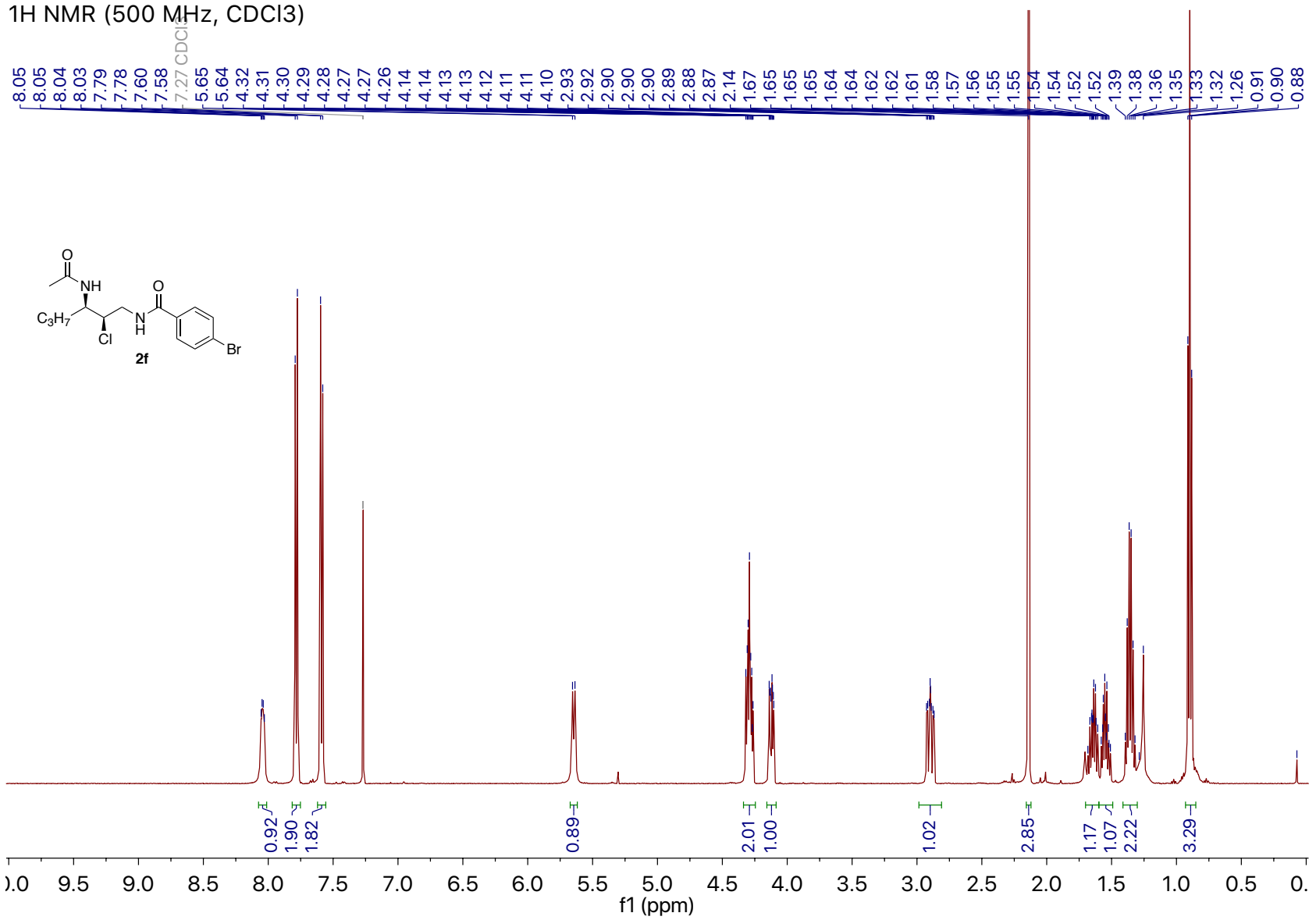
2d

1H NMR (500 MHz, CDCl3)

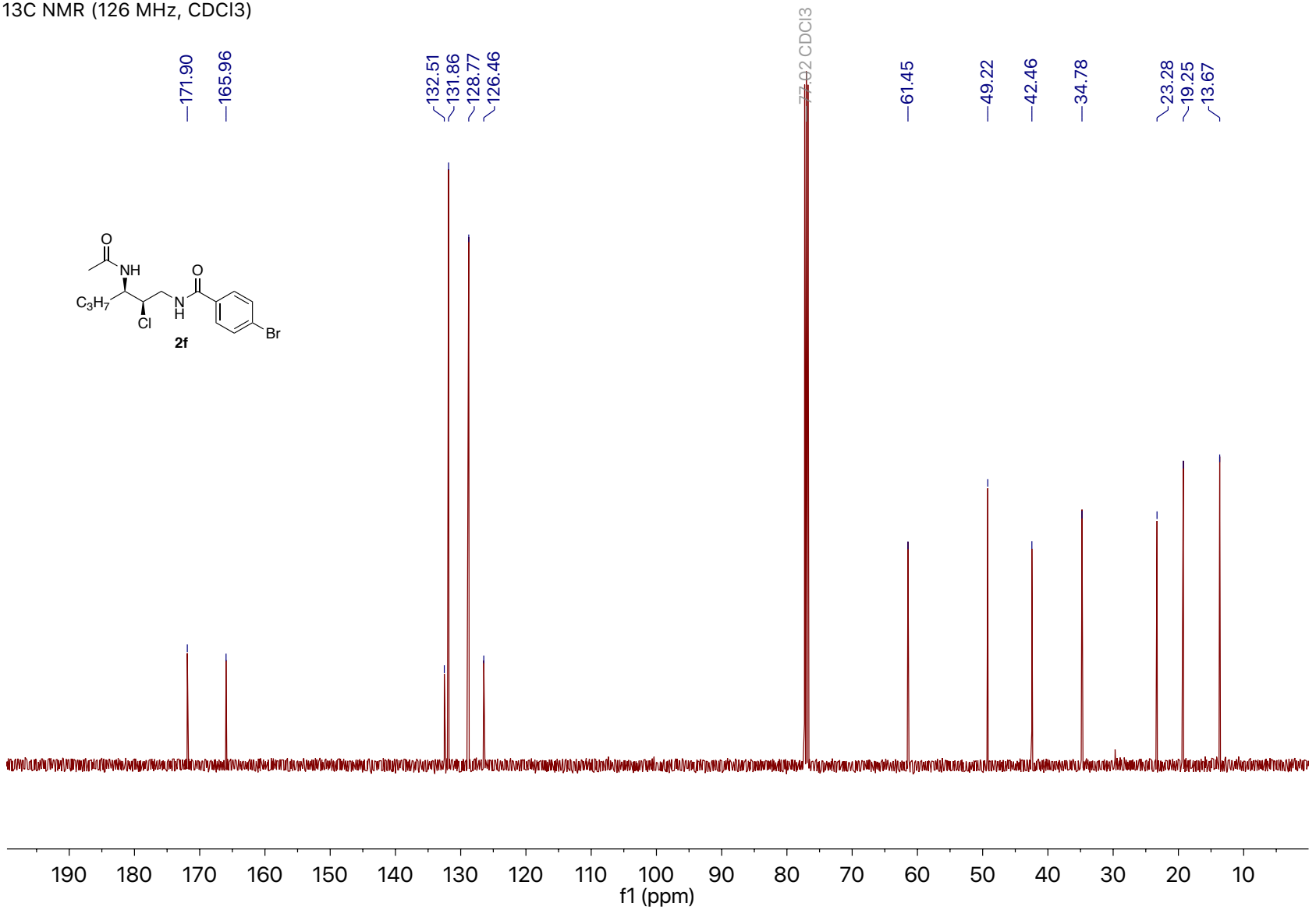


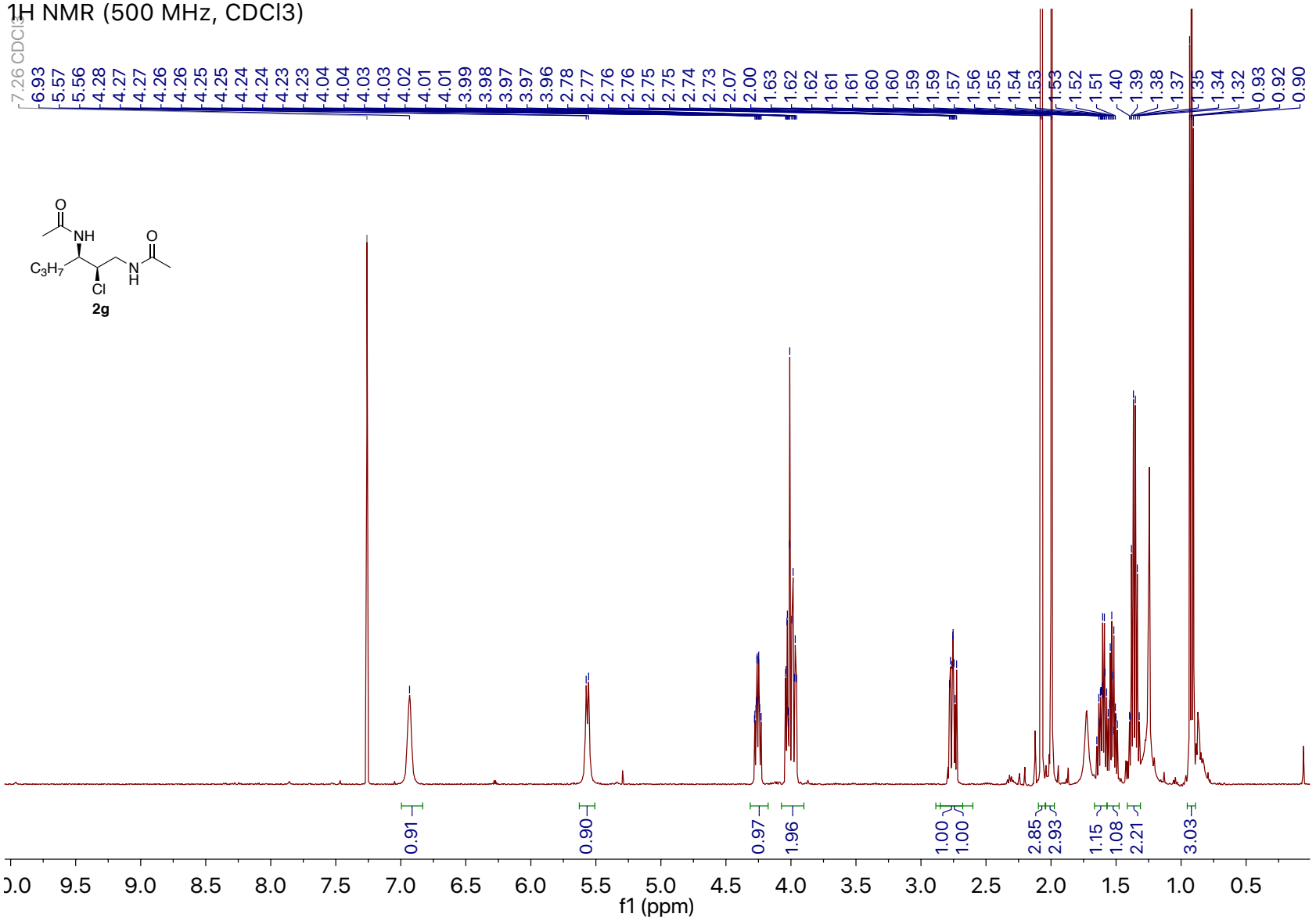
13C NMR (126 MHz, CDCl3)



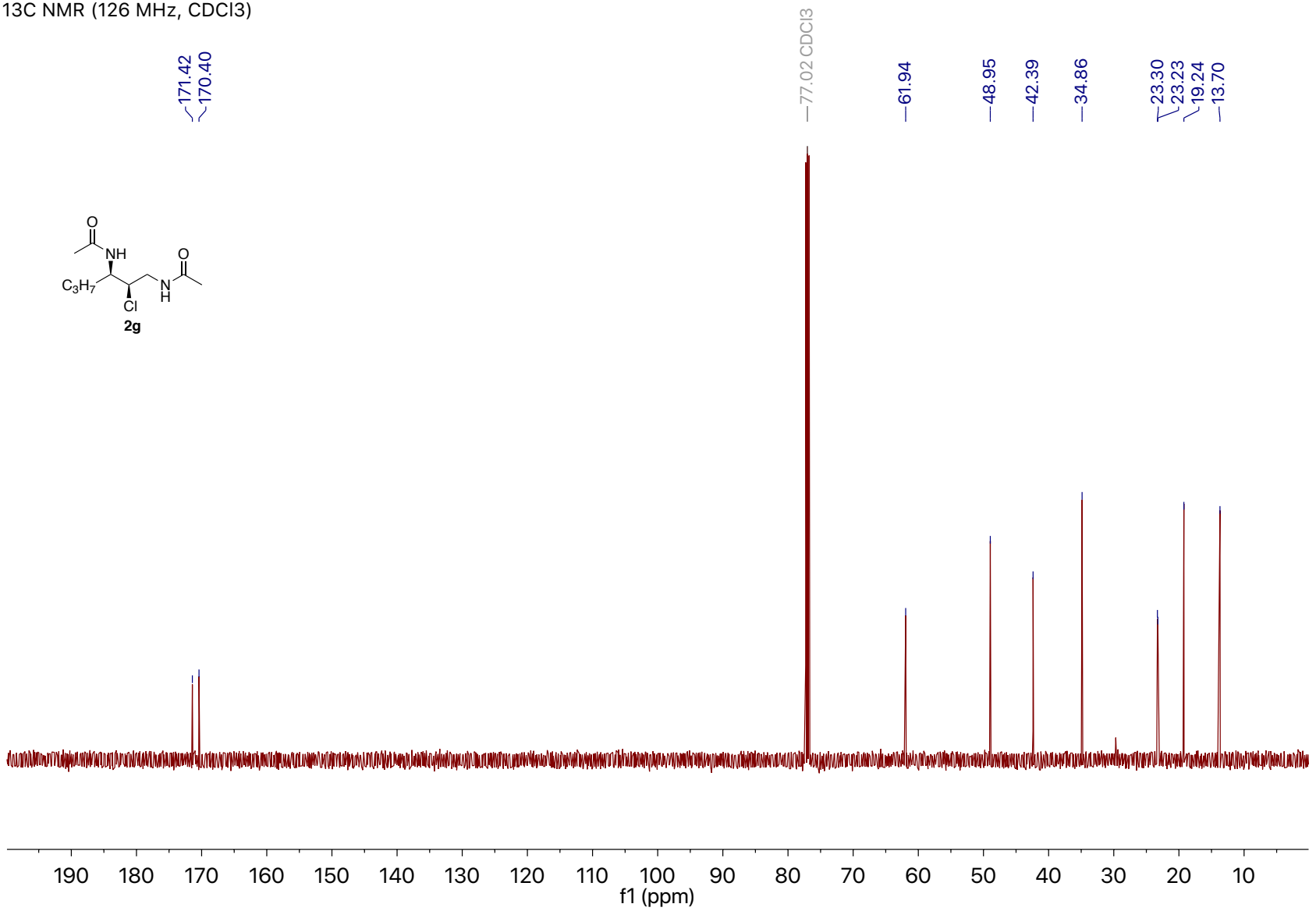

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
8.05 8.05 8.04 8.03 7.79 7.78 7.60 7.58 5.65 5.64 4.32 4.31 4.30 4.29 4.28 4.27 4.27 4.26 4.14 4.14 4.13 4.13 4.12 4.11 4.11 4.10 2.93 2.92 2.90 2.90 2.90 2.89 2.88 2.87 2.14 1.67 1.65 1.65 1.65 1.64 1.64 1.62 1.62 1.61 1.58 1.57 1.56 1.55 1.55 1.54 1.54 1.52 1.52 1.39 1.38 1.36 1.35 1.33 1.32 1.26 0.91 0.90 0.88
O
NH
O
C3H7
N
H
Cl
Br
2f
0.92 1.90 1.82 0.89 2.01 1.00 1.02 2.85 1.17 1.07 2.22 3.29
f1 (ppm)

13C NMR (126 MHz, CDCl3)

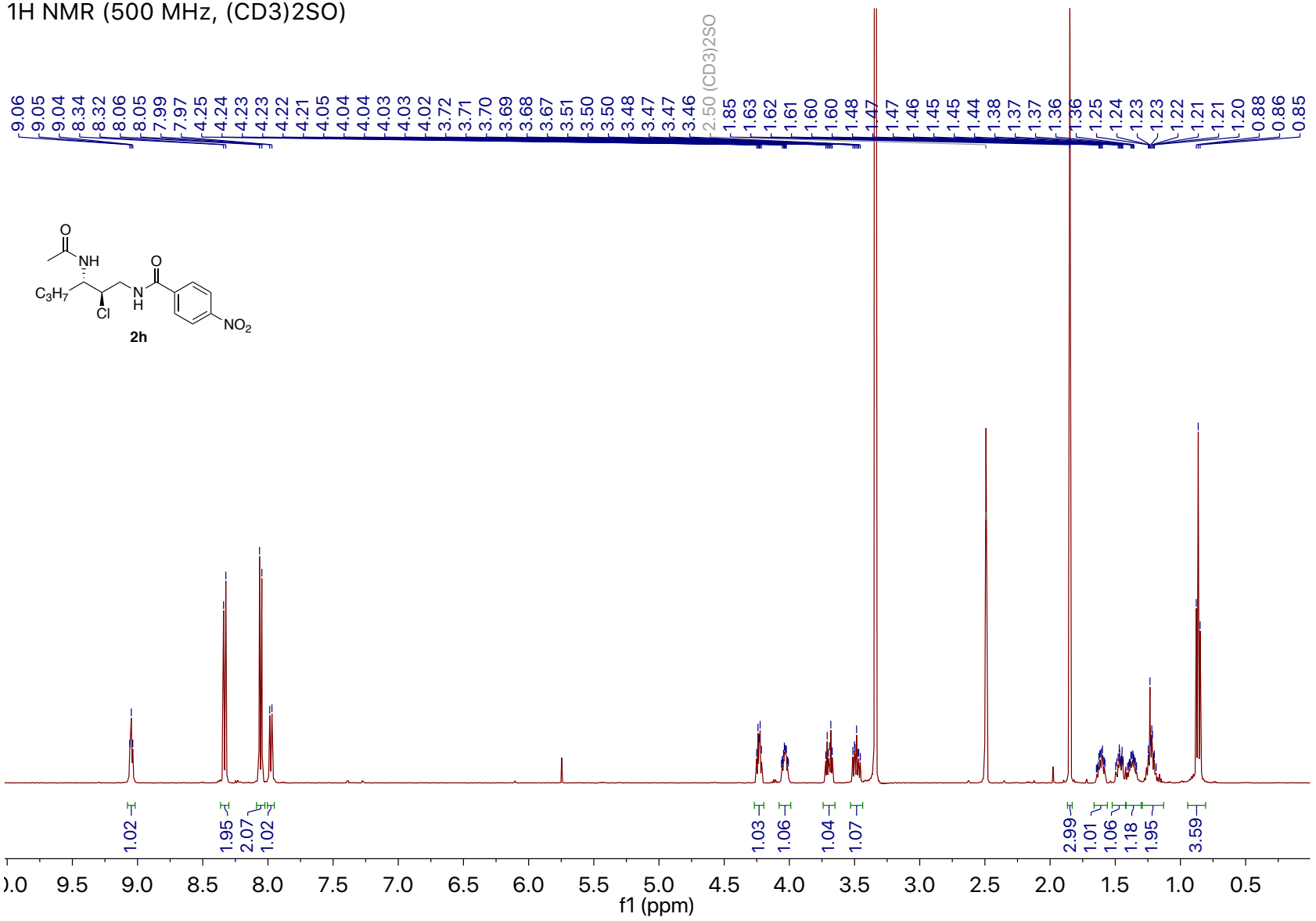



1H NMR (500 MHz, CDCl3)
7.26 CDCl3
6.93
5.57
5.56
4.28
4.27
4.27
4.26
4.26
4.25
4.25
4.24
4.24
4.23
4.23
4.04
4.04
4.03
4.03
4.02
4.01
4.01
3.99
3.98
3.97
3.97
3.96
2.78
2.77
2.76
2.76
2.75
2.75
2.74
2.73
2.07
2.00
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.57
1.56
1.55
1.54
1.53
1.53
1.52
1.51
1.40
1.39
1.38
1.37
1.35
1.34
1.32
0.93
0.92
0.90
O
NH
O
C3H7
N
H
Cl
2g
0.91
0.90
0.97
1.96
1.00
1.00
2.85
2.93
1.15
1.08
2.21
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

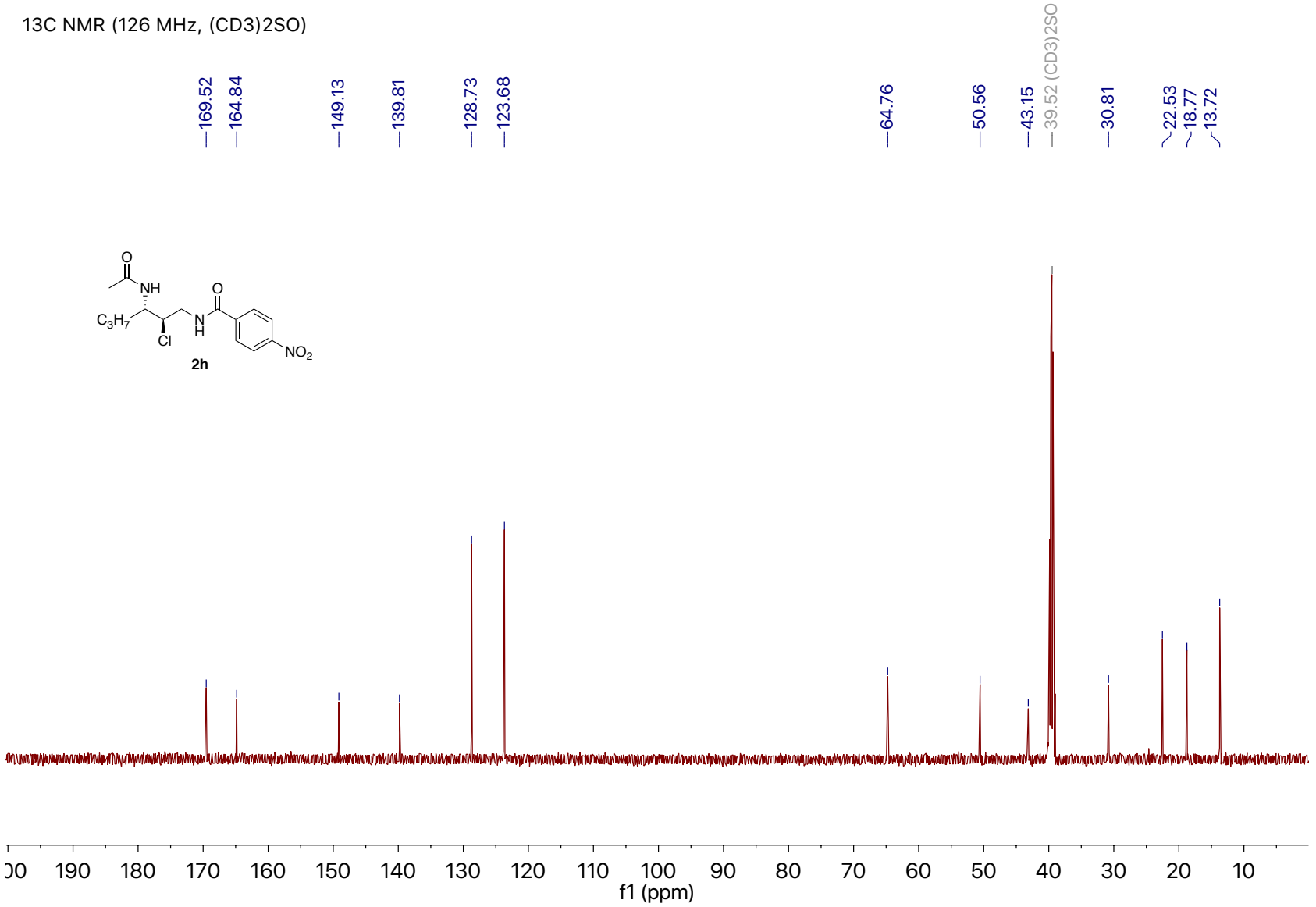
13C NMR (126 MHz, CDCl3)



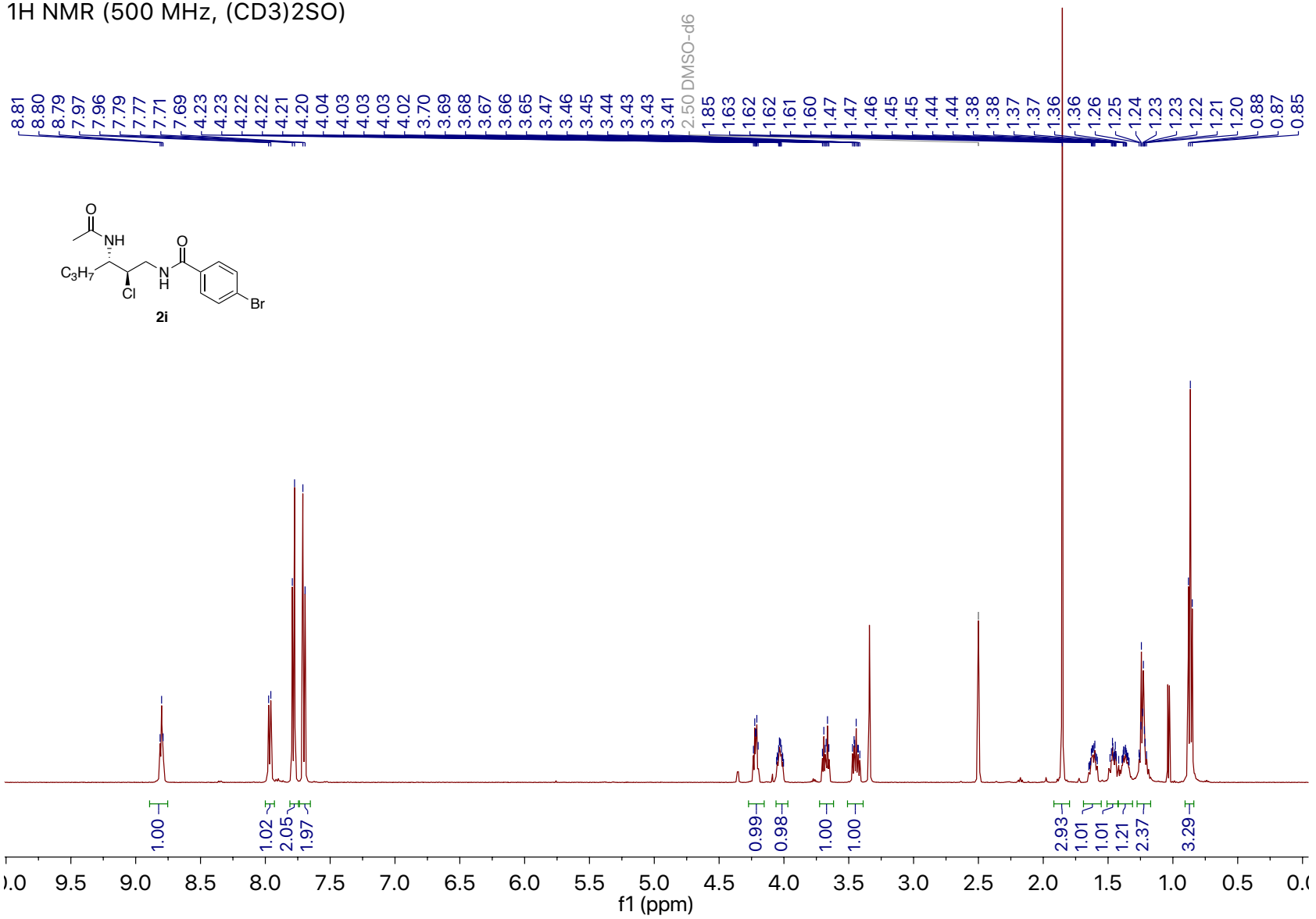
1H NMR (500 MHz, (CD3)2SO)



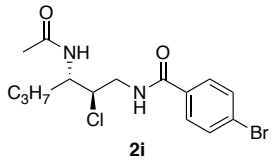
13C NMR (126 MHz, (CD3)2SO)



1H NMR (500 MHz, (CD3)2SO)

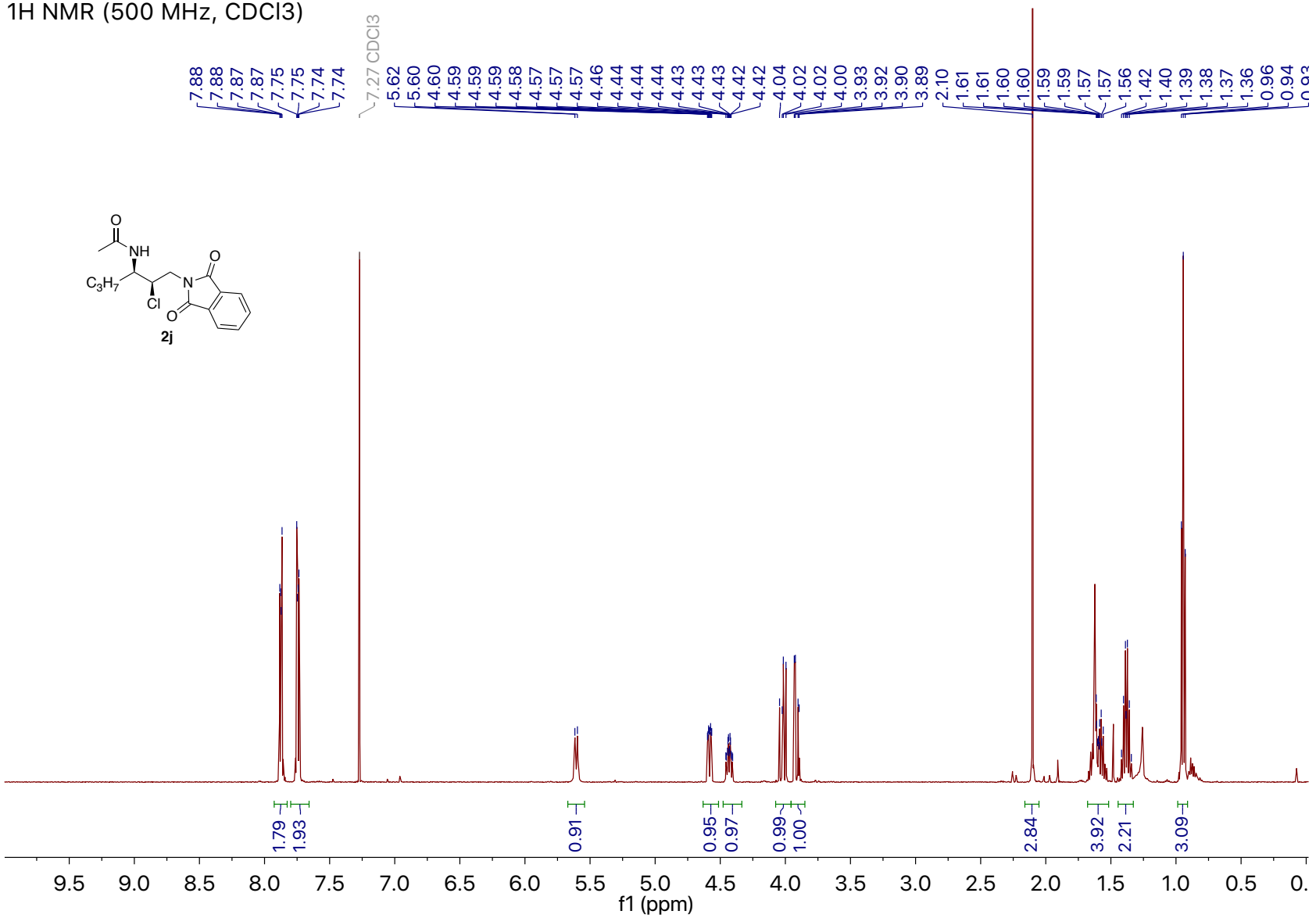


13C NMR (126 MHz, (CD3)2SO)

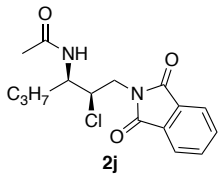


2i

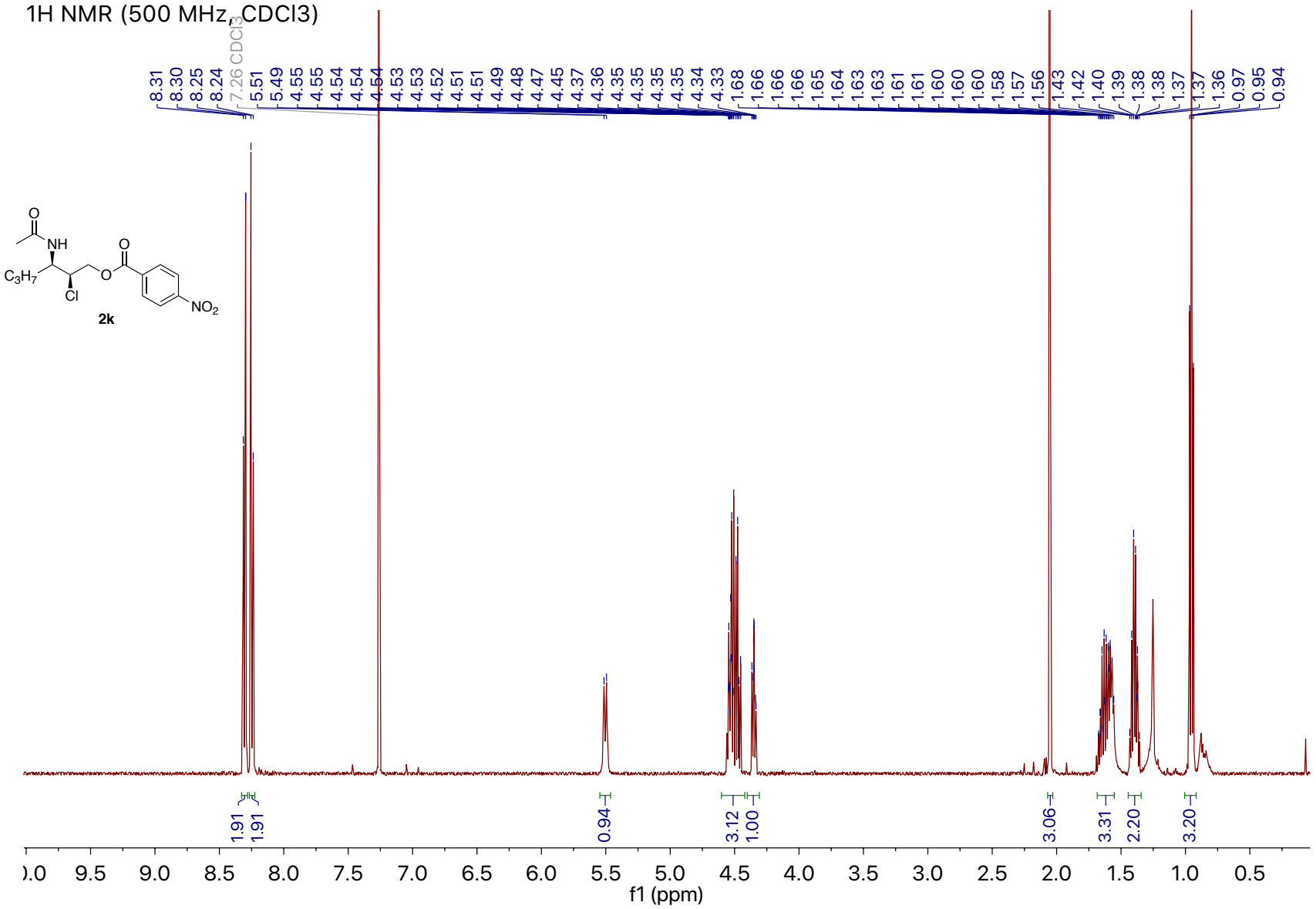
1H NMR (500 MHz, CDCl3)

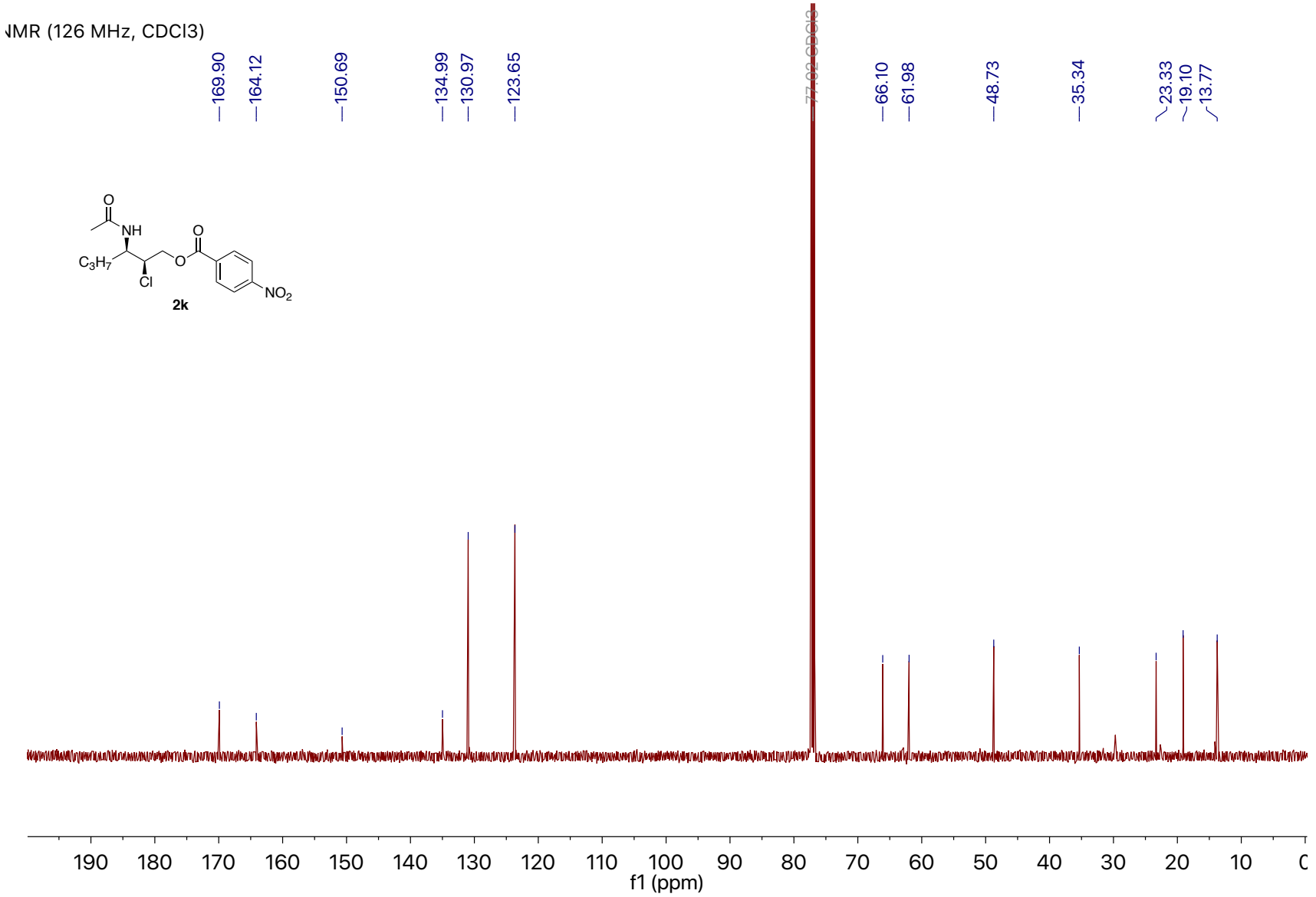


13C NMR (126 MHz, CDCl3)

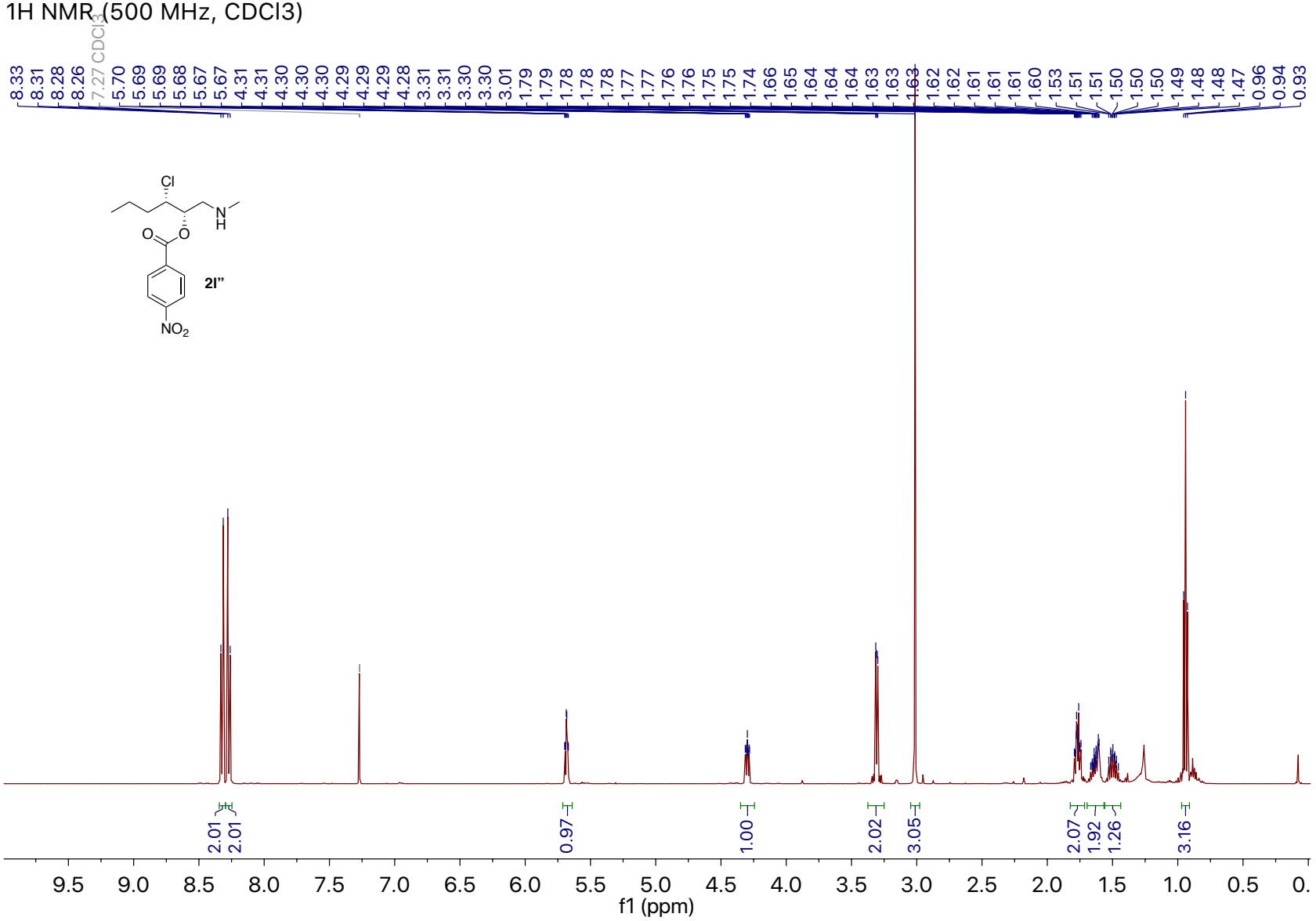


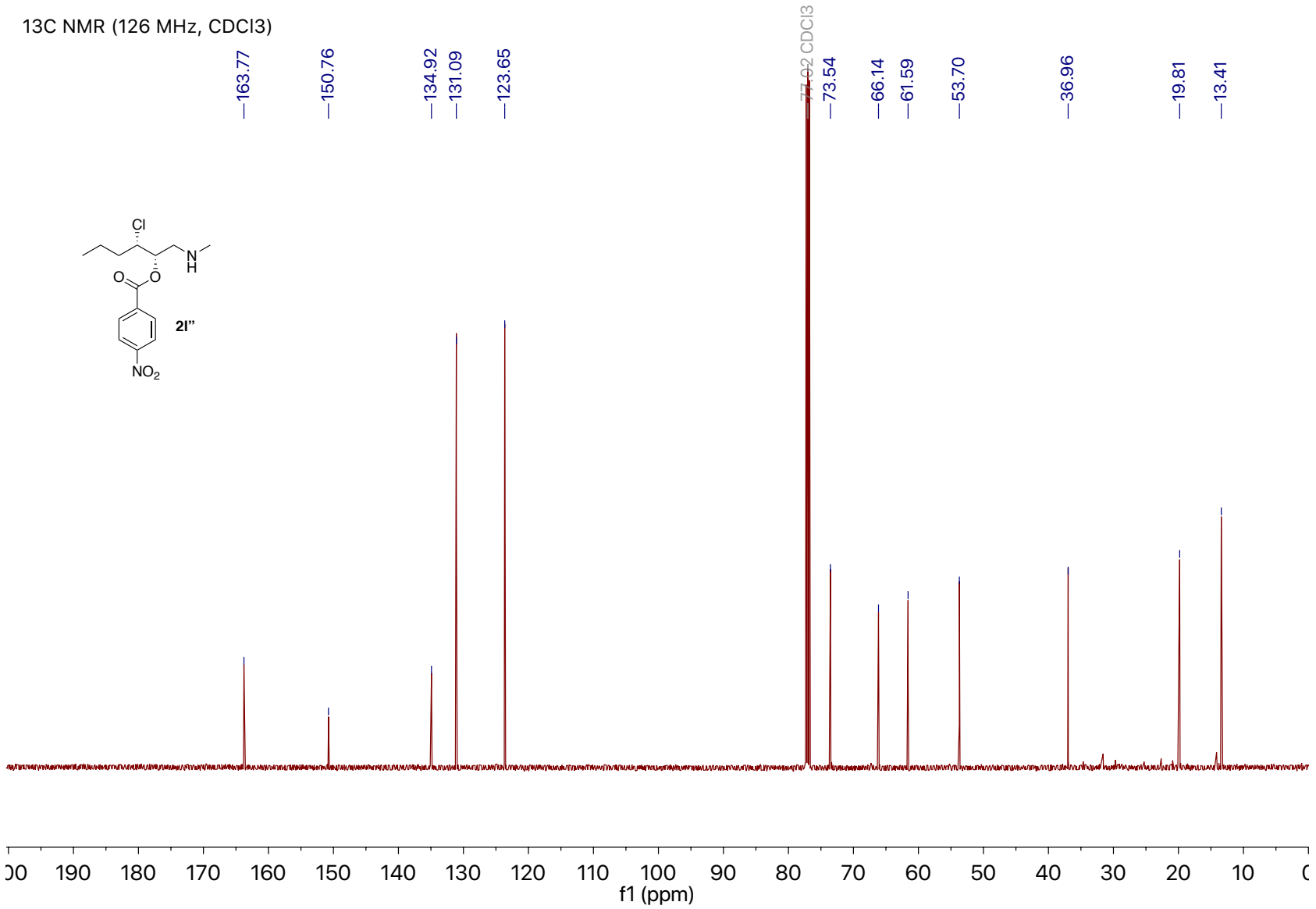
2j

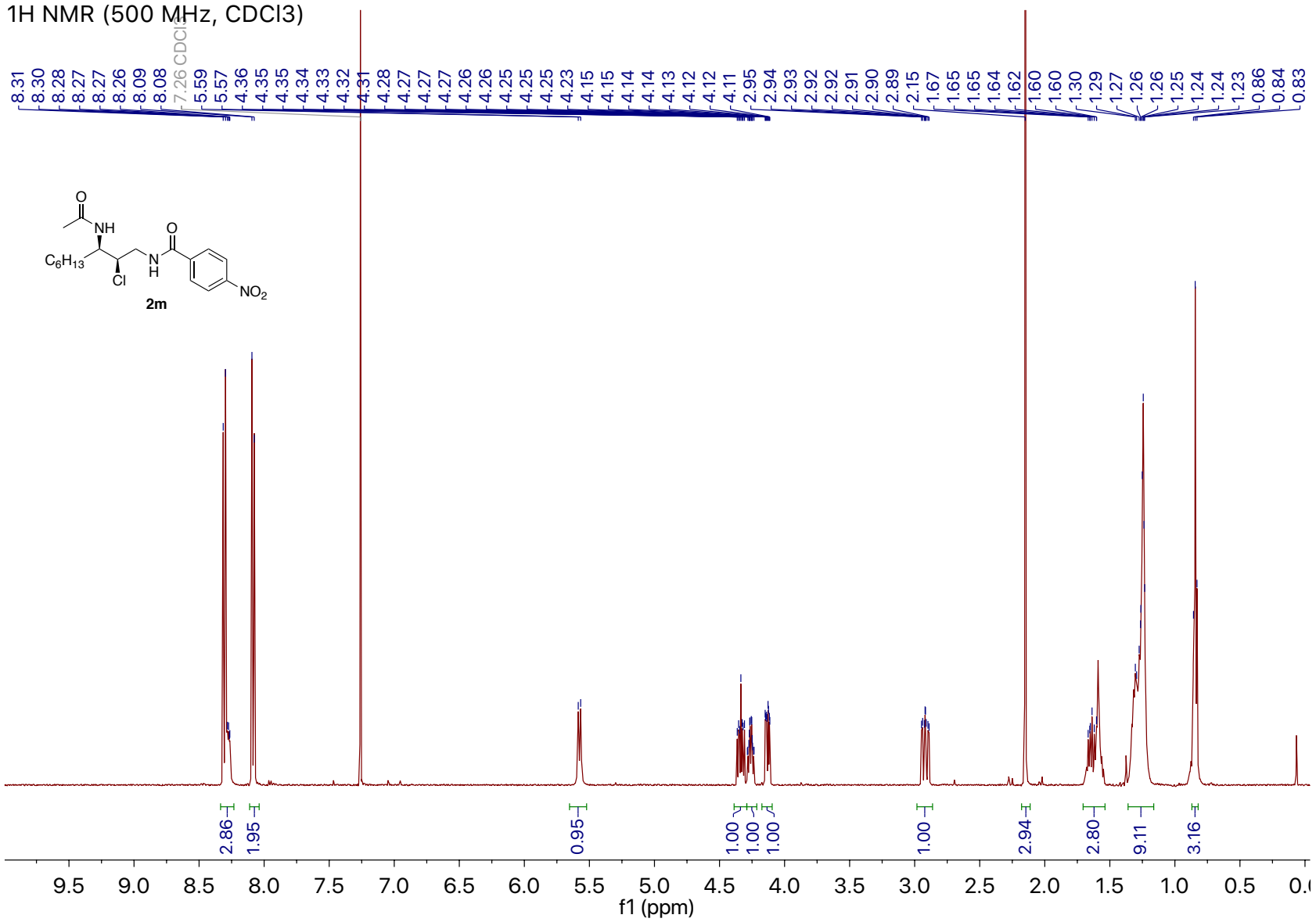

1H NMR (500 MHz, CDCl3)
7.26 CDCl3
8.31 8.30 8.25 8.24 5.51 5.49 4.55 4.55 4.54 4.54 4.54 4.53 4.53 4.52 4.51 4.51 4.49 4.48 4.47 4.45 4.37 4.36 4.35 4.35 4.35 4.34 4.33 1.68 1.66 1.66 1.66 1.65 1.64 1.63 1.63 1.61 1.61 1.60 1.60 1.60 1.58 1.57 1.56 1.43 1.42 1.40 1.39 1.38 1.38 1.37 1.37 1.36 0.97 0.95 0.94
O
NH
O
C3H7
O
Cl
NO2
2k
1.91
1.91
0.94
3.12
1.00
3.06
3.31
2.20
3.20
f1 (ppm)


NMR (126 MHz, CDCl3)
169.90
164.12
150.69
134.99
130.97
123.65
77.02 CDCl3
66.10
61.98
48.73
35.34
23.33
19.10
13.77
O
NH
O
C3H7
O
Cl
NO2
2k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

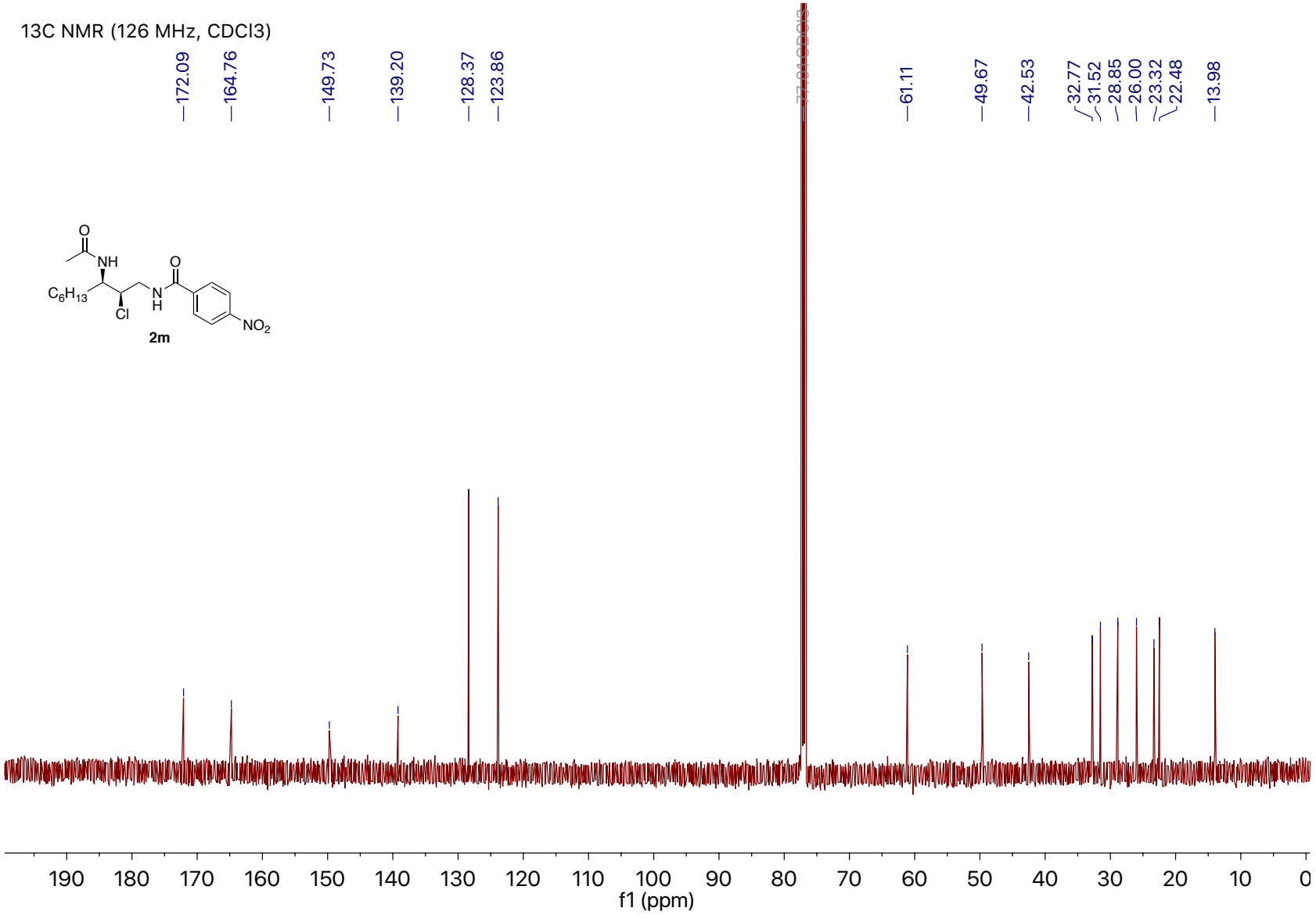
1H NMR (500 MHz, CDCl3)

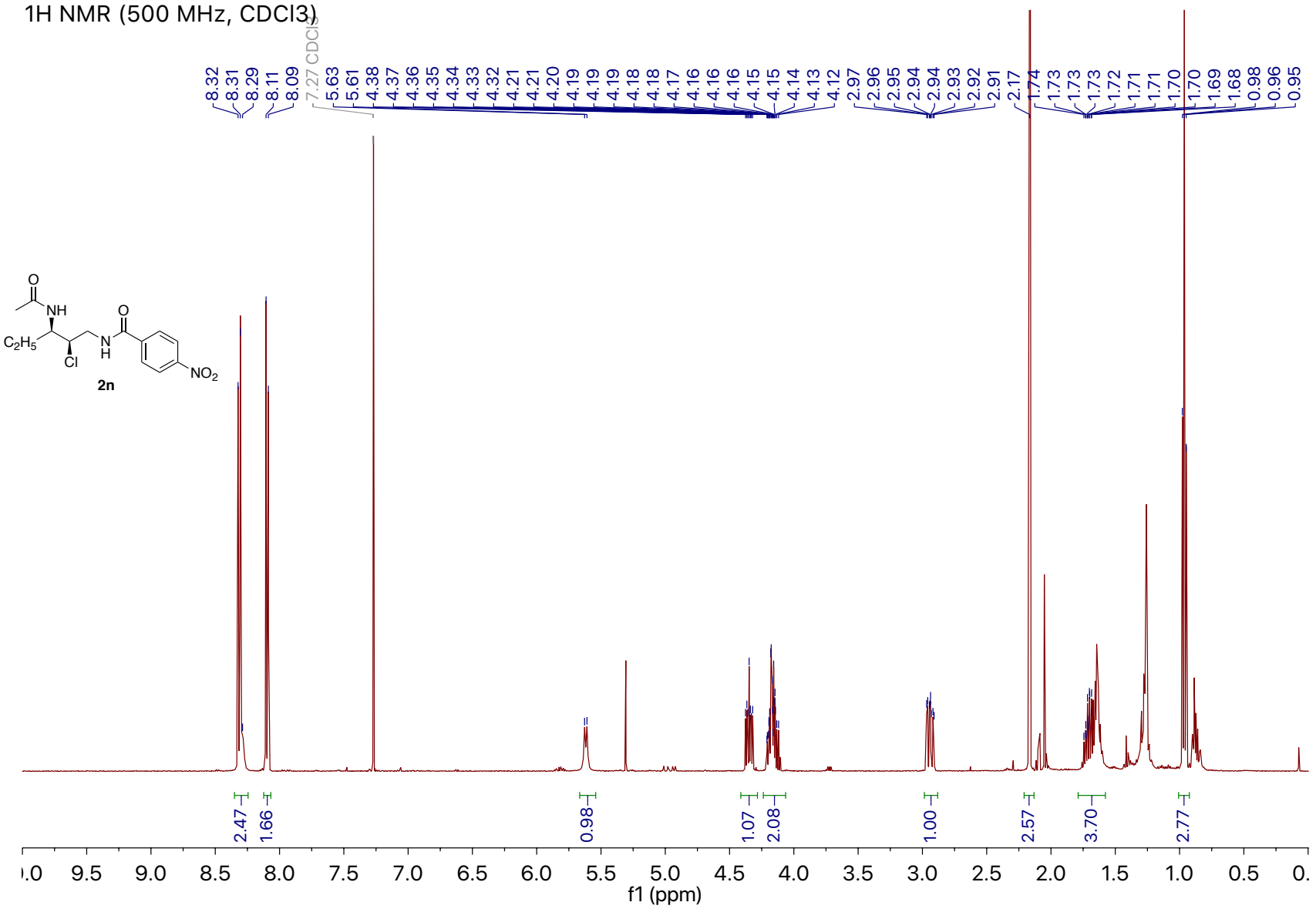


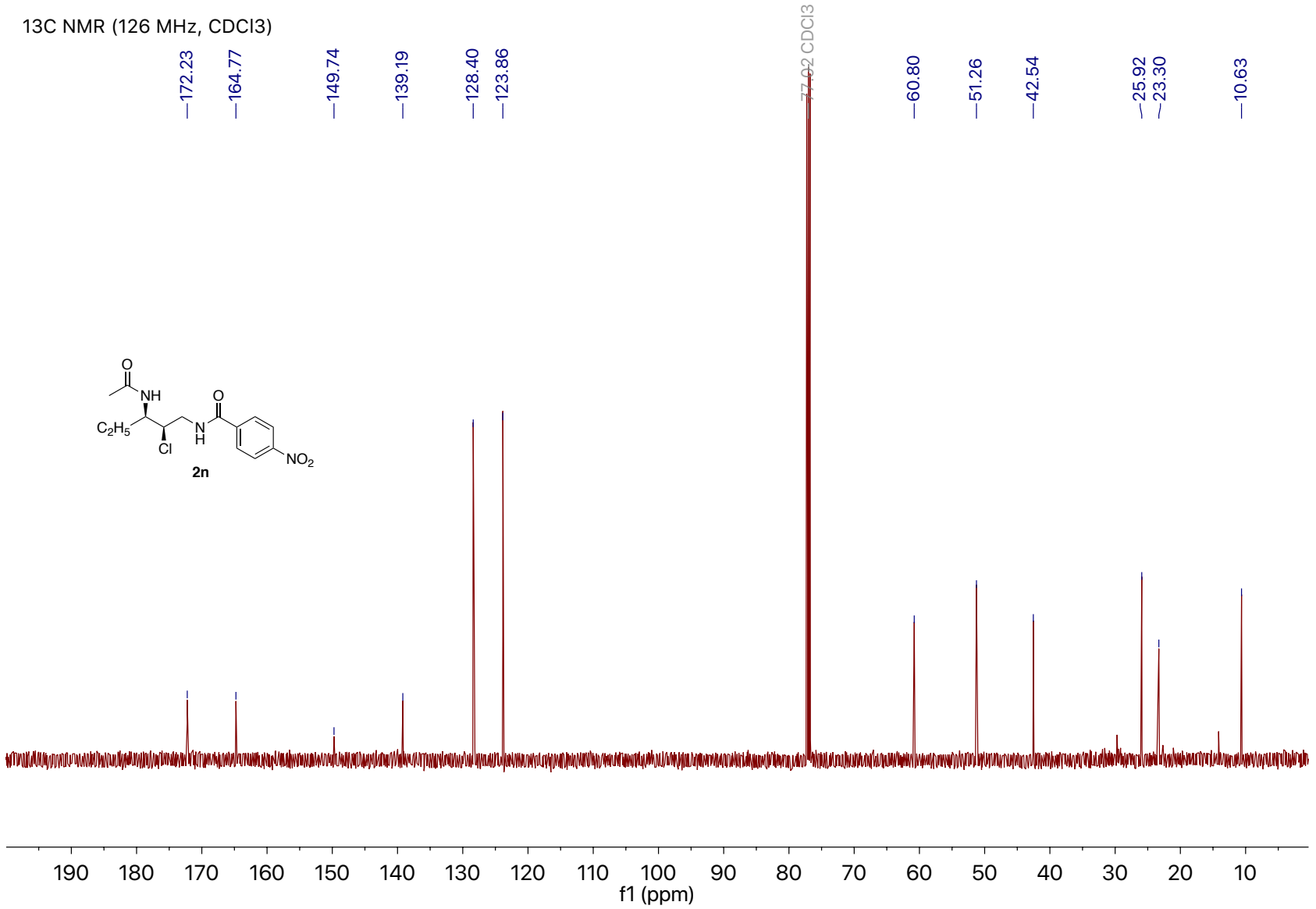

13C NMR (126 MHz, CDCl3)
163.77
150.76
134.92
131.09
123.65
77.02 CDCl3
73.54
66.14
61.59
53.70
36.96
19.81
13.41
Cl
N
H
O
O
2l”
NO2
f1 (ppm)


1H NMR (500 MHz, CDCl3)
8.31 8.30 8.28 8.27 8.27 8.26 8.09 8.08 7.26 CDCl3 5.59 5.57 4.36 4.35 4.35 4.34 4.33 4.32 4.31 4.28 4.27 4.27 4.27 4.26 4.26 4.25 4.25 4.25 4.23 4.15 4.15 4.14 4.14 4.13 4.12 4.12 4.11 2.95 2.94 2.93 2.92 2.92 2.91 2.90 2.89 2.15 1.67 1.65 1.65 1.64 1.62 1.60 1.60 1.30 1.29 1.27 1.26 1.26 1.25 1.24 1.24 1.23 0.86 0.84 0.83
O
NH
O
C6H13
N
H
Cl
NO2
2m
2.86 1.95 0.95 1.00 1.00 1.00 1.00 2.94 2.80 9.11 3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

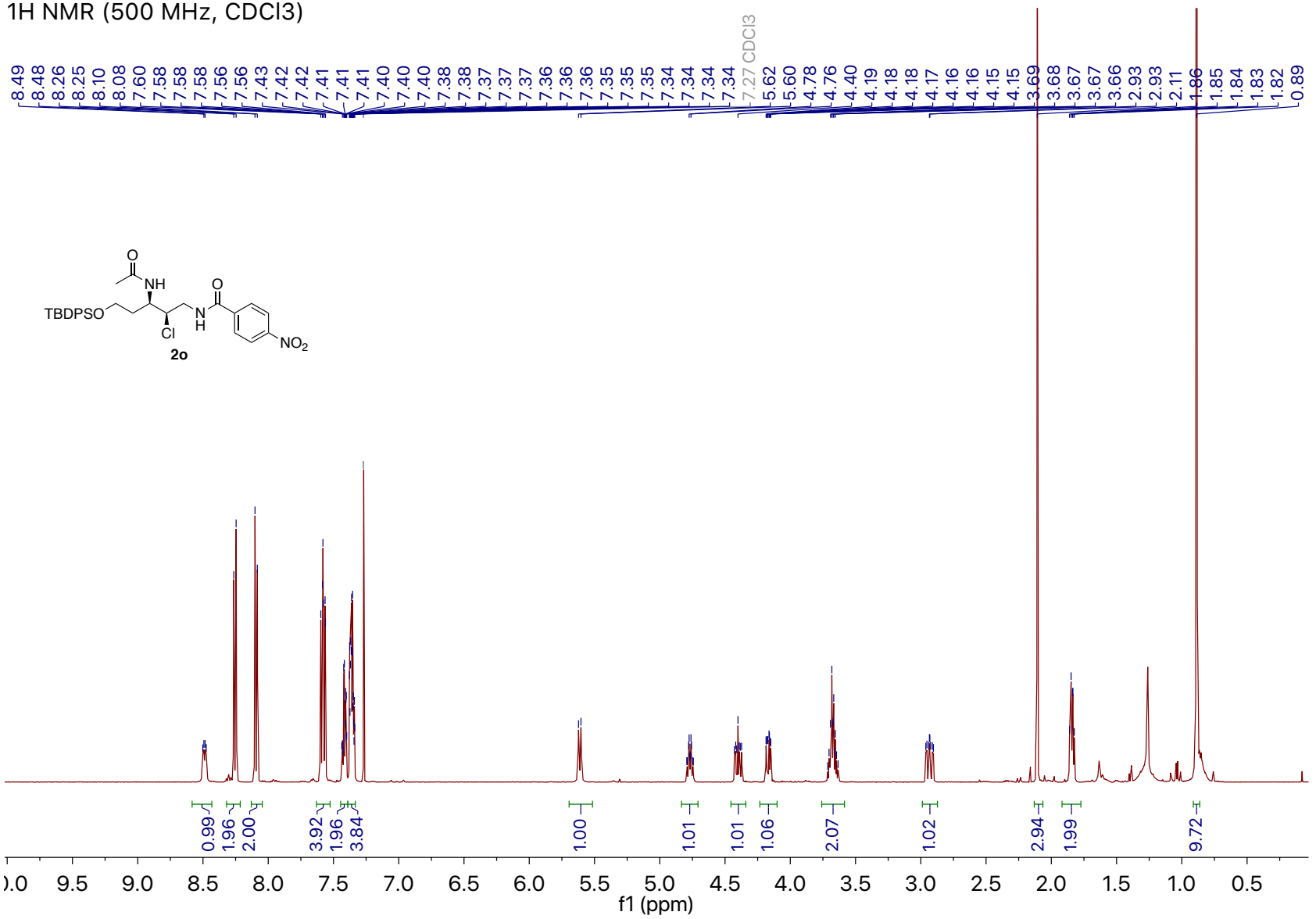
13C NMR (126 MHz, CDCl3)



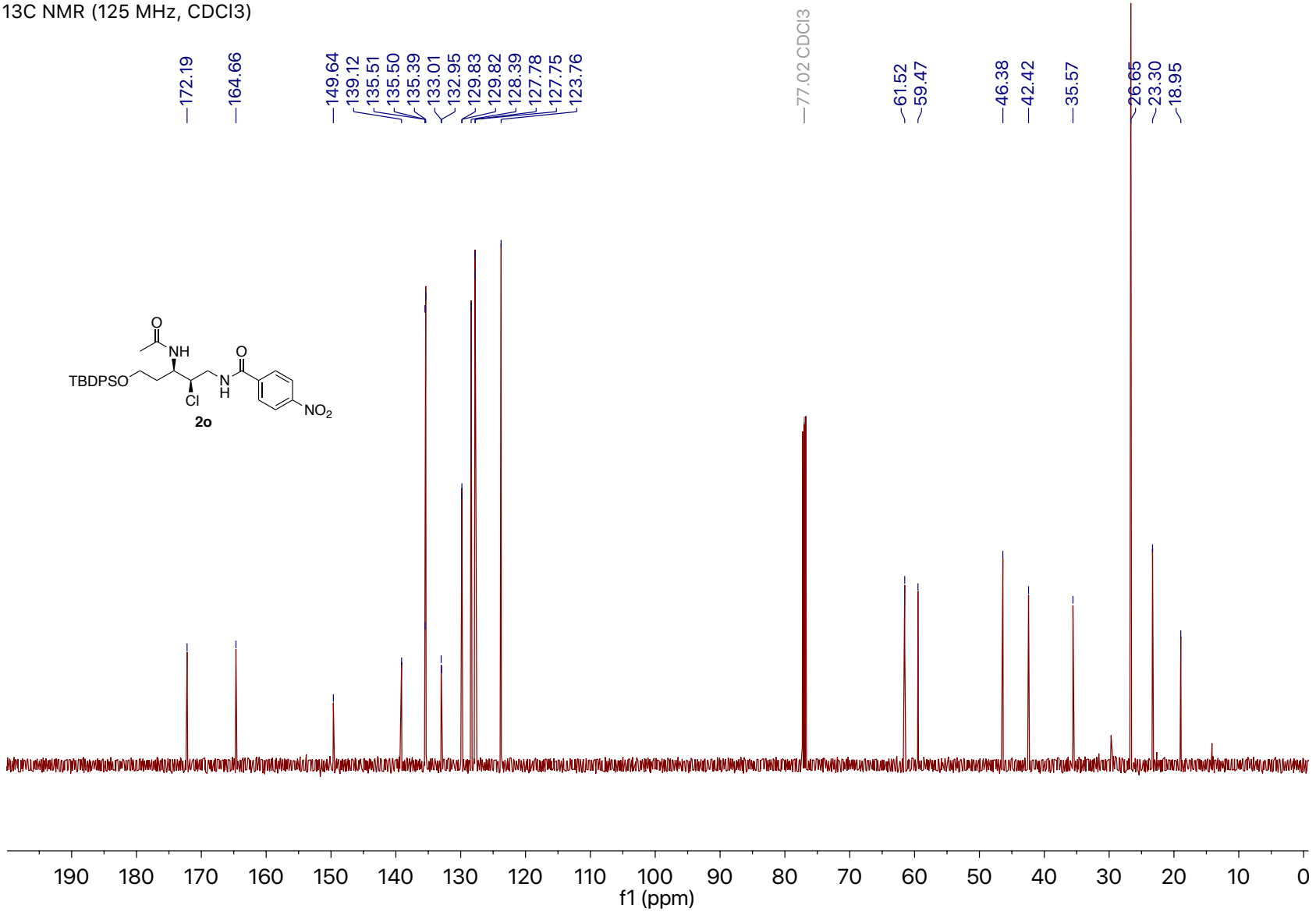

1H NMR (500 MHz, CDCl3)
8.32
8.31
8.29
8.11
8.09
7.27 CDCl3
5.63
5.61
4.38
4.37
4.36
4.35
4.34
4.33
4.32
4.21
4.21
4.20
4.19
4.19
4.19
4.18
4.18
4.17
4.16
4.16
4.16
4.15
4.15
4.14
4.13
4.12
2.97
2.96
2.95
2.94
2.94
2.93
2.92
2.91
2.17
1.74
1.73
1.73
1.73
1.72
1.71
1.71
1.70
1.70
1.69
1.68
0.98
0.96
0.95
O
NH
O
C2H5
N
H
Cl
NO2
2n
2.47
1.66
0.98
1.07
2.08
1.00
2.57
3.70
2.77
f1 (ppm)

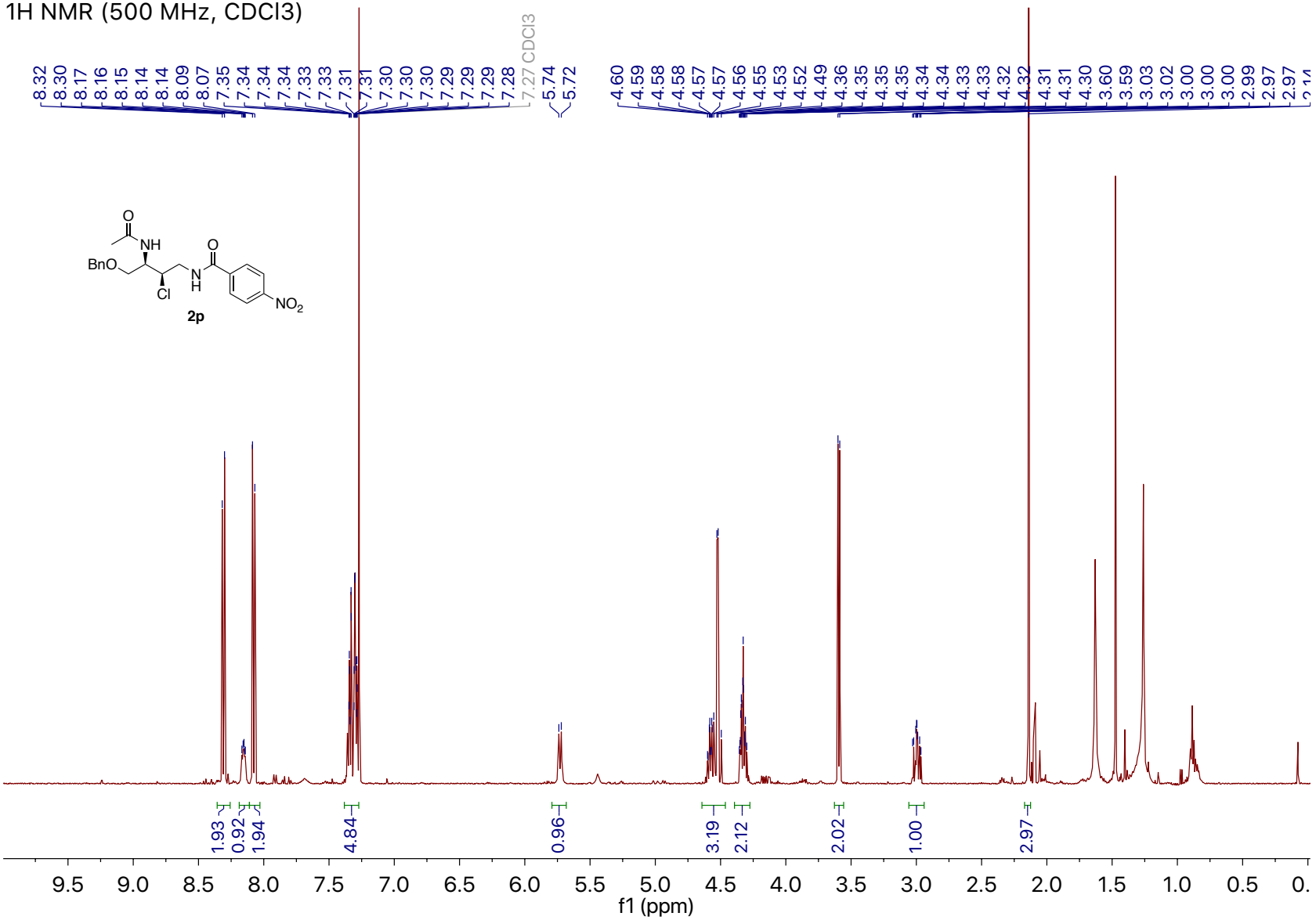

13C NMR (126 MHz, CDCl3)
172.23
164.77
149.74
139.19
128.40
123.86
77.02 CDCl3
60.80
51.26
42.54
25.92
23.30
10.63
O
NH
C2H5
Cl
N
H
O
NO2
2n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1H NMR (500 MHz, CDCl3)

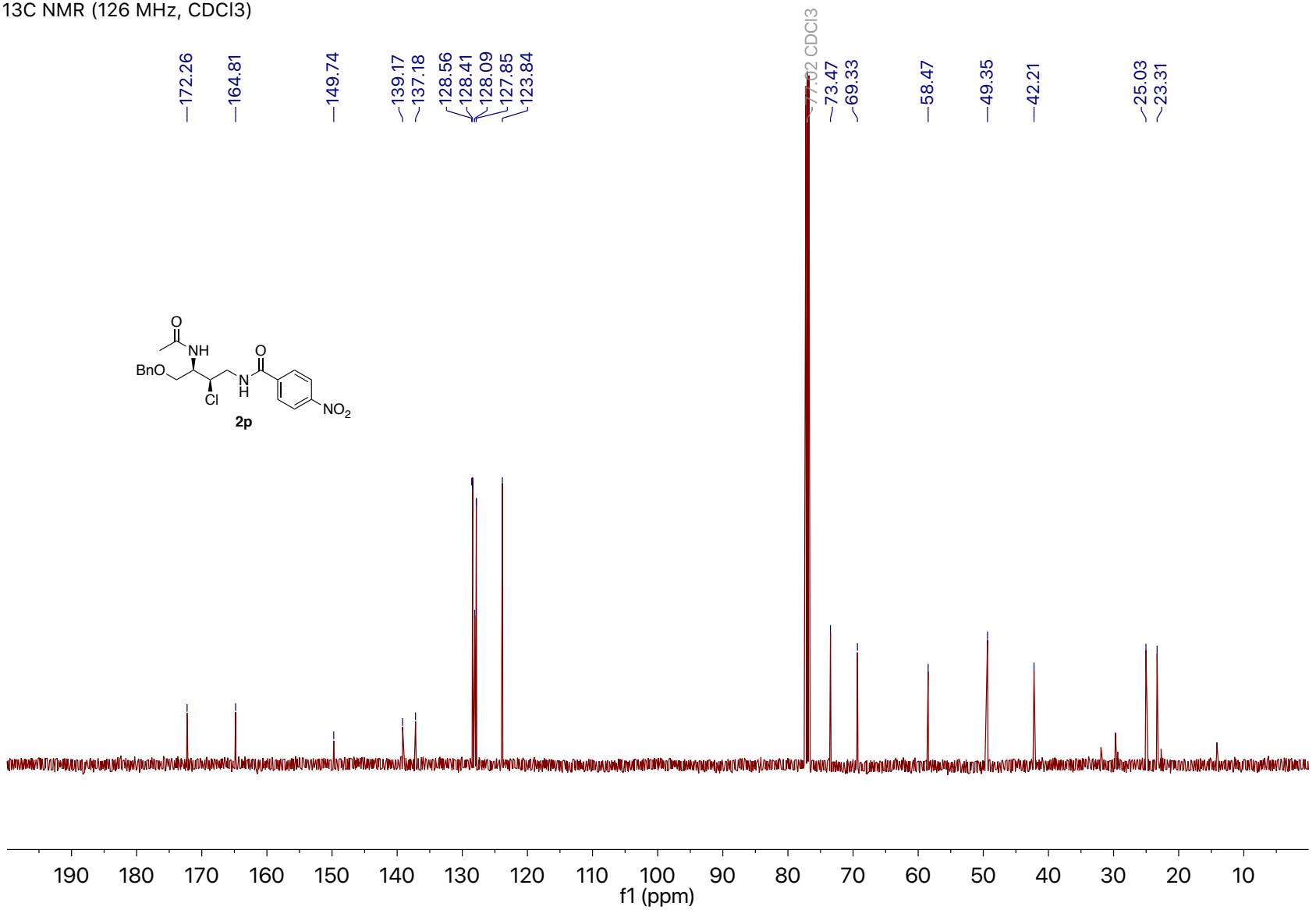


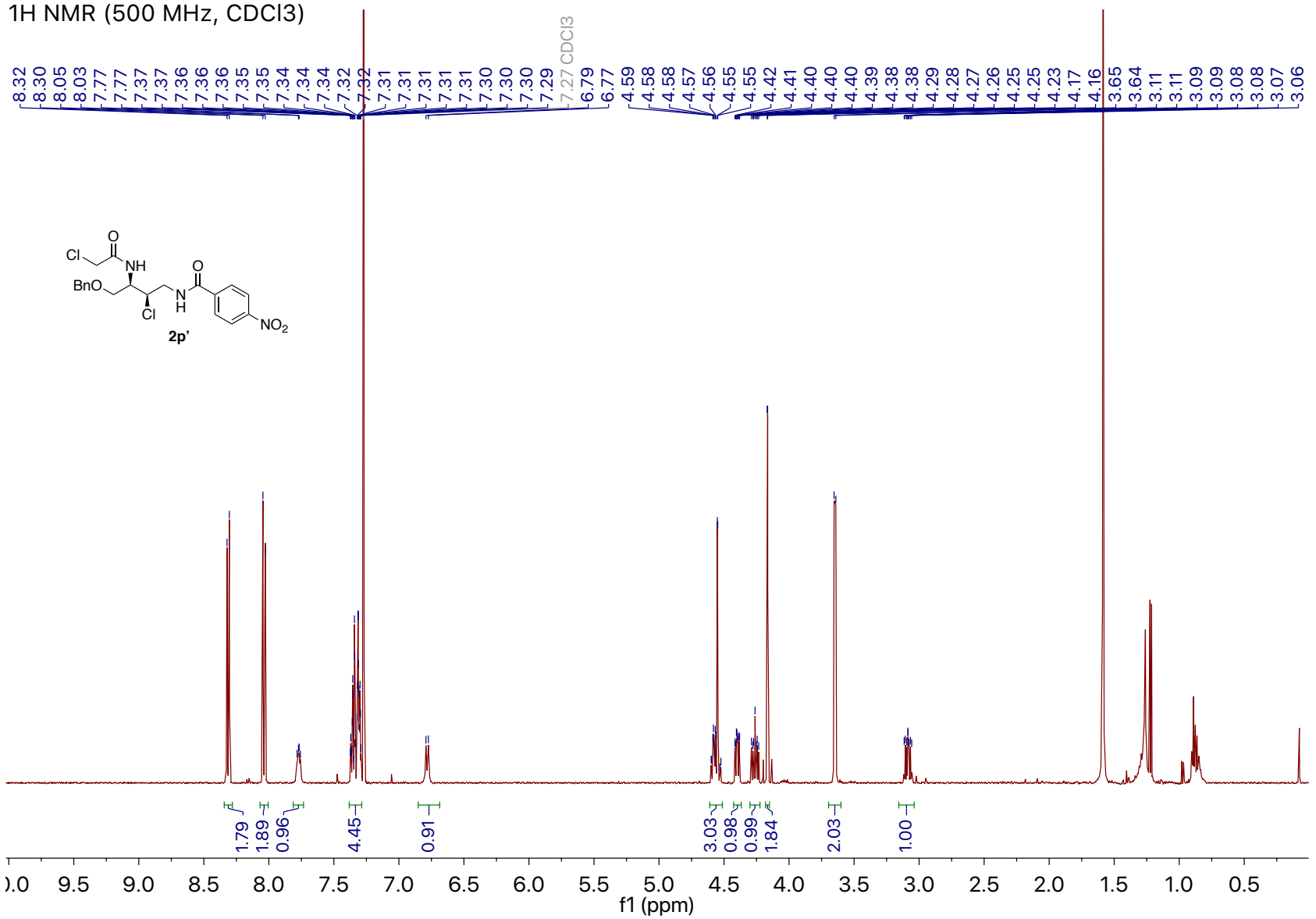
13C NMR (125 MHz, CDCl3)

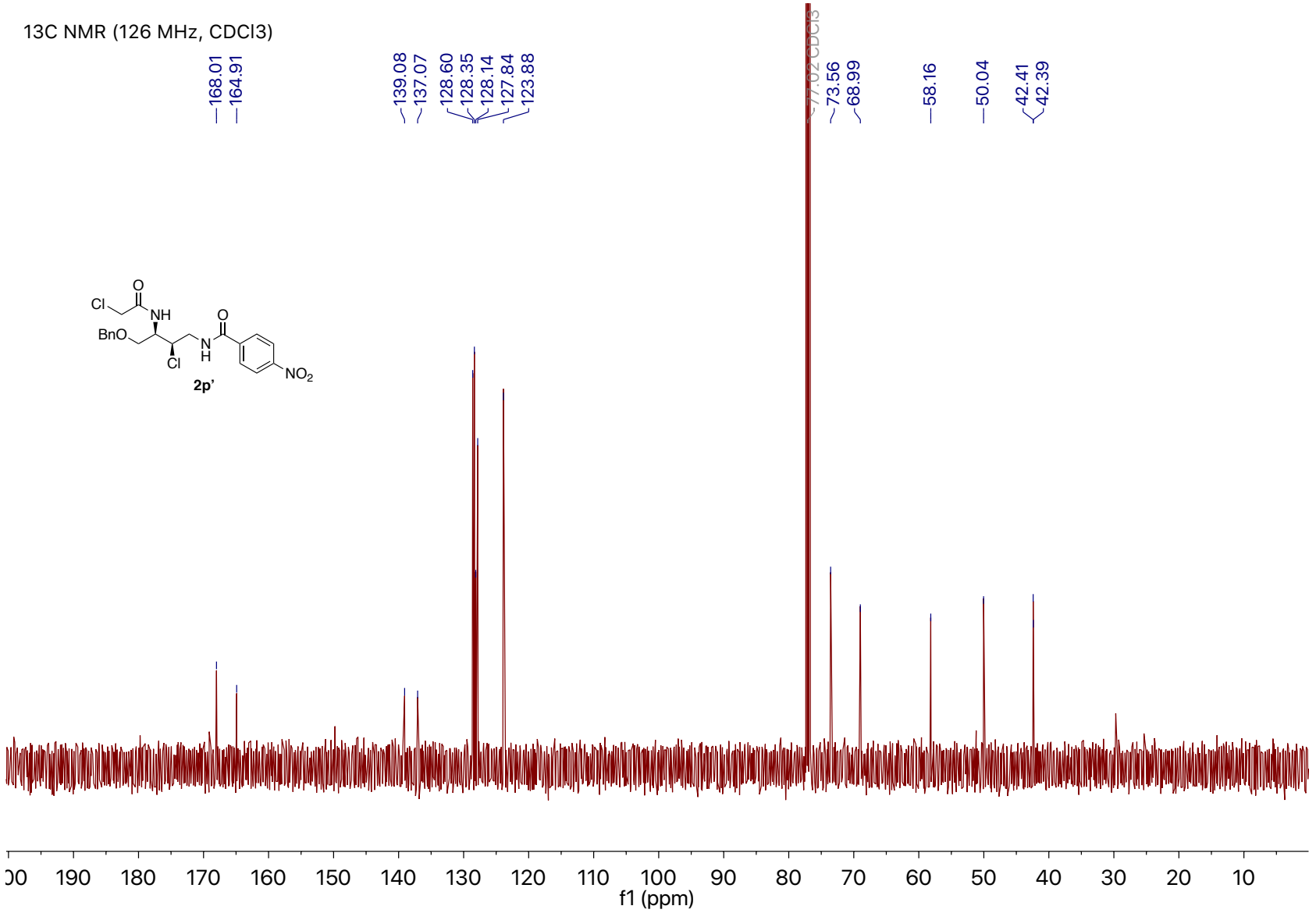


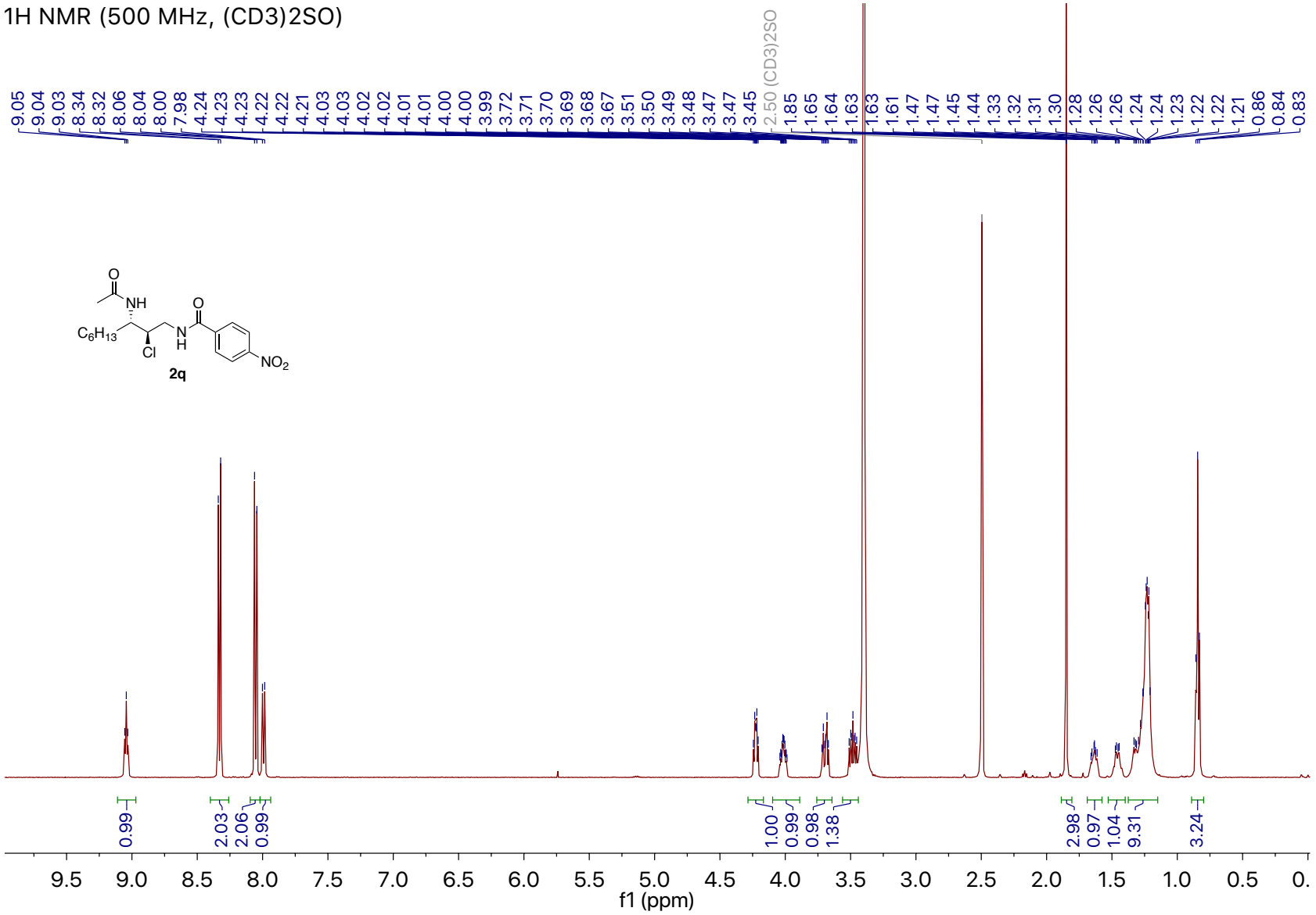

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
BnO
NH
Cl
N
H
O
NO2
2p
1.93
0.92
1.94
4.84
0.96
3.19
2.12
2.02
1.00
2.97
f1 (ppm)

13C NMR (126 MHz, CDCl3)

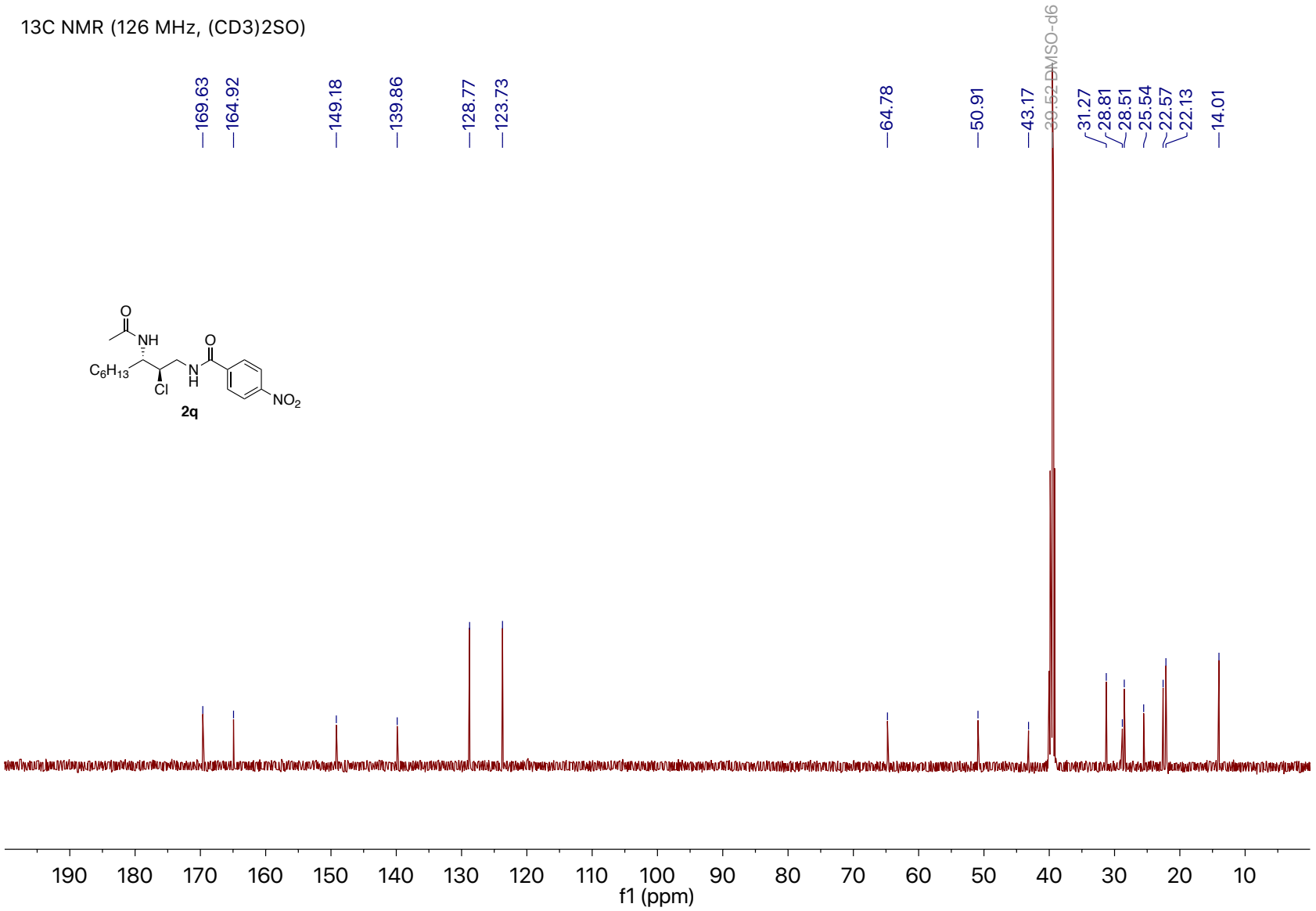


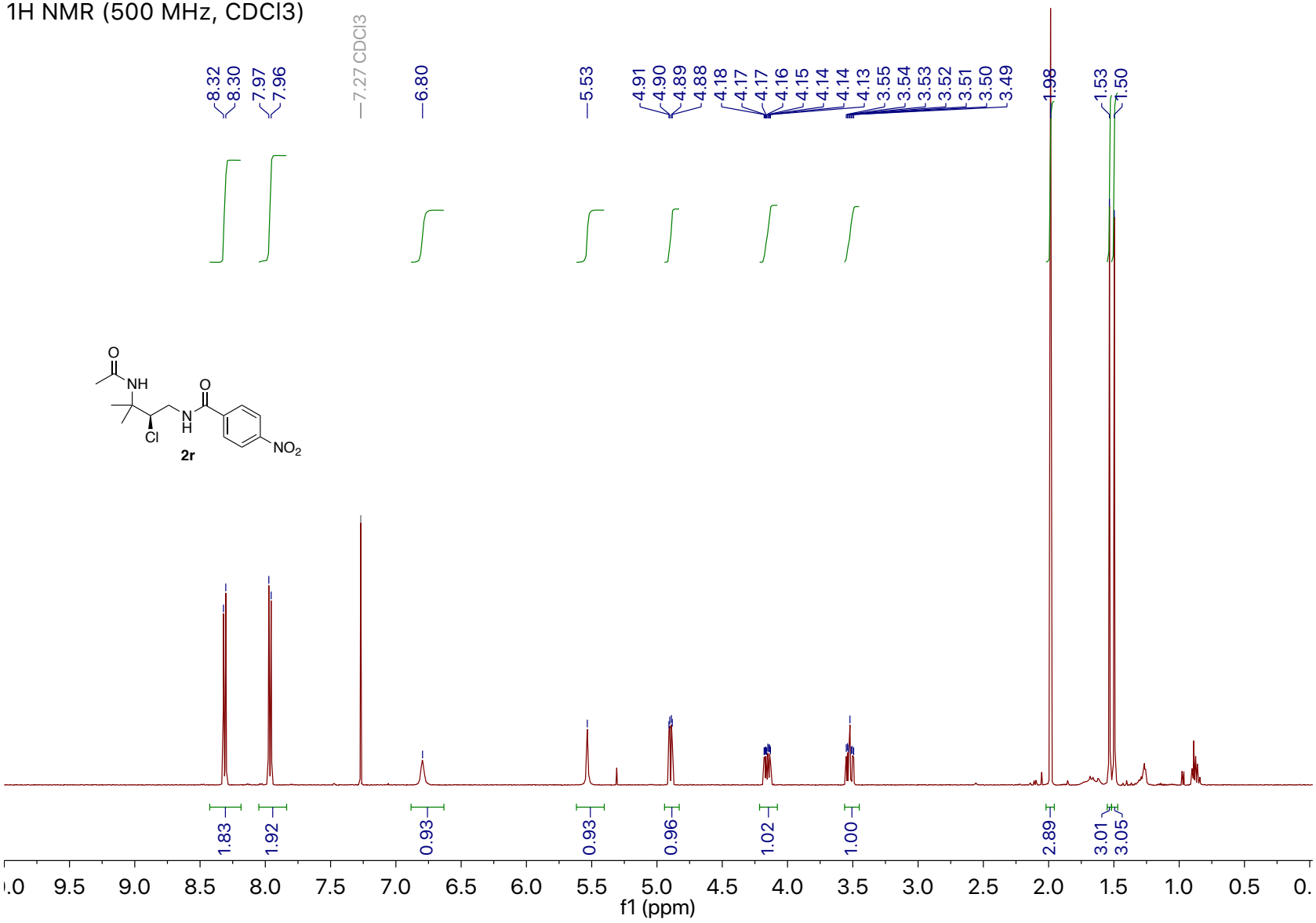

1H NMR (500 MHz, CDCl3)
8.32 8.30 8.05 8.03 7.77 7.77 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.32 7.32 7.31 7.31 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.27 CDCl3 6.79 6.77 4.59 4.58 4.58 4.57 4.56 4.55 4.55 4.42 4.41 4.40 4.40 4.40 4.39 4.38 4.38 4.29 4.28 4.27 4.26 4.25 4.25 4.23 4.17 4.16 3.65 3.64 3.11 3.11 3.09 3.09 3.08 3.08 3.07 3.06
Cl
O
NH
BnO
Cl
N
H
O
NO2
2p'
1.79 1.89 0.96 4.45 0.91 3.03 0.98 0.99 1.84 2.03 1.00
f1 (ppm)

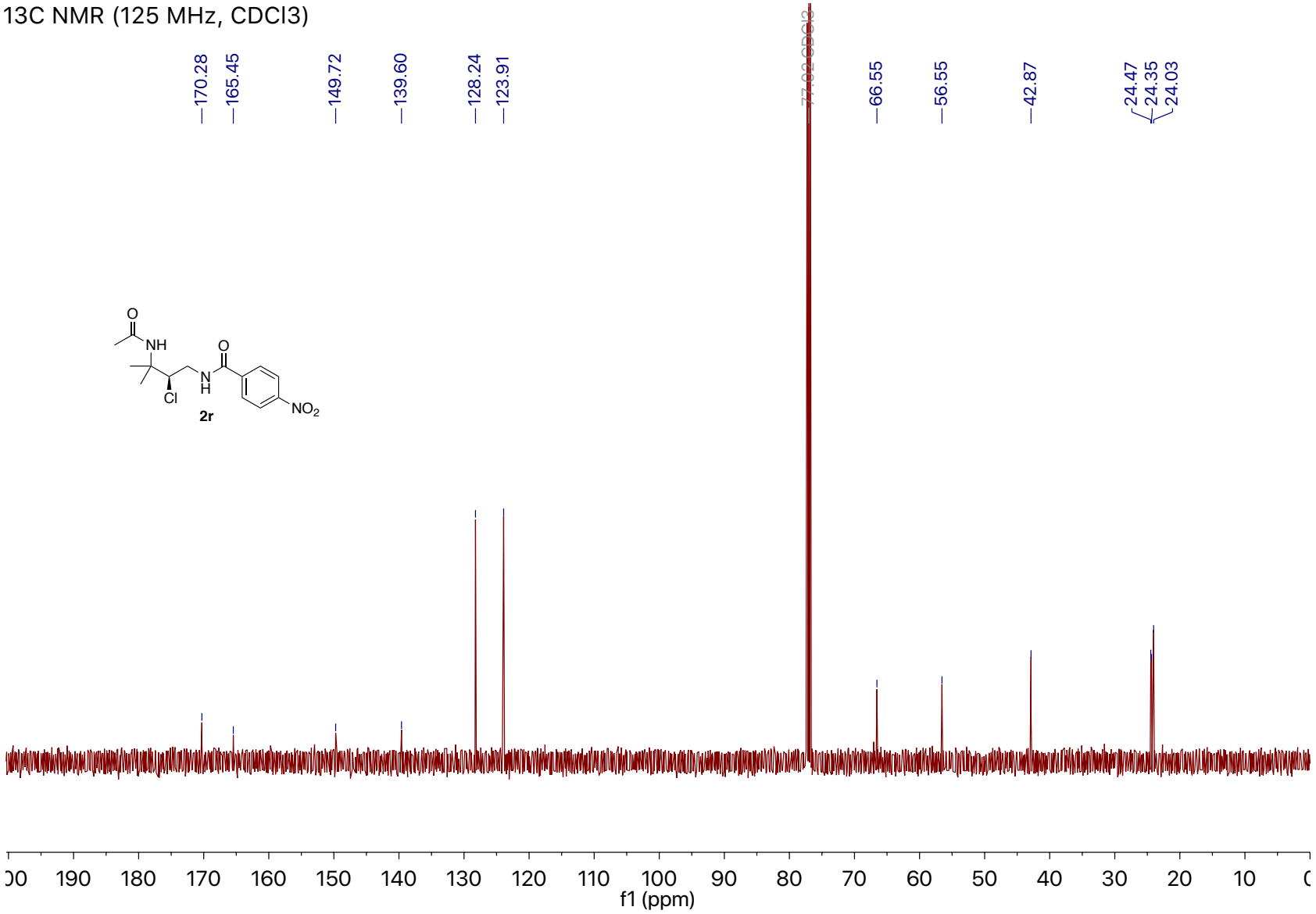

13C NMR (126 MHz, CDCl3)
168.01
164.91
139.08
137.07
128.60
128.35
128.14
127.84
123.88
77.02 CDCl3
73.56
68.99
58.16
50.04
42.41
42.39
Cl
O
NH
BnO
Cl
O
N
H
NO2
2p'
f1 (ppm)


1H NMR (500 MHz, (CD3)2SO)
2.50 (CD3)2SO
2q
f1 (ppm)

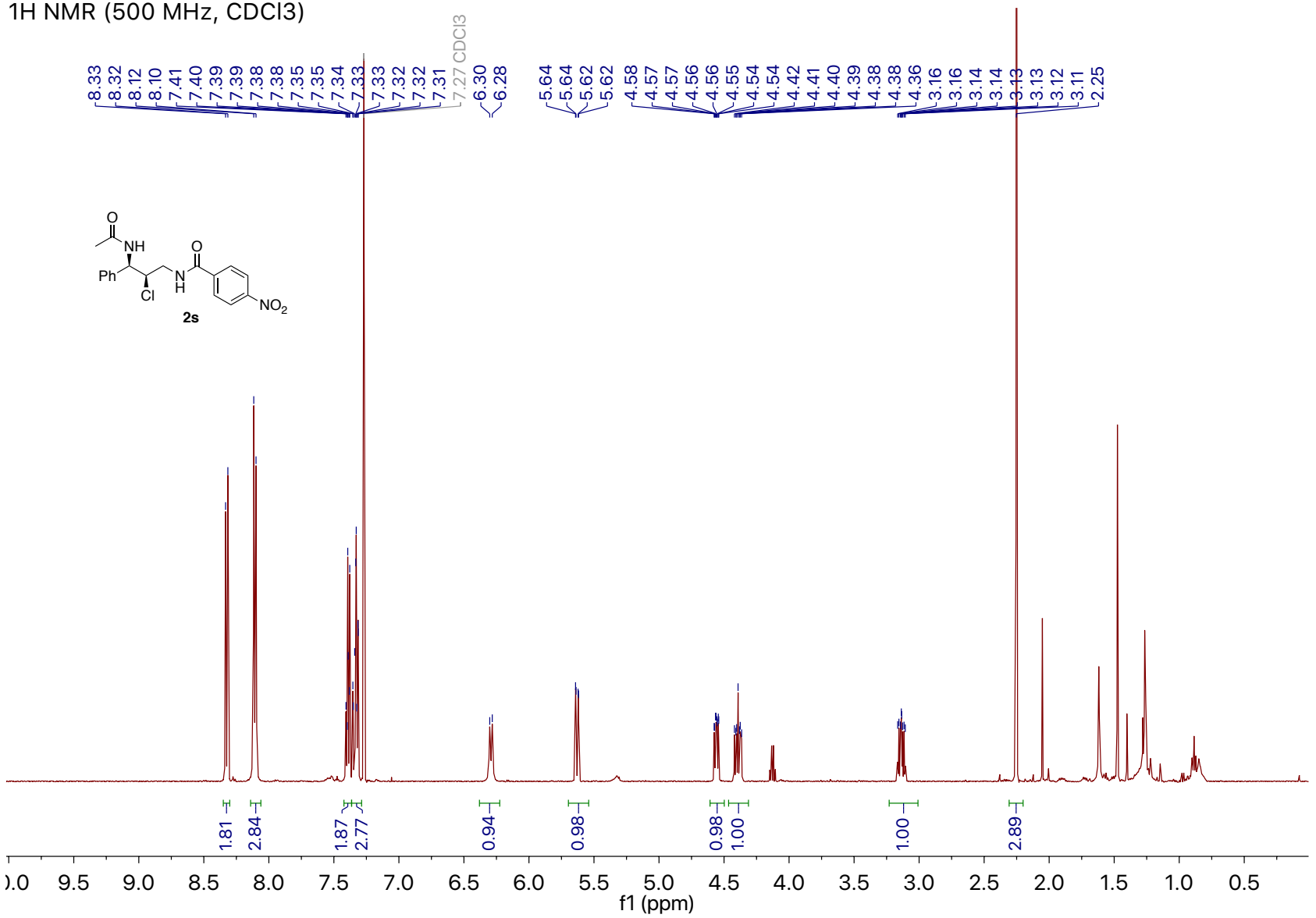
13C NMR (126 MHz, (CD3)2SO)



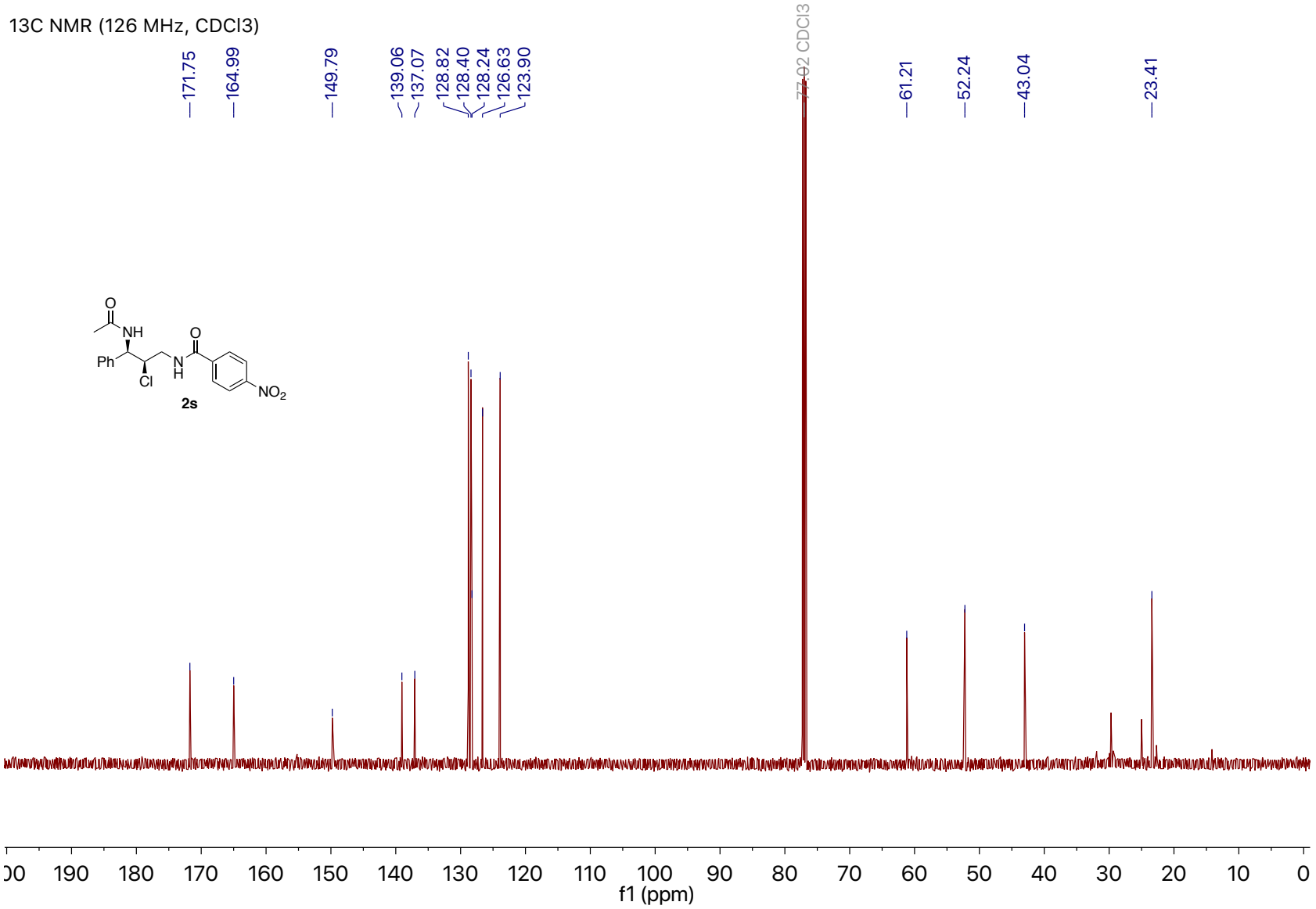

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
8.32
8.30
7.97
7.96
6.80
5.53
4.91
4.90
4.89
4.88
4.18
4.17
4.17
4.16
4.15
4.14
4.14
4.13
3.55
3.54
3.53
3.52
3.51
3.50
3.49
1.98
1.53
1.50
O
NH
O
N
H
Cl
NO2
2r
1.83
1.92
0.93
0.93
0.96
1.02
1.00
2.89
3.01
3.05
f1 (ppm)

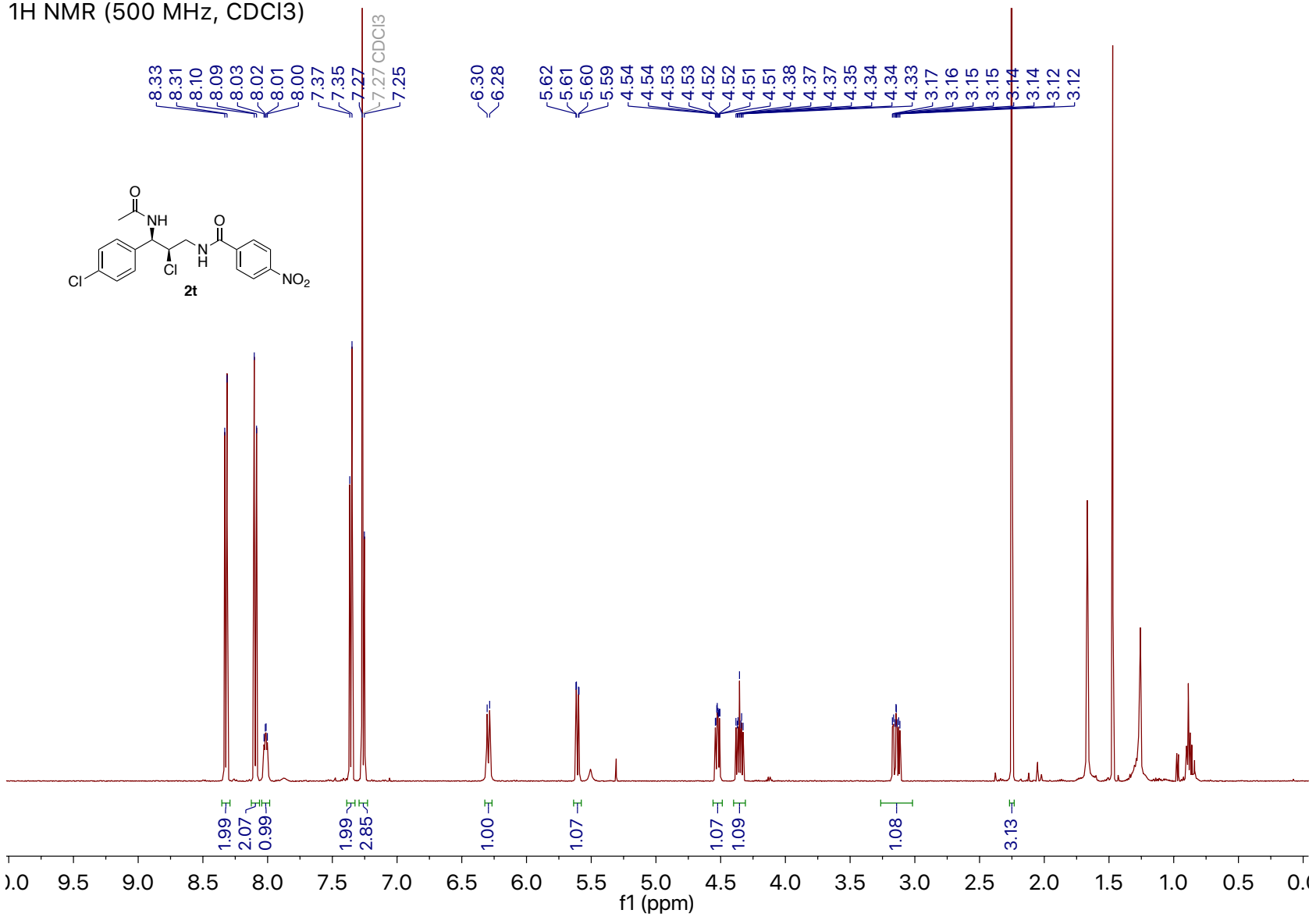

13C NMR (125 MHz, CDCl3)
170.28
165.45
149.72
139.60
128.24
123.91
77.02 CDCl3
66.55
56.55
42.87
24.47
24.35
24.03
O
NH
O
N
H
Cl
NO2
2r
f1 (ppm)

1H NMR (500 MHz, CDCl3)

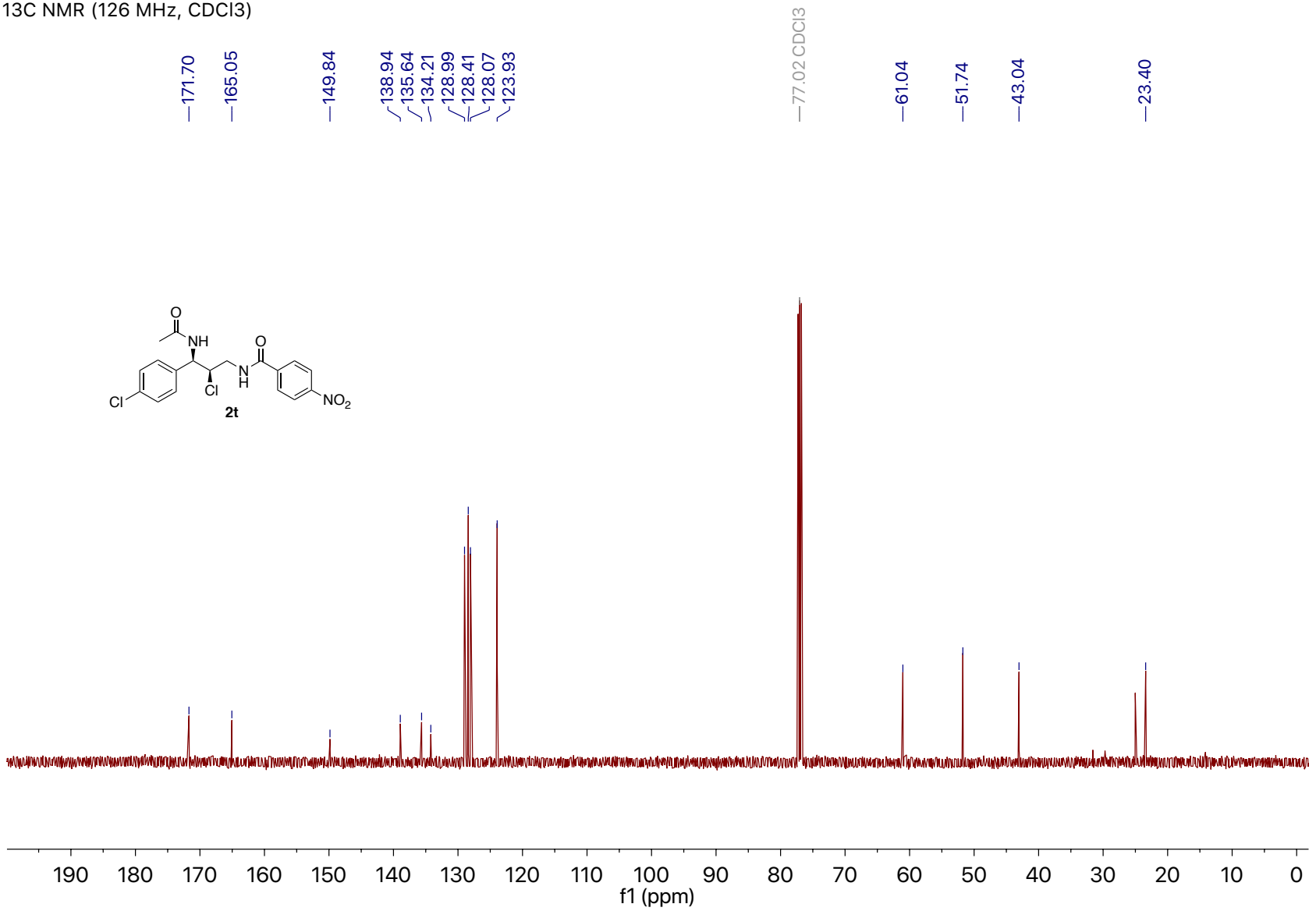


13C NMR (126 MHz, CDCl3)

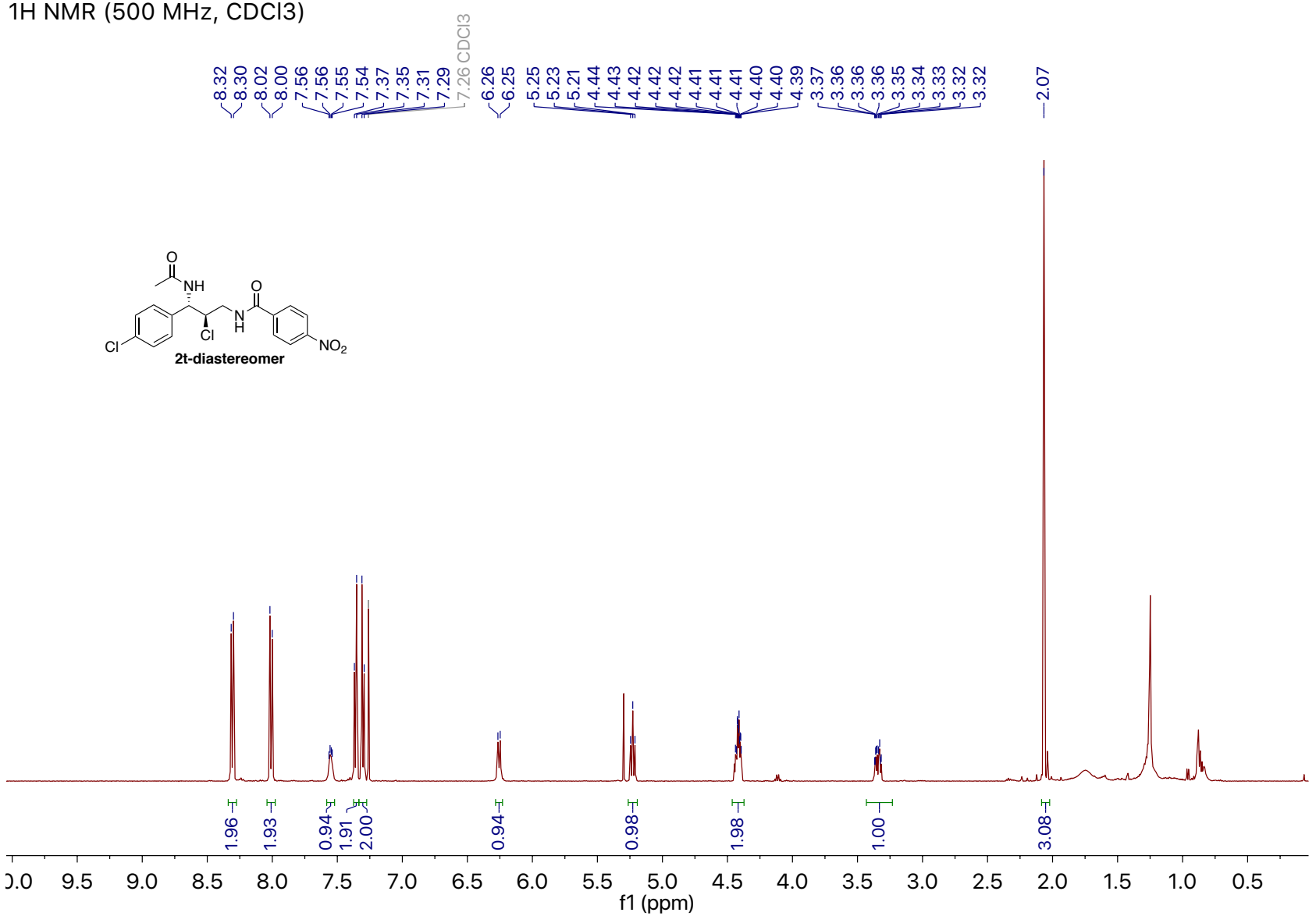



1H NMR (500 MHz, CDCl3)
8.33
8.31
8.10
8.09
8.03
8.02
8.01
8.00
7.37
7.35
7.27
7.27 CDCl3
7.25
6.30
6.28
5.62
5.61
5.60
5.59
4.54
4.54
4.53
4.53
4.52
4.52
4.51
4.51
4.38
4.37
4.37
4.35
4.34
4.34
4.33
3.17
3.16
3.15
3.15
3.14
3.14
3.12
3.12
O
NH
O
N
H
Cl
Cl
NO2
2t
1.99
2.07
0.99
1.99
2.85
1.00
1.07
1.07
1.09
1.08
3.13
f1 (ppm)

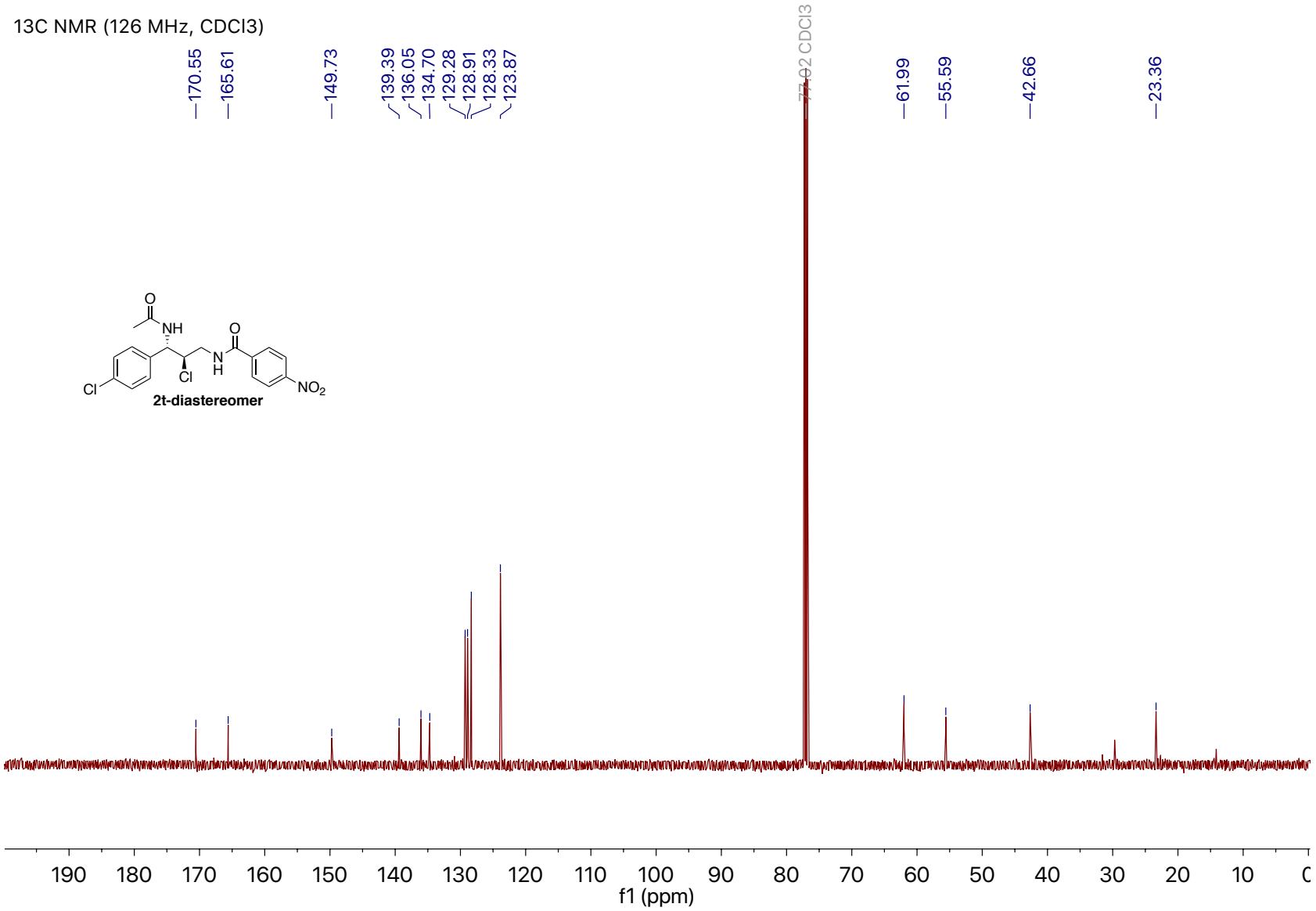
13C NMR (126 MHz, CDCl3)



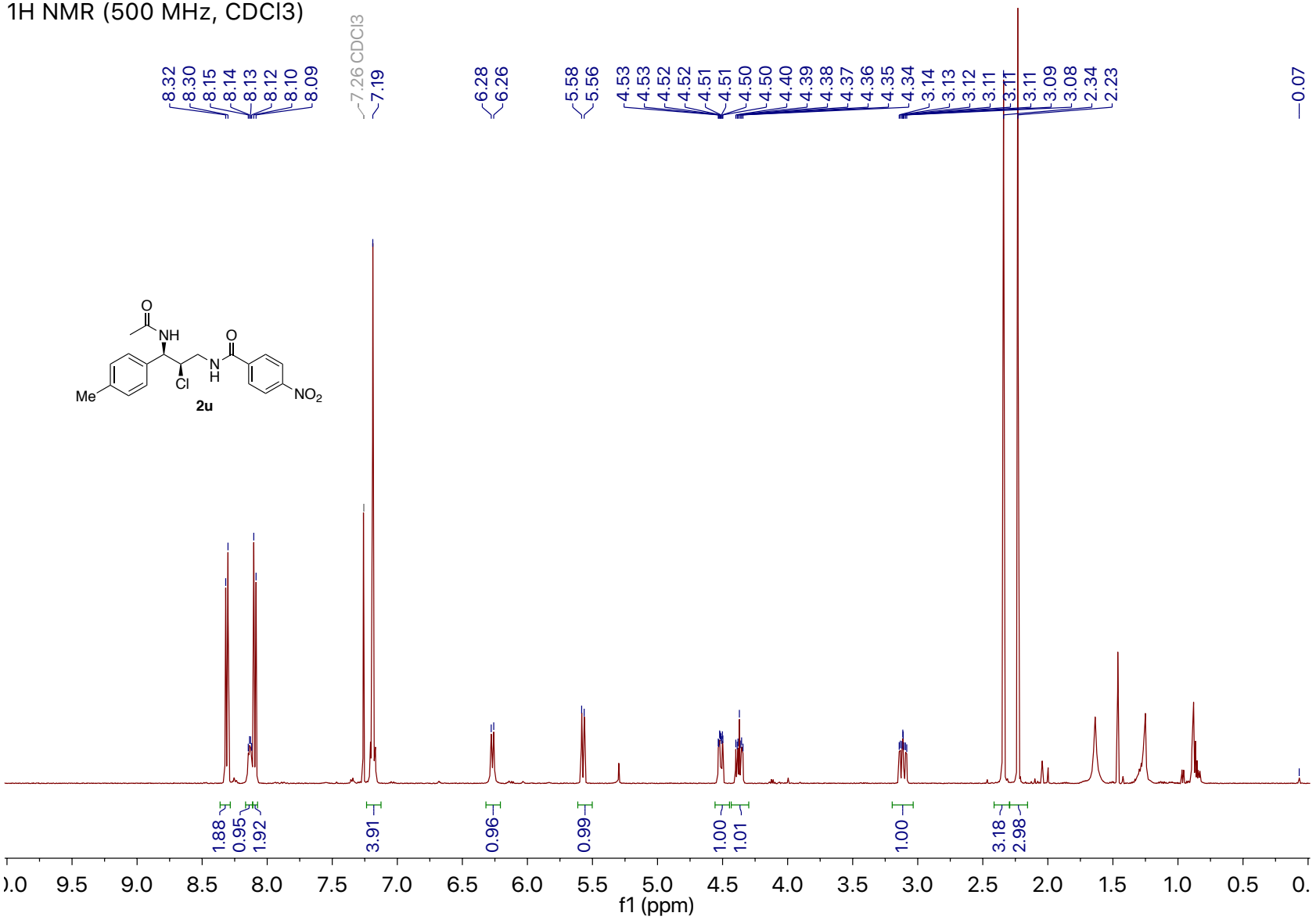
1H NMR (500 MHz, CDCl3)



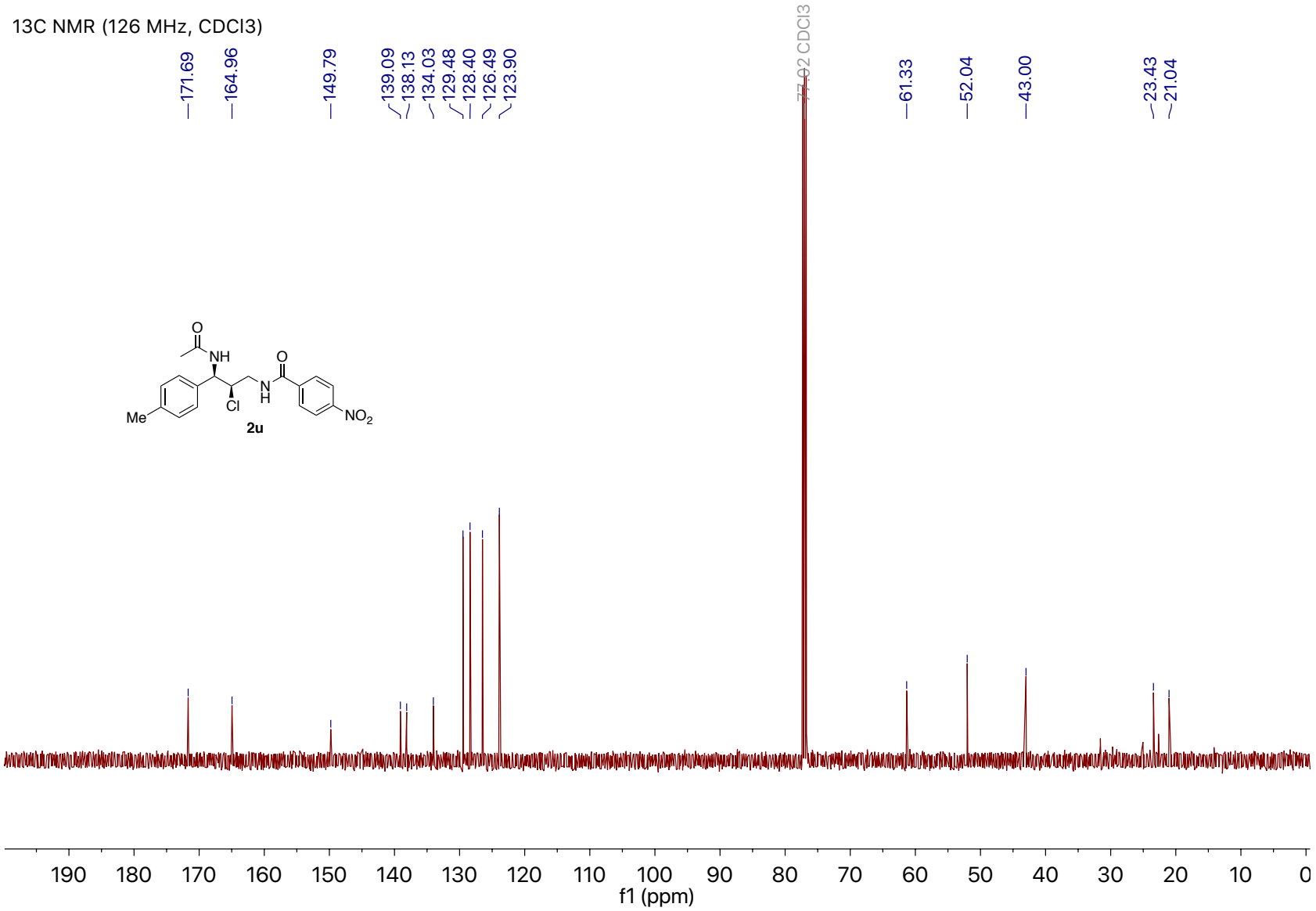
13C NMR (126 MHz, CDCl3)



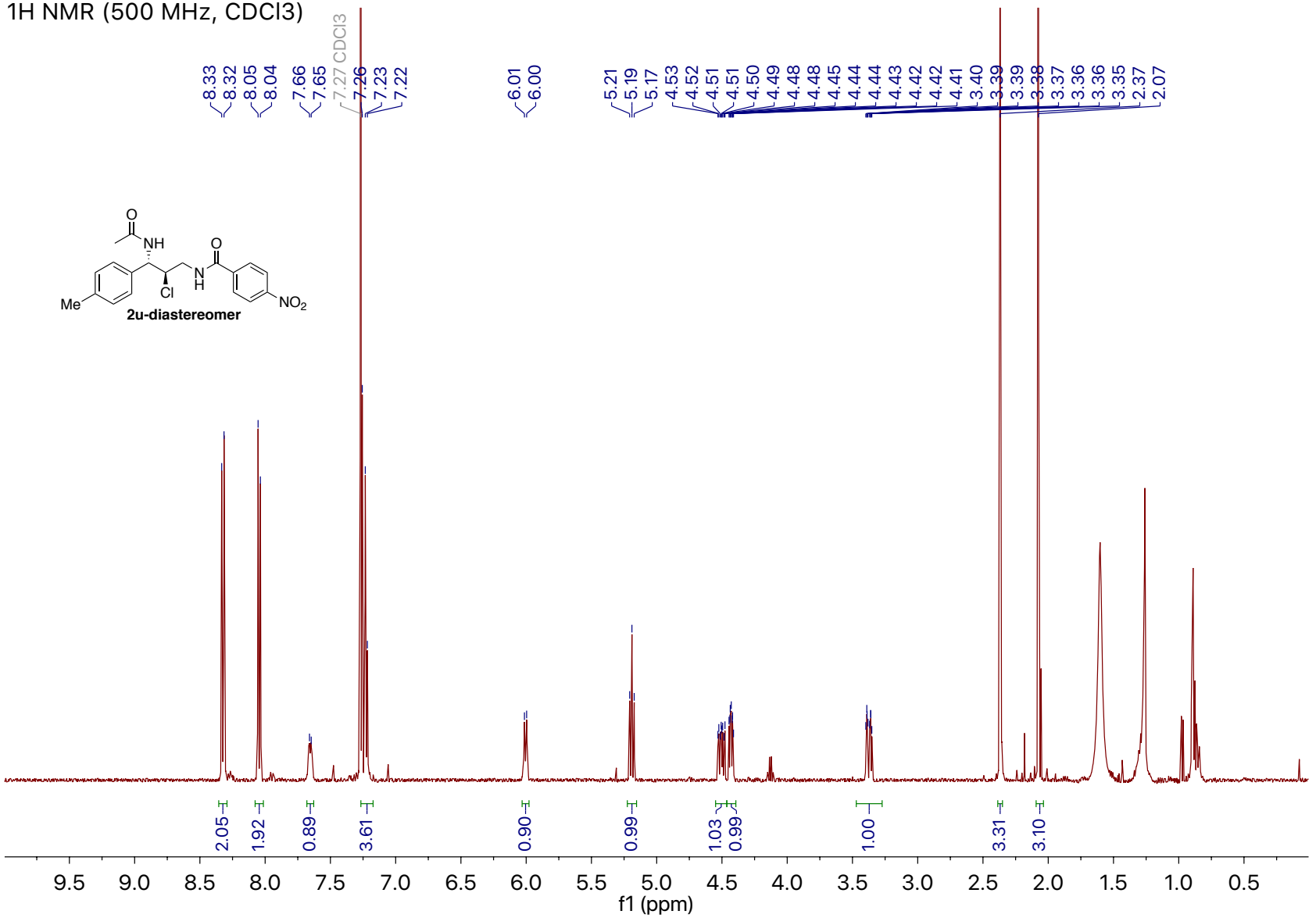
1H NMR (500 MHz, CDCl3)



13C NMR (126 MHz, CDCl3)

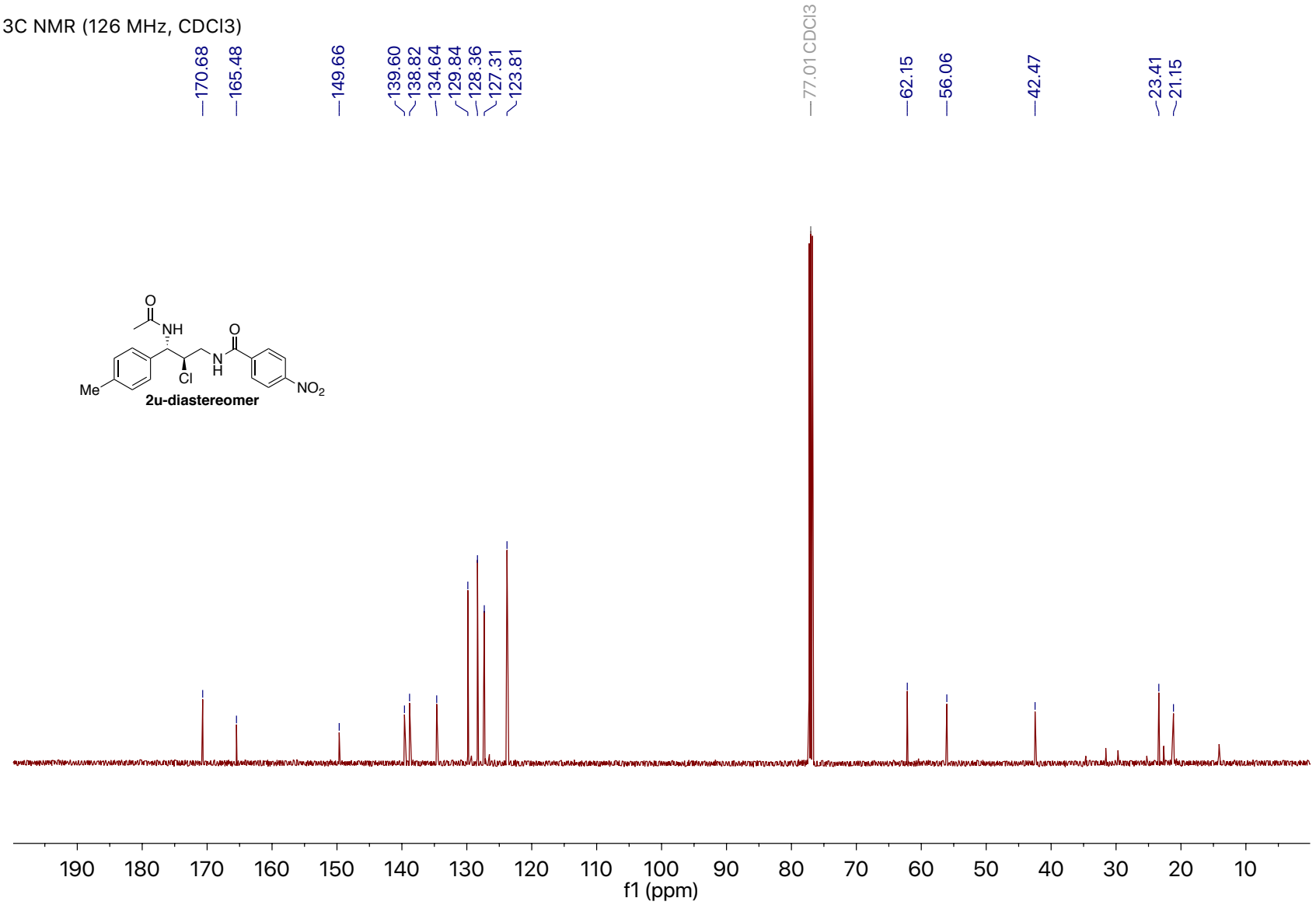


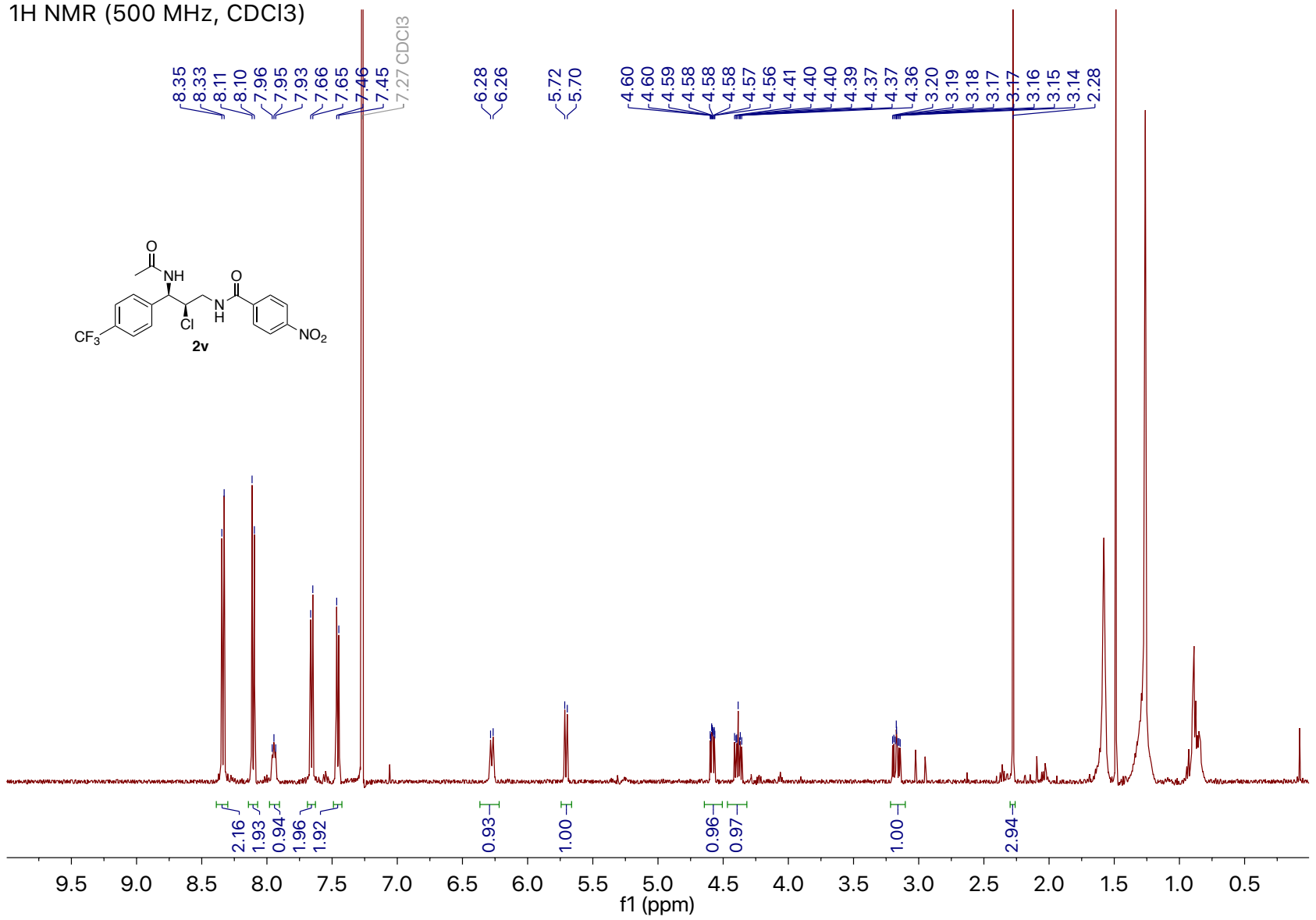
1H NMR (500 MHz, CDCl3)



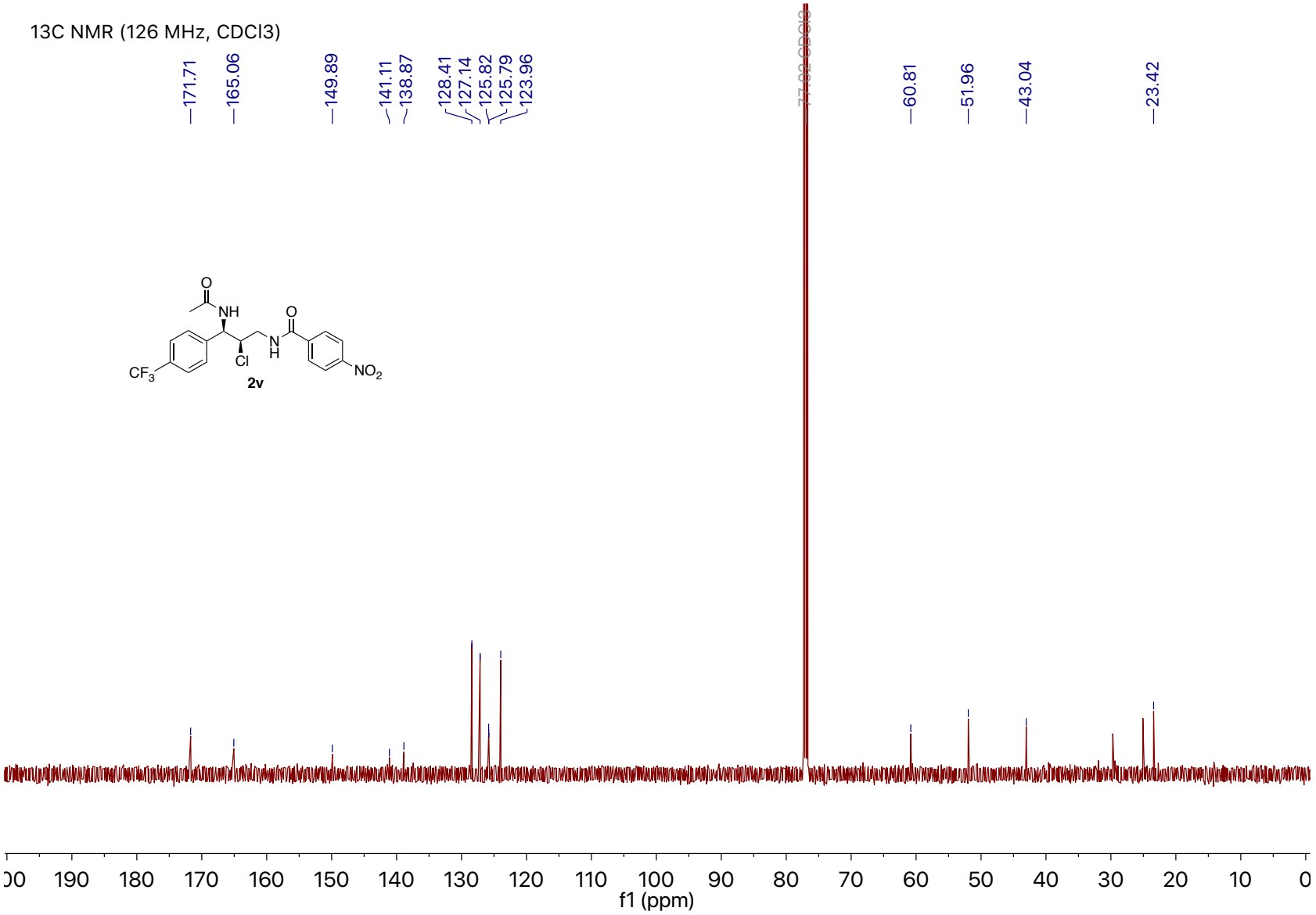
2u-diastereomer

13C NMR (126 MHz, CDCl3)



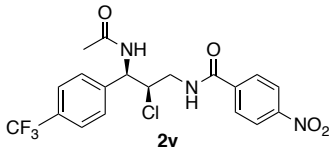

1H NMR (500 MHz, CDCl3)
8.35
8.33
8.11
8.10
7.96
7.95
7.93
7.66
7.65
7.46
7.45
7.27 CDCl3
6.28
6.26
5.72
5.70
4.60
4.60
4.59
4.58
4.58
4.58
4.57
4.56
4.41
4.40
4.40
4.39
4.37
4.37
4.36
3.20
3.19
3.18
3.17
3.17
3.16
3.15
3.14
2.28
O
NH
O
N
H
Cl
CF3
NO2
2v
2.16
1.93
0.94
1.96
1.92
0.93
1.00
0.96
0.97
1.00
2.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

13C NMR (126 MHz, CDCl3)



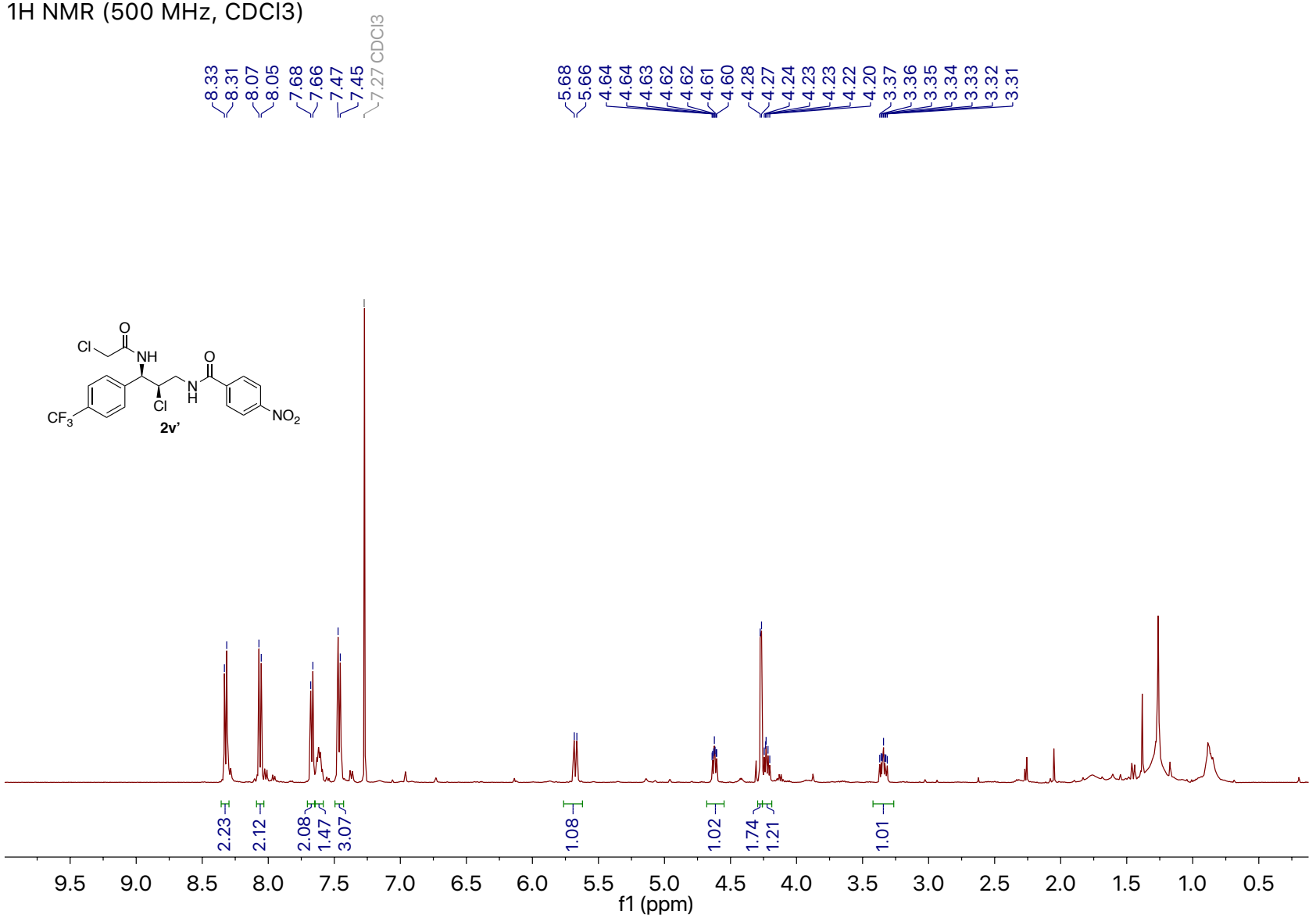
2v

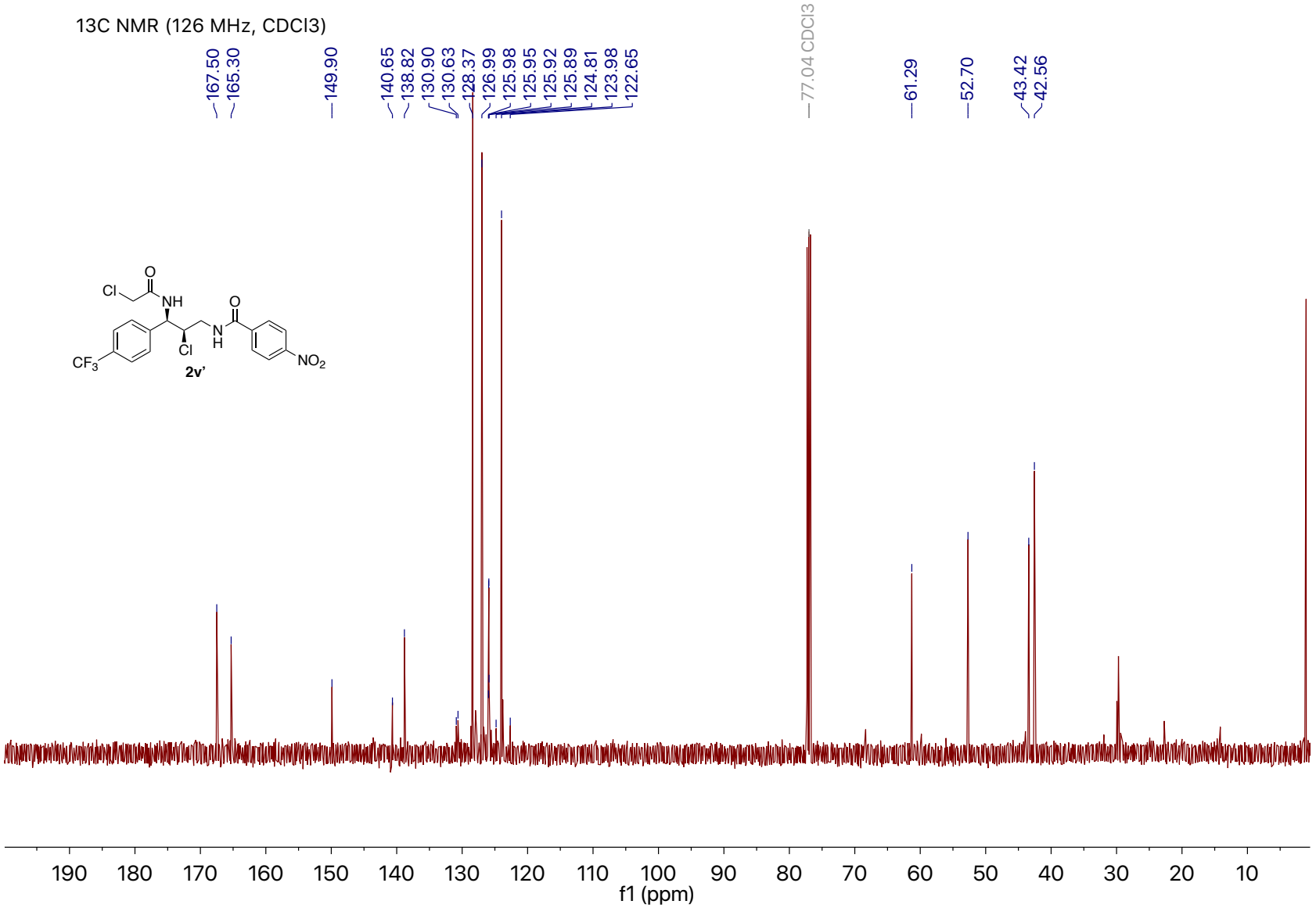
19F NMR (470 MHz, CDCl3)



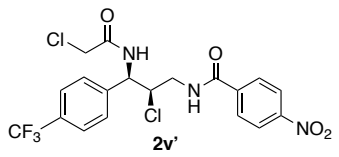
2v

1H NMR (500 MHz, CDCl3)



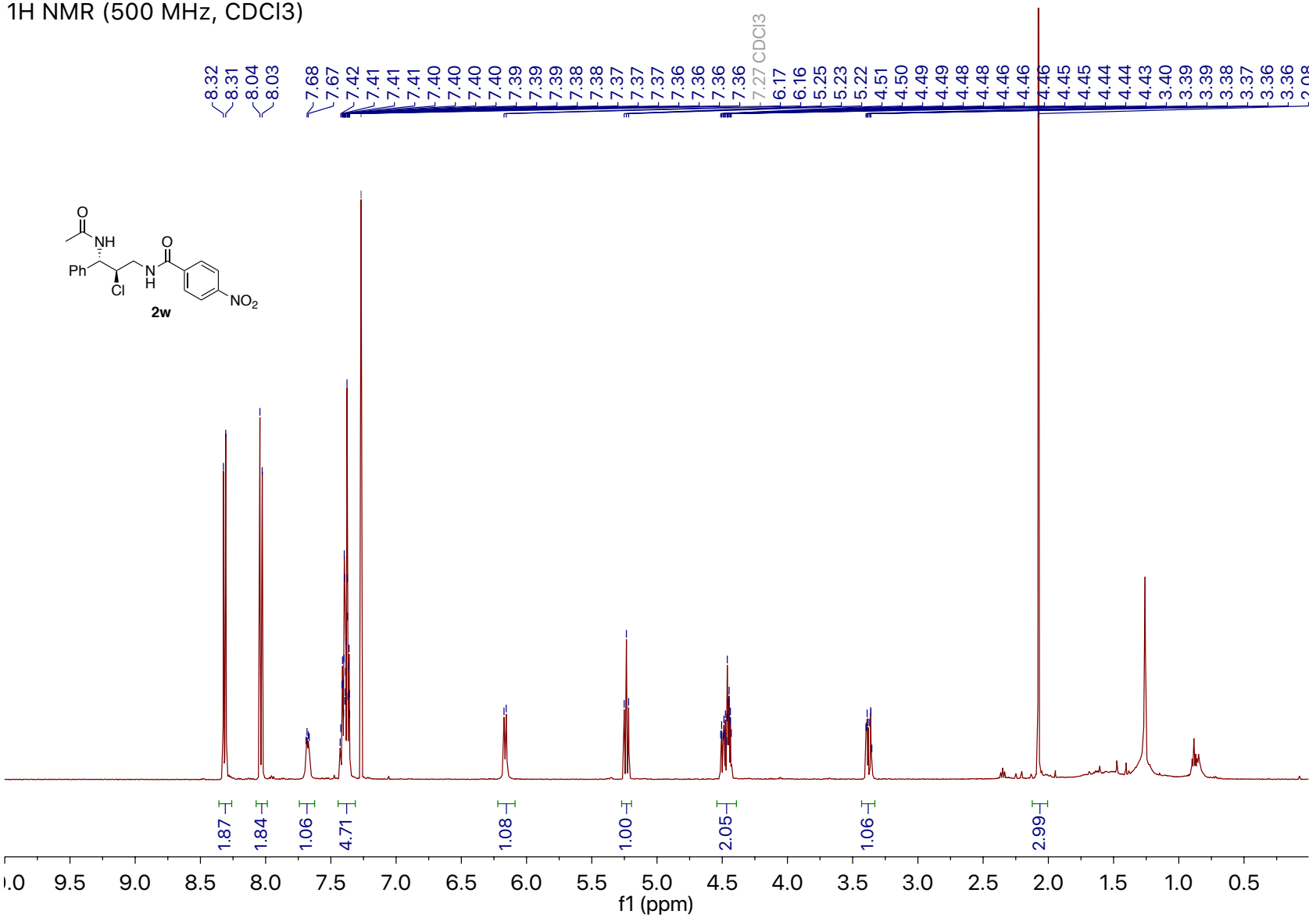

13C NMR (126 MHz, CDCl3)
167.50
165.30
149.90
140.65
138.82
130.90
130.63
128.37
126.99
125.98
125.95
125.92
125.89
124.81
123.98
122.65
77.04 CDCl3
61.29
52.70
43.42
42.56
Cl
O
NH
O
N
H
Cl
CF3
NO2
2v'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

19F NMR (470 MHz, CDCl3)

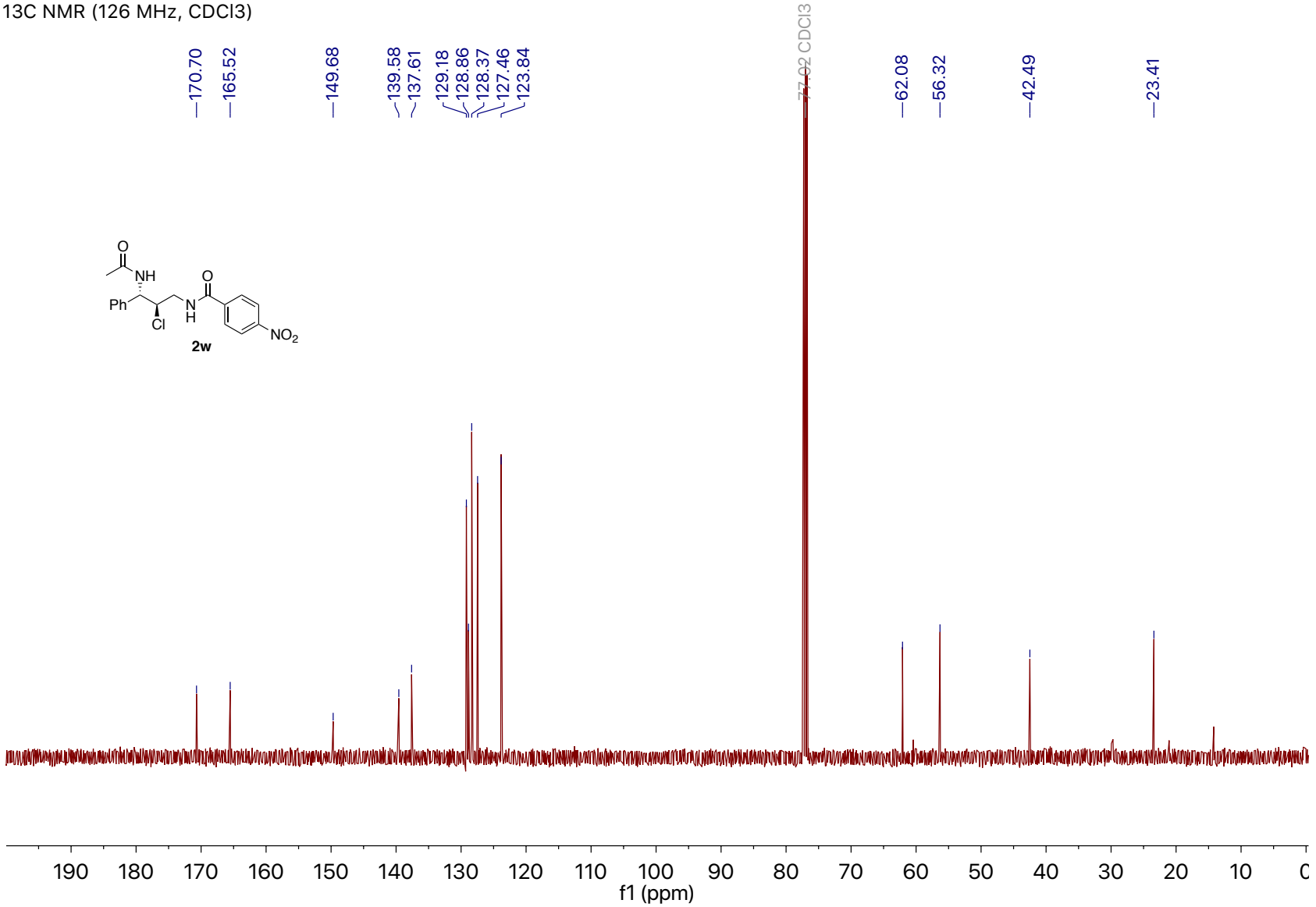


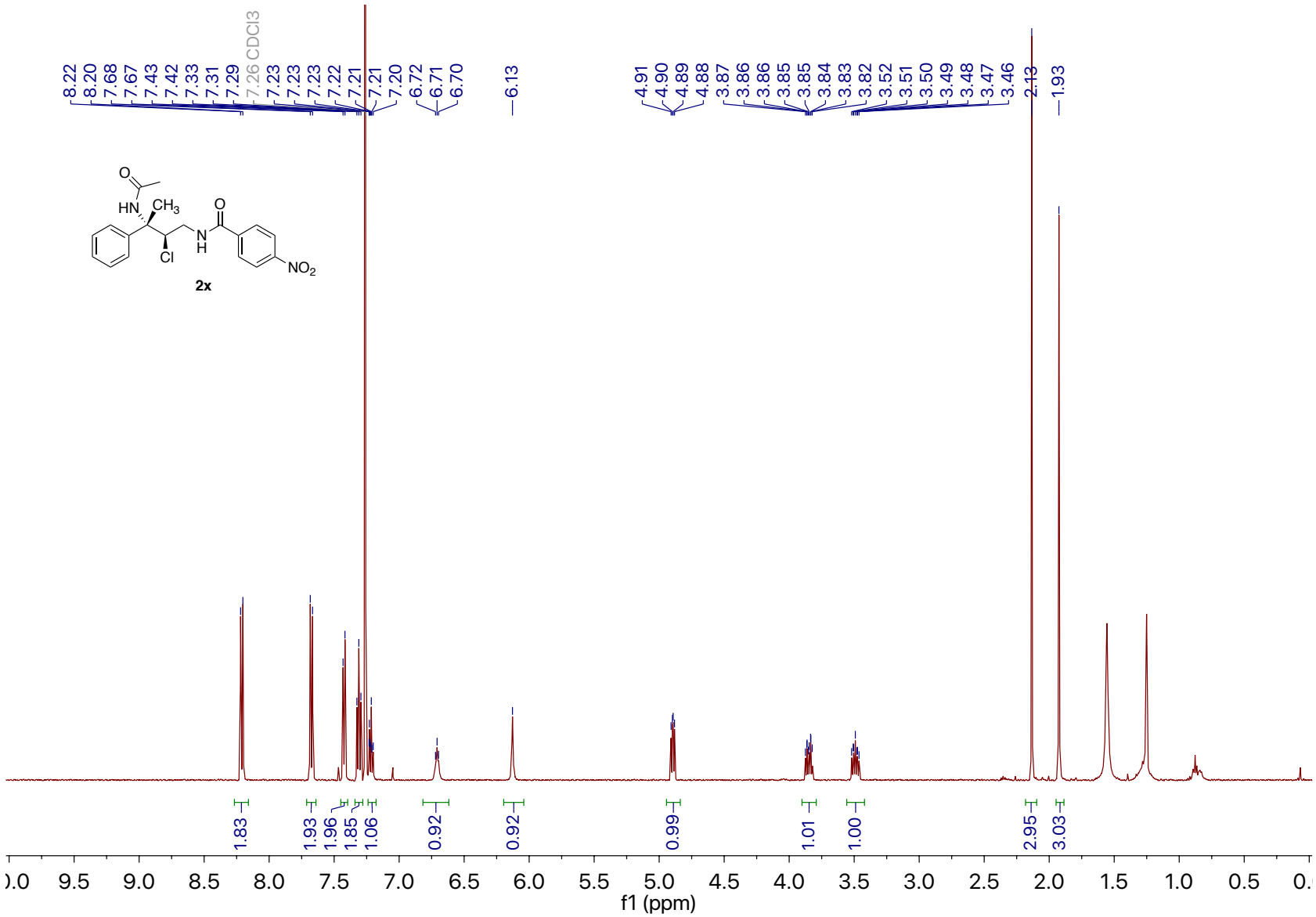
2v'

1H NMR (500 MHz, CDCl3)

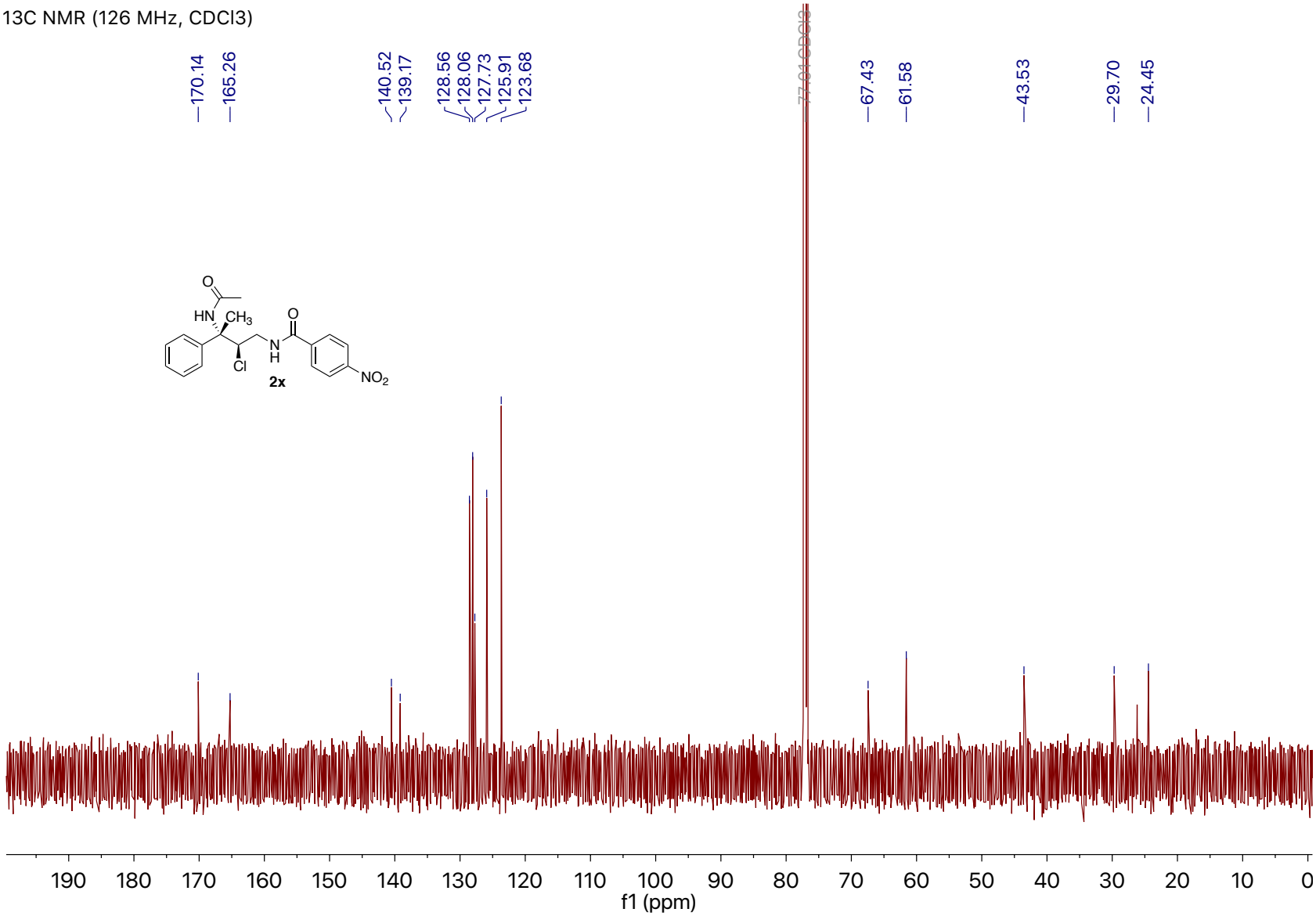


13C NMR (126 MHz, CDCl3)

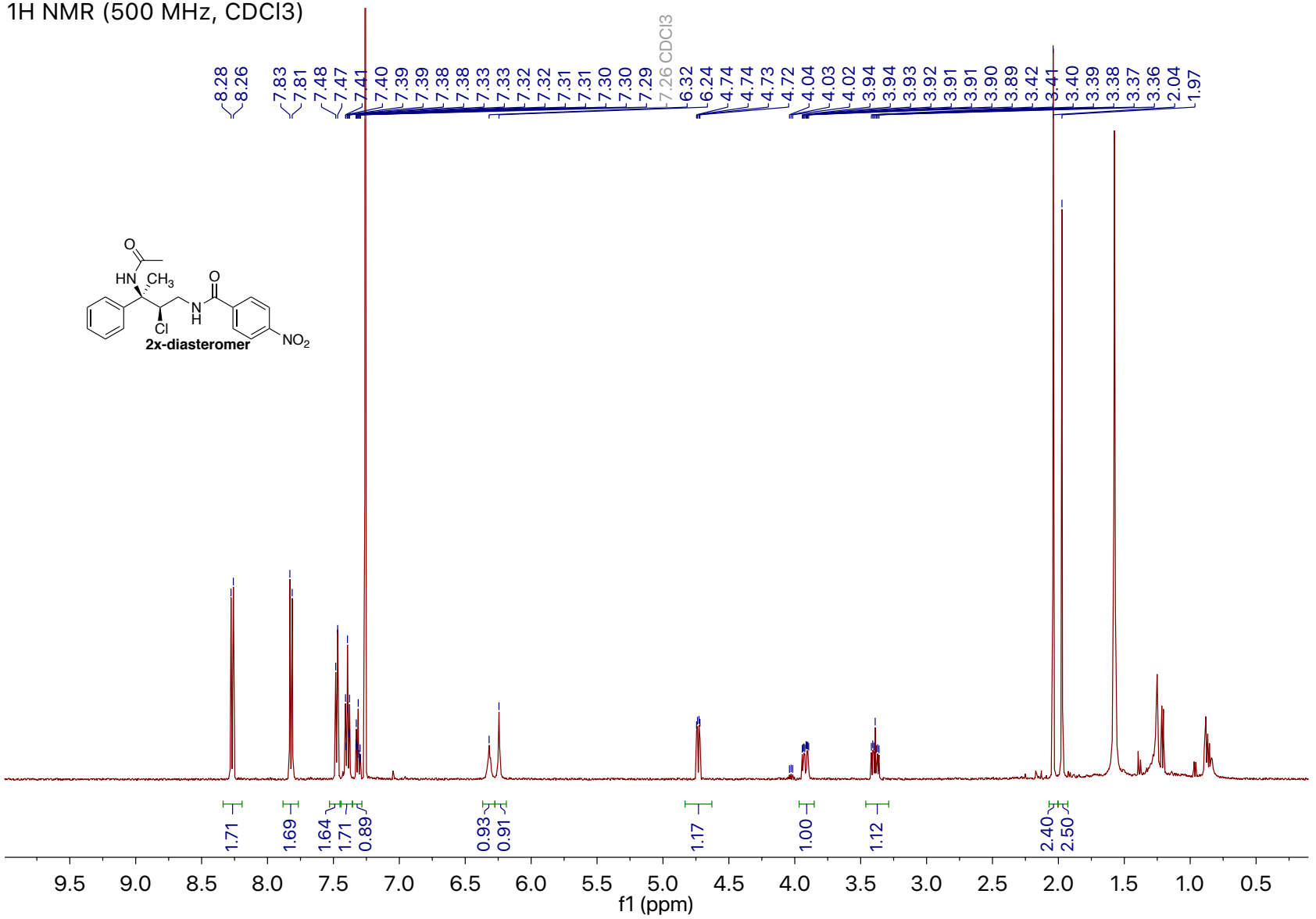



8.22
8.20
7.68
7.67
7.43
7.42
7.33
7.31
7.29
7.26 CDCl3
7.23
7.23
7.23
7.22
7.21
7.21
7.20
6.72
6.71
6.70
6.13
4.91
4.90
4.89
4.88
3.87
3.86
3.86
3.85
3.85
3.84
3.83
3.82
3.52
3.51
3.50
3.49
3.48
3.47
3.46
2.13
1.93
O
HN
CH3
O
N
H
Cl
NO2
2x
1.83
1.93
1.96
1.85
1.06
0.92
0.92
0.99
1.01
1.00
2.95
3.03
f1 (ppm)

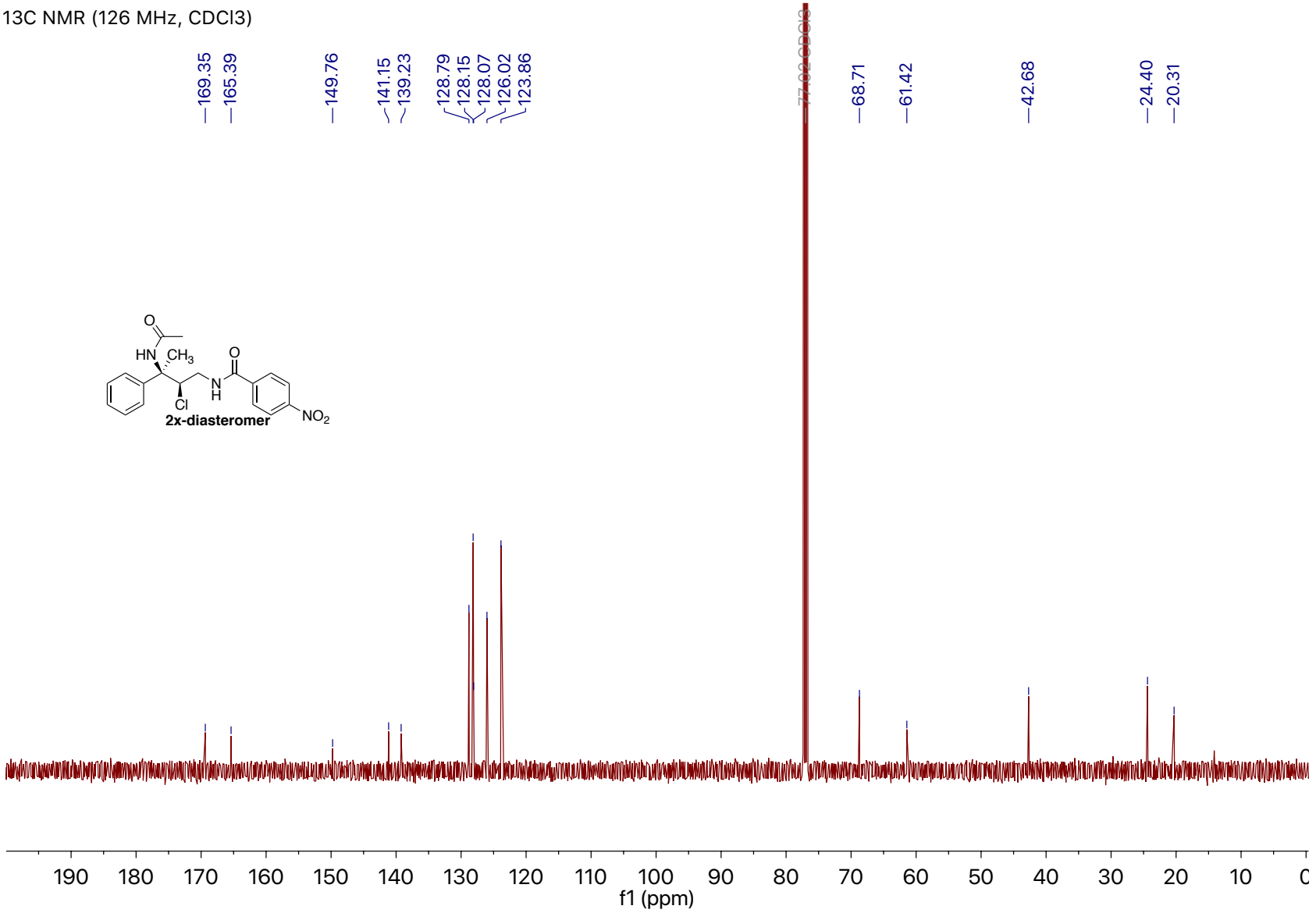
13C NMR (126 MHz, CDCl3)



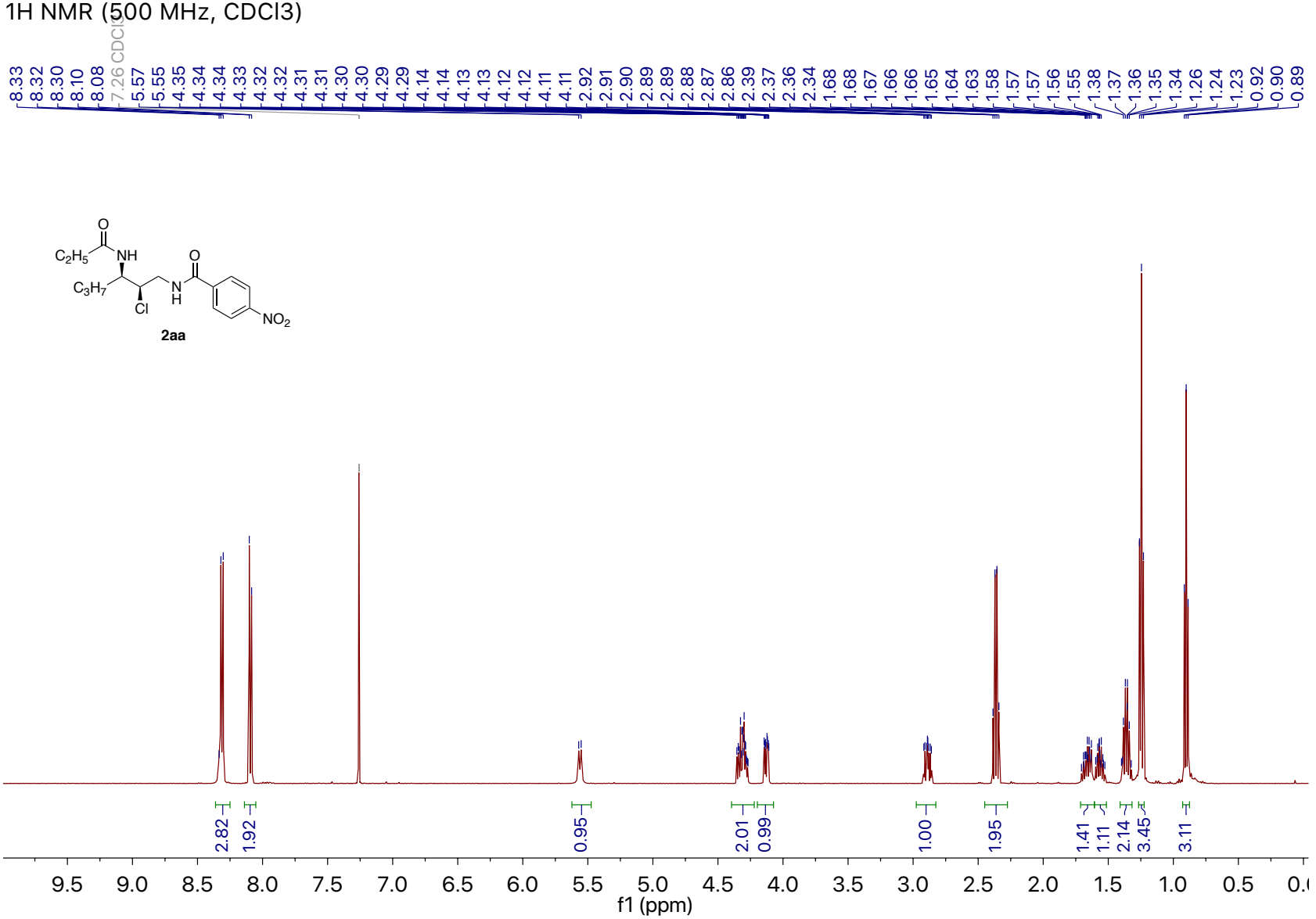
1H NMR (500 MHz, CDCl3)



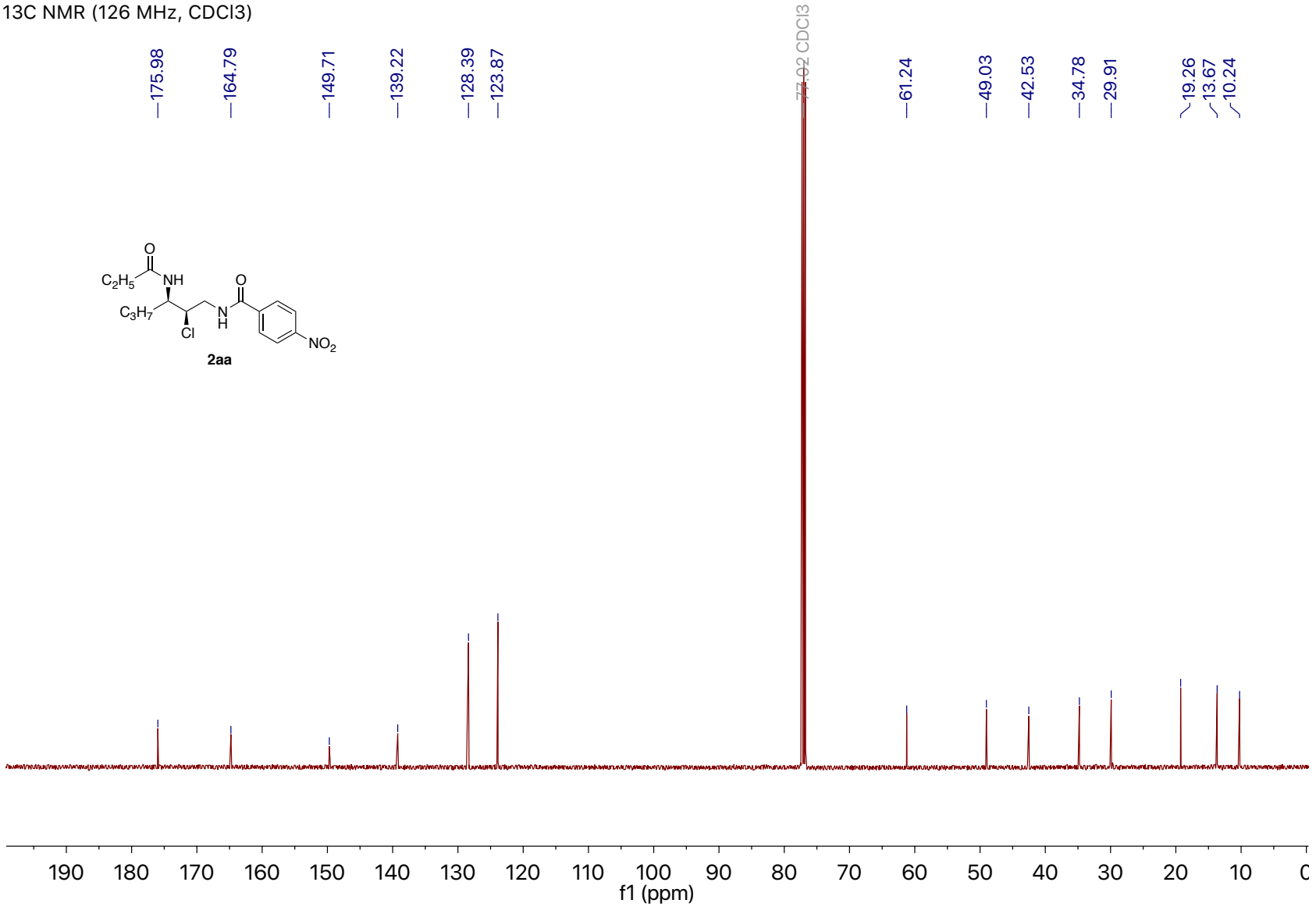
13C NMR (126 MHz, CDCl3)



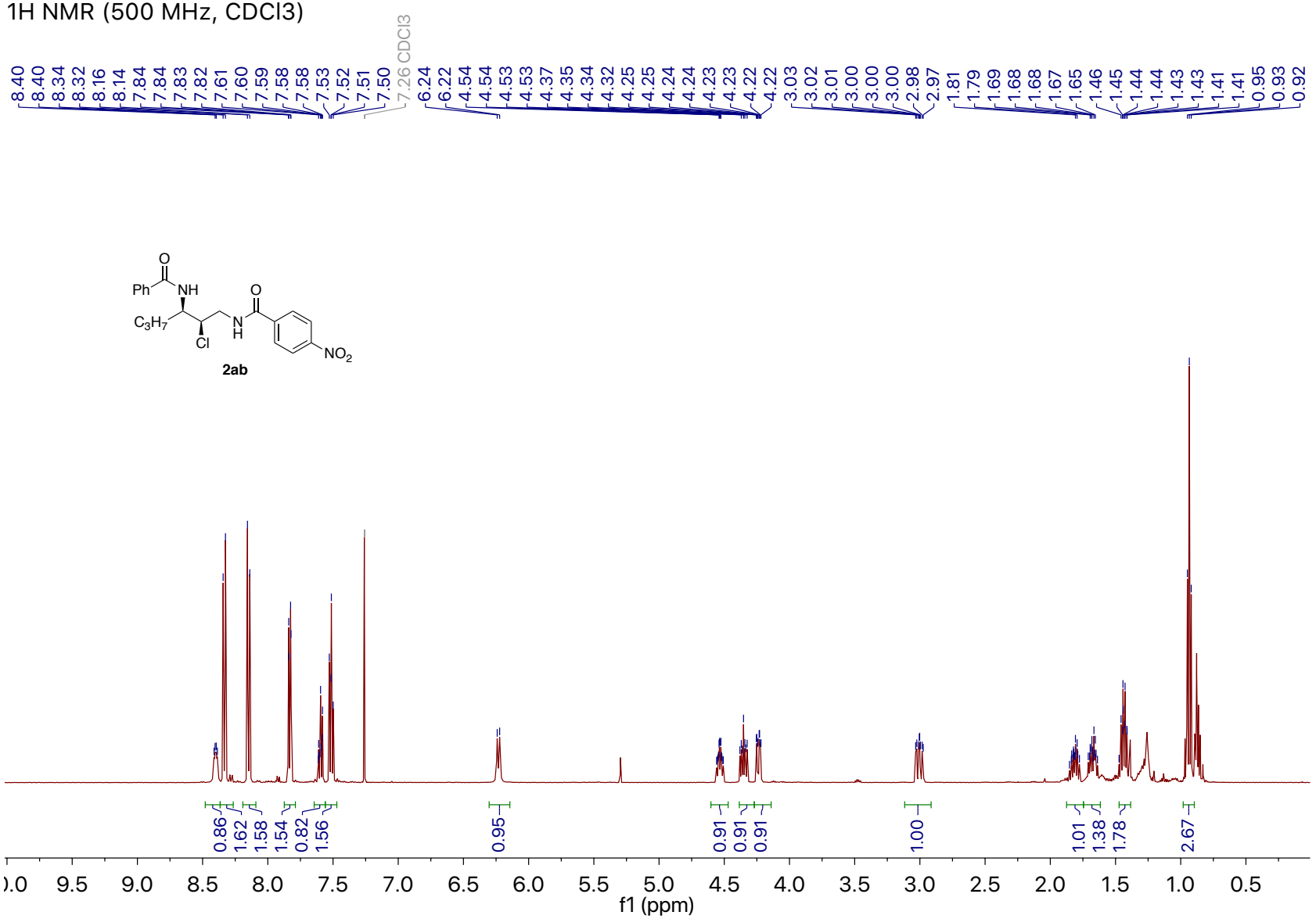
1H NMR (500 MHz, CDCl3)



13C NMR (126 MHz, CDCl3)

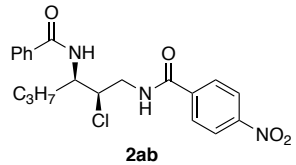


1H NMR (500 MHz, CDCl3)

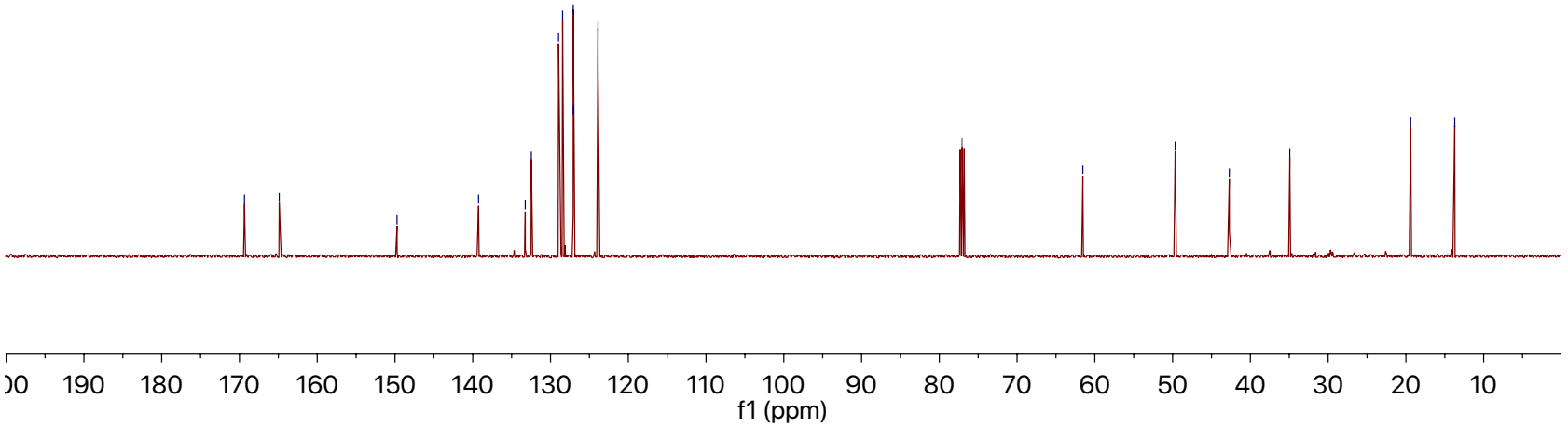


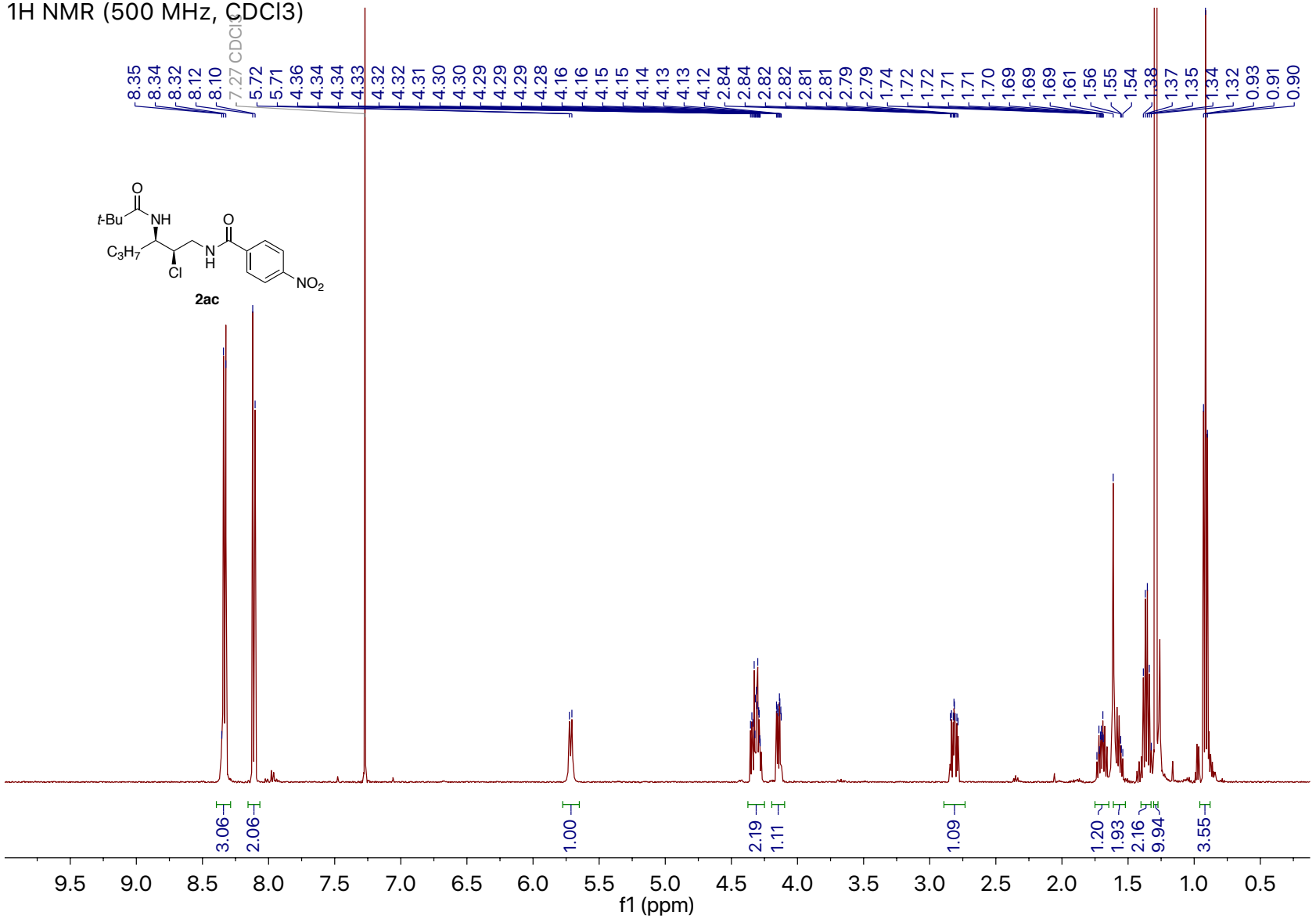
13C NMR (126 MHz, CDCl3)

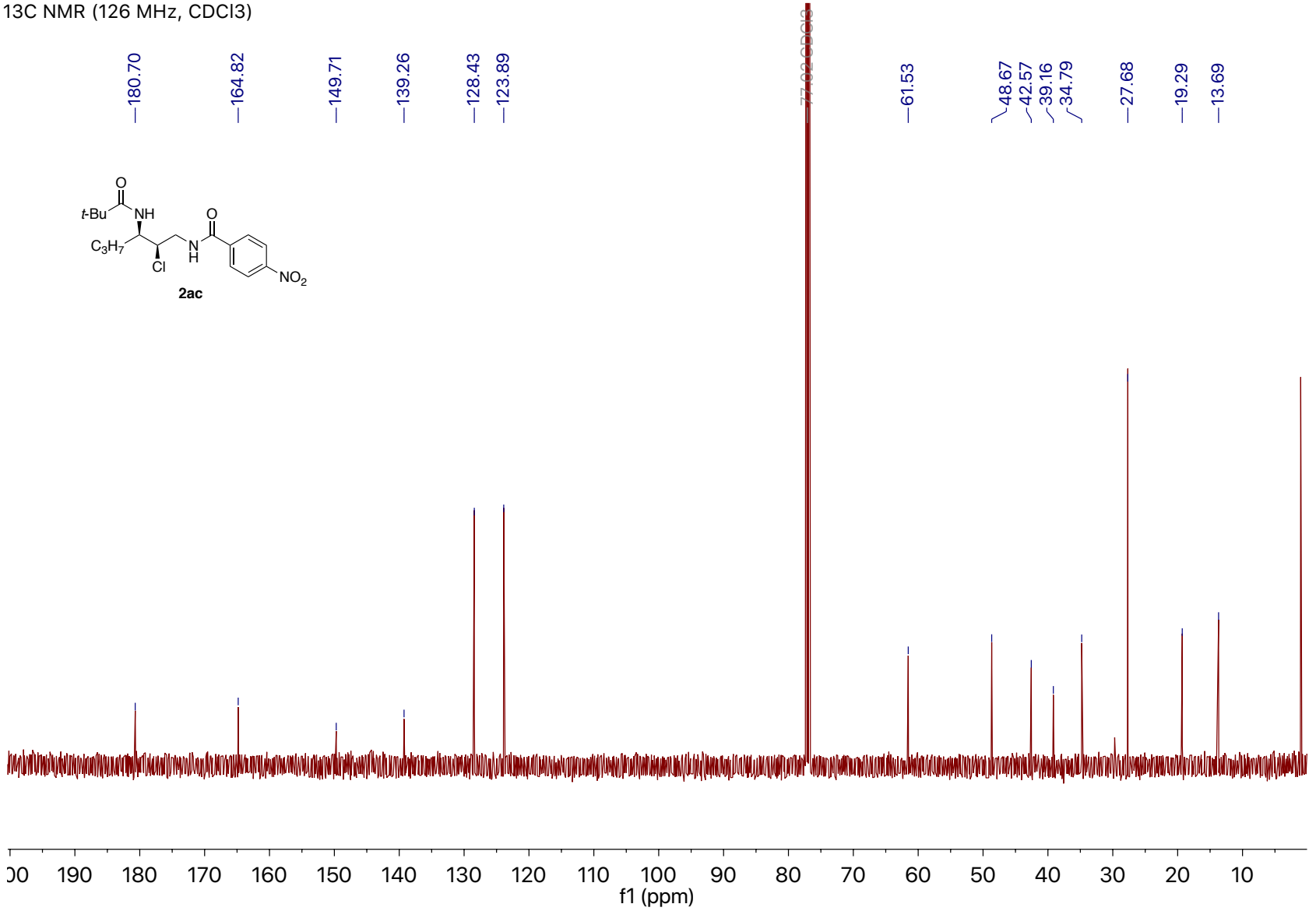
169.36
164.88
149.74
139.26
133.25
132.47
128.97
128.45
127.08
127.08
123.89
77.06 CDCl3
61.54
49.68
42.71
34.93
19.38
13.72

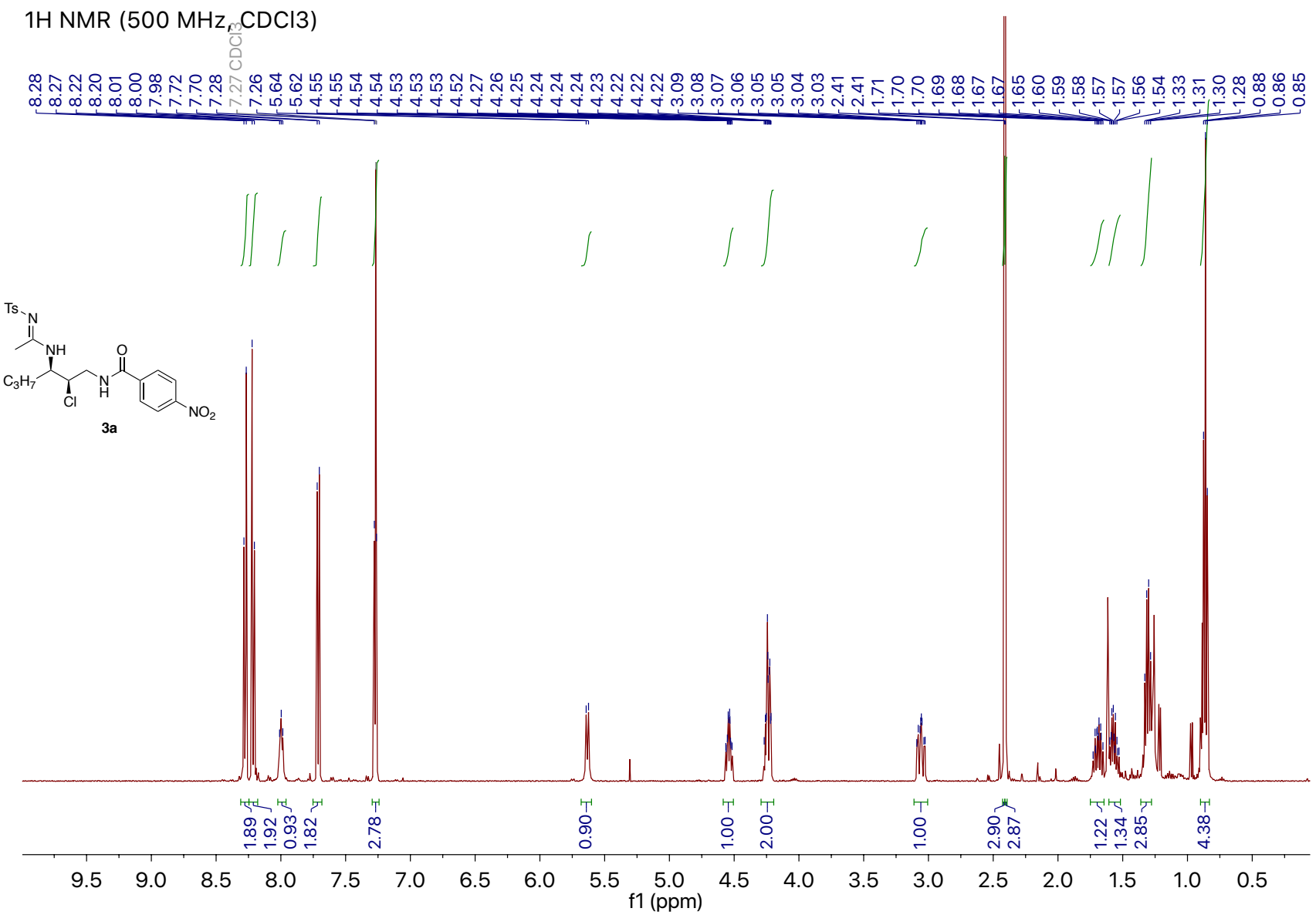


2ab

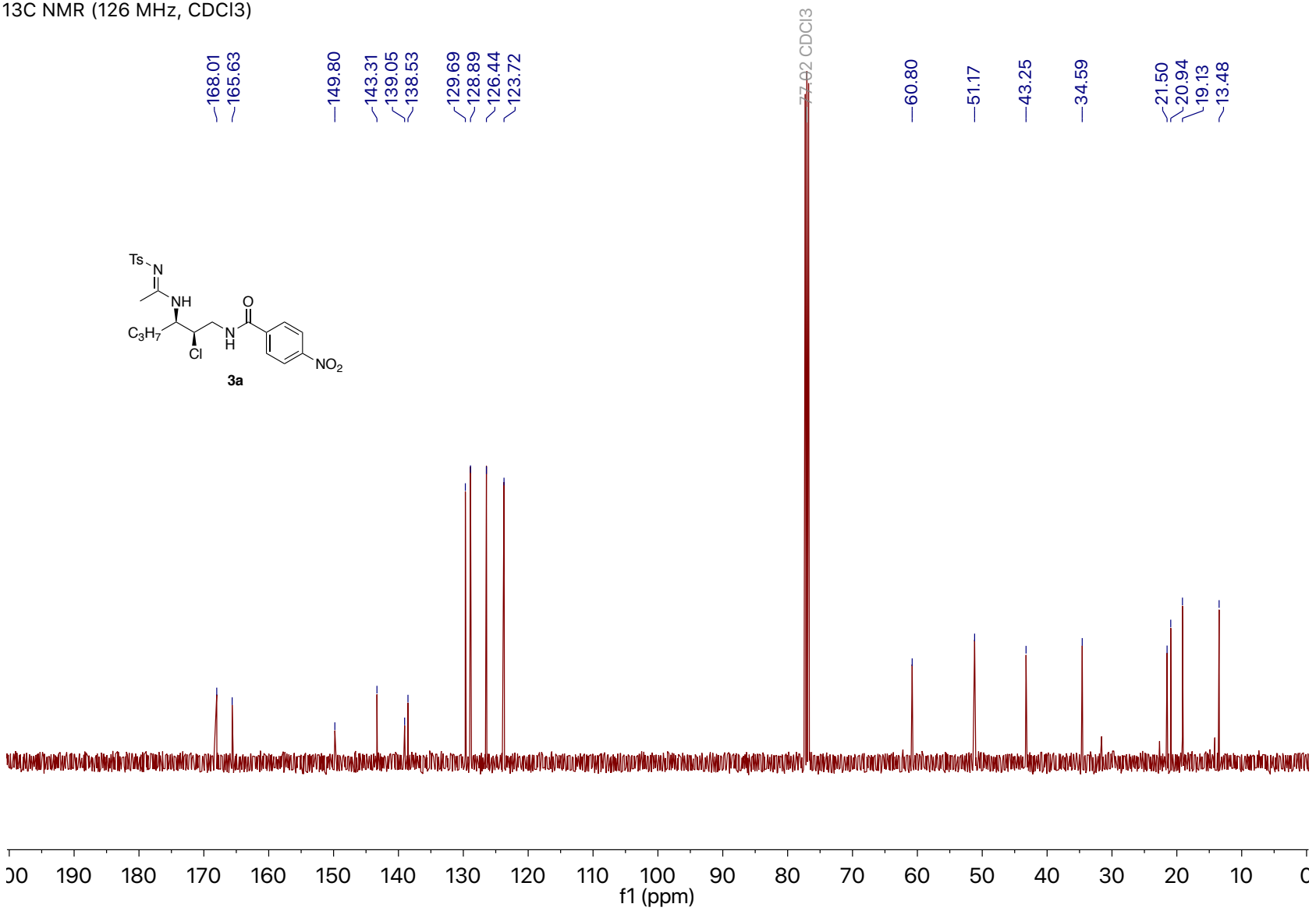



1H NMR (500 MHz, CDCl3)
7.27 CDCl3
8.35 8.34 8.32 8.12 8.10 5.72 5.71 4.36 4.34 4.34 4.33 4.32 4.32 4.31 4.30 4.30 4.29 4.29 4.29 4.28 4.16 4.16 4.15 4.15 4.14 4.13 4.13 4.12 2.84 2.84 2.82 2.82 2.81 2.81 2.79 2.79 1.74 1.72 1.72 1.71 1.71 1.70 1.69 1.69 1.69 1.61 1.56 1.55 1.54 1.38 1.37 1.35 1.34 1.32 0.93 0.91 0.90
t-Bu
NH
O
C3H7
Cl
N
H
O
NO2
2ac
3.06
2.06
1.00
2.19
1.11
1.09
1.20
1.93
2.16
9.94
3.55
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

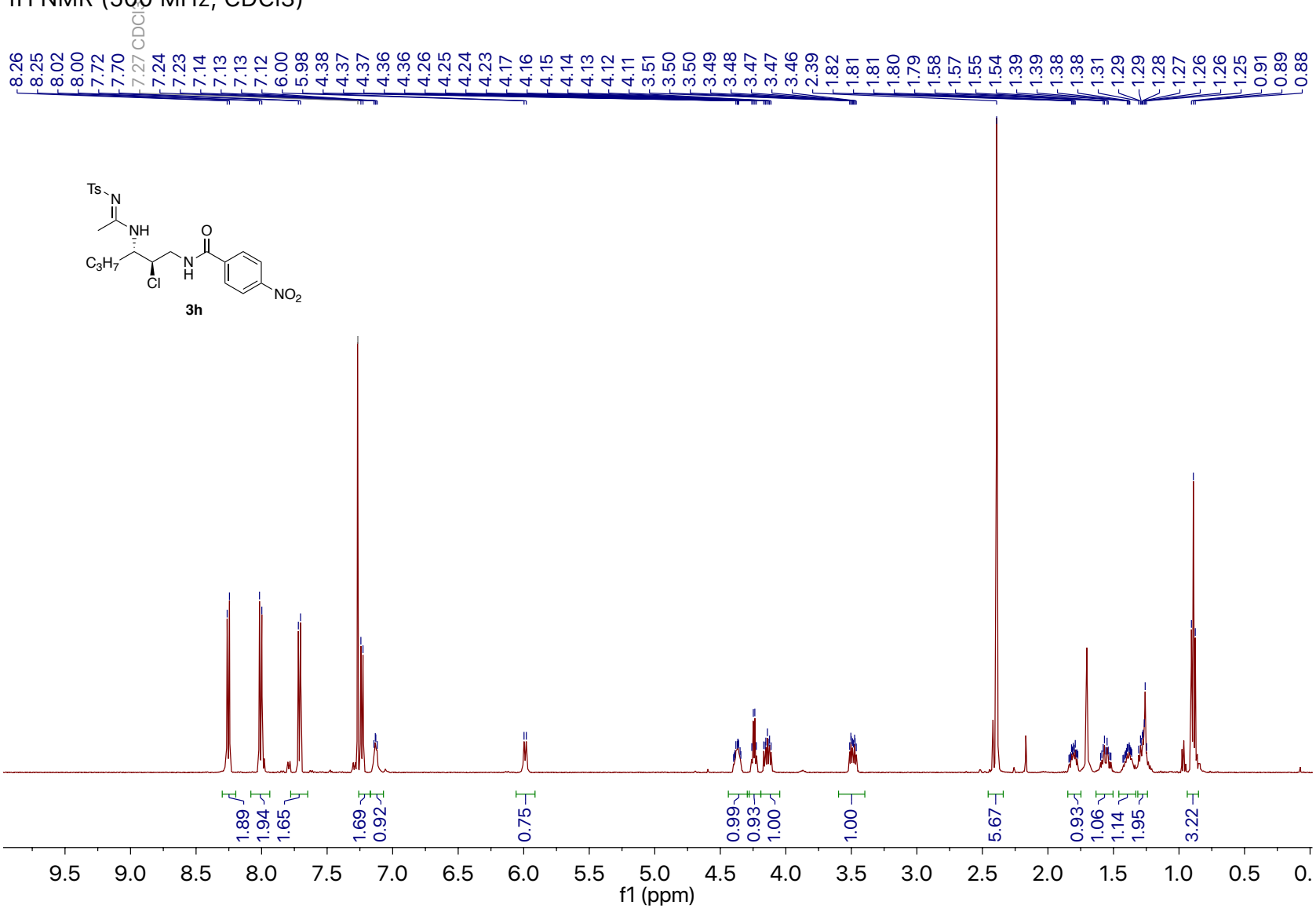

13C NMR (126 MHz, CDCl3)
180.70
164.82
149.71
139.26
128.43
123.89
77.02 CDCl3
61.53
48.67
42.57
39.16
34.79
27.68
19.29
13.69
t-Bu
NH
O
C3H7
Cl
N
H
O
NO2
2ac
f1 (ppm)


1H NMR (500 MHz, CDCl3)
7.27 CDCl3
f1 (ppm)
3a

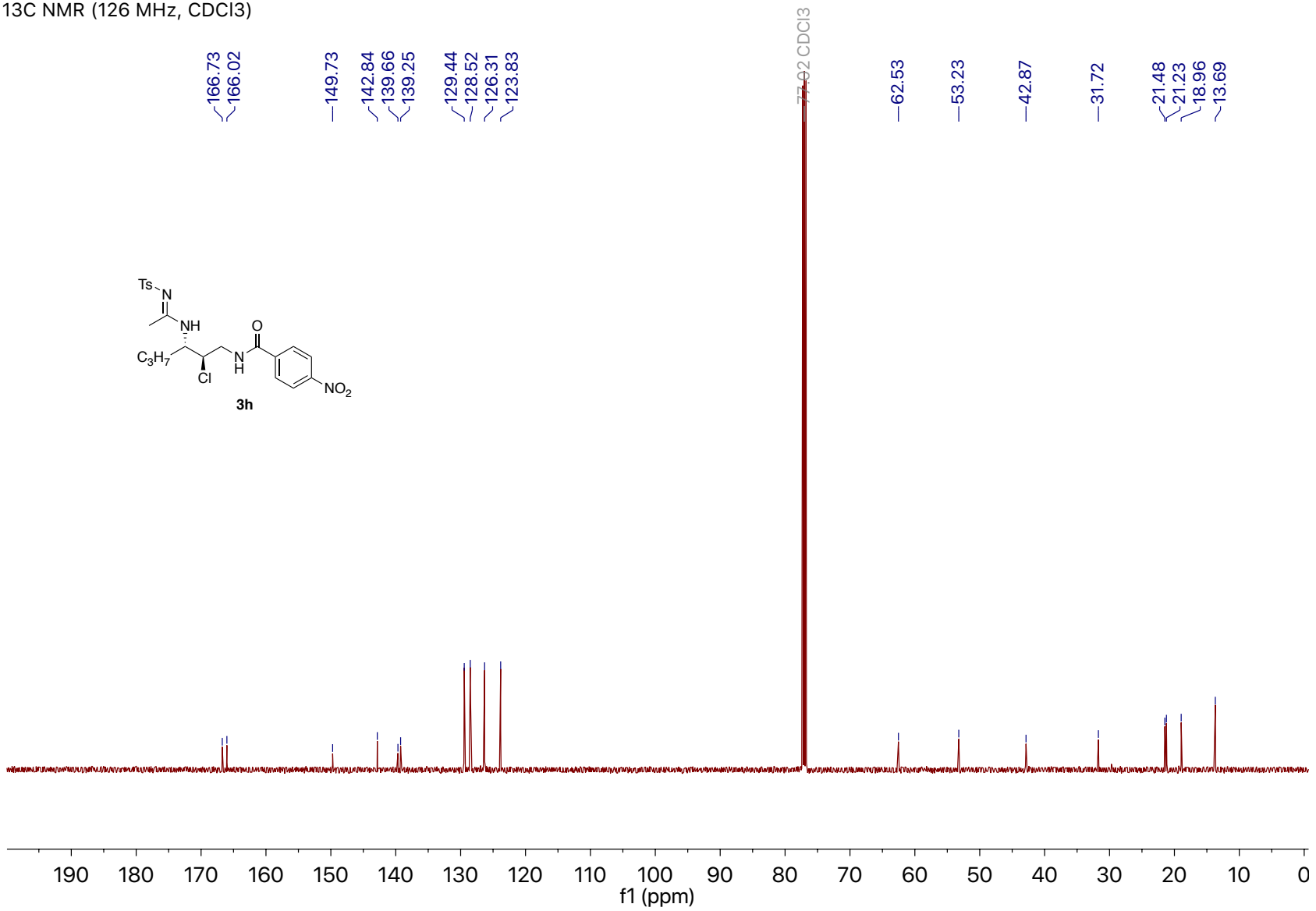
13C NMR (126 MHz, CDCl3)



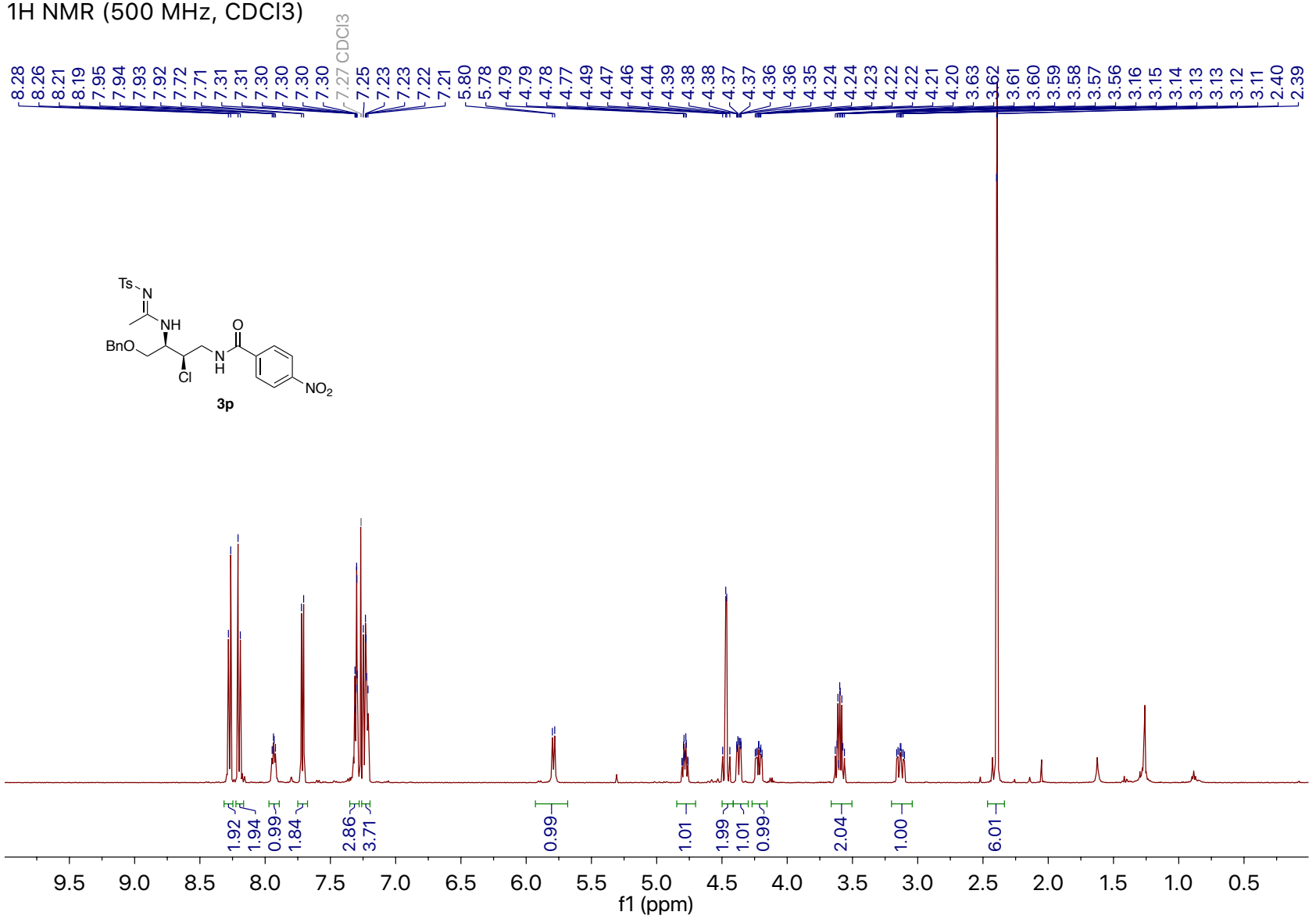
1H NMR (500 MHz, CDCl3)



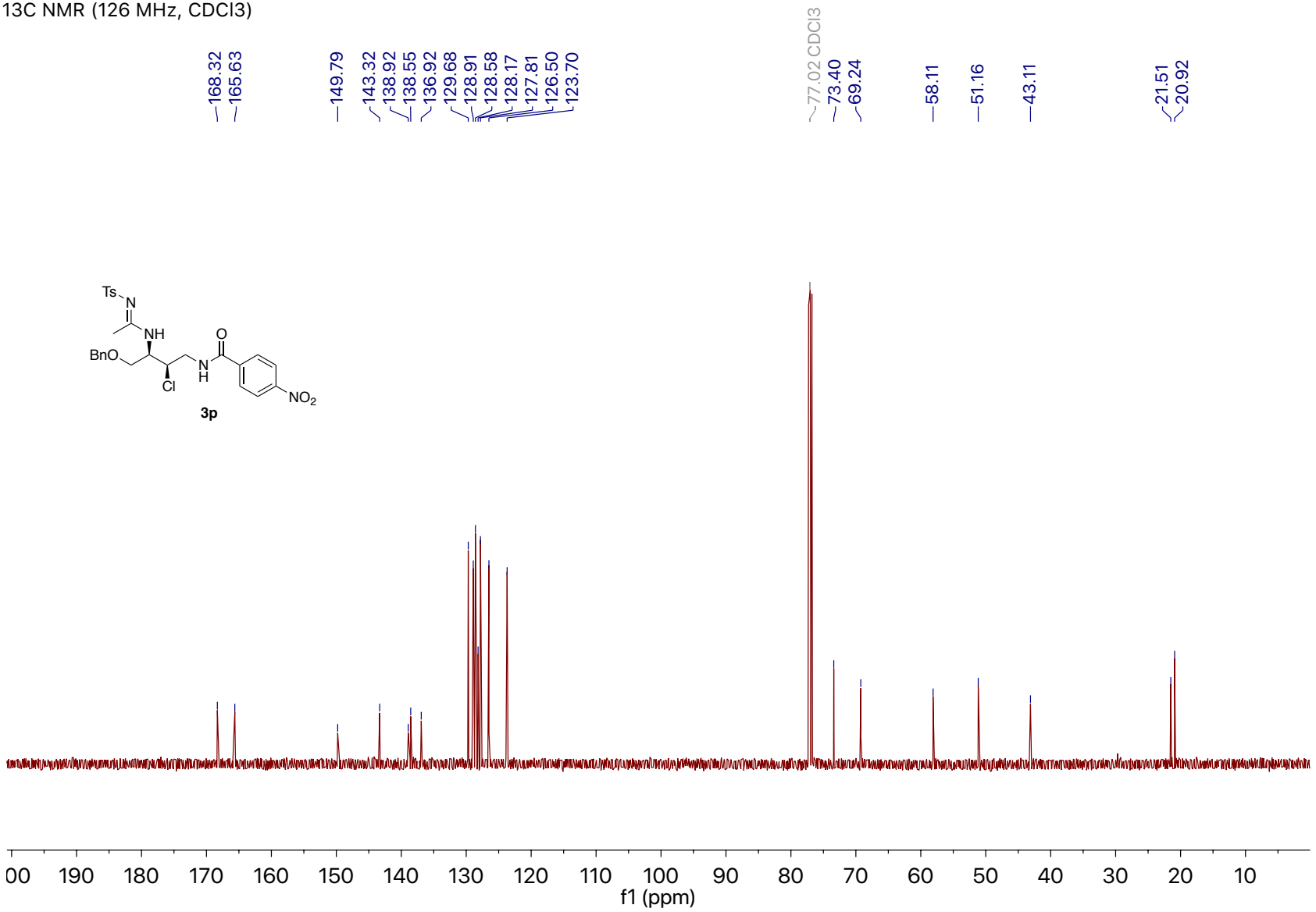
13C NMR (126 MHz, CDCl3)



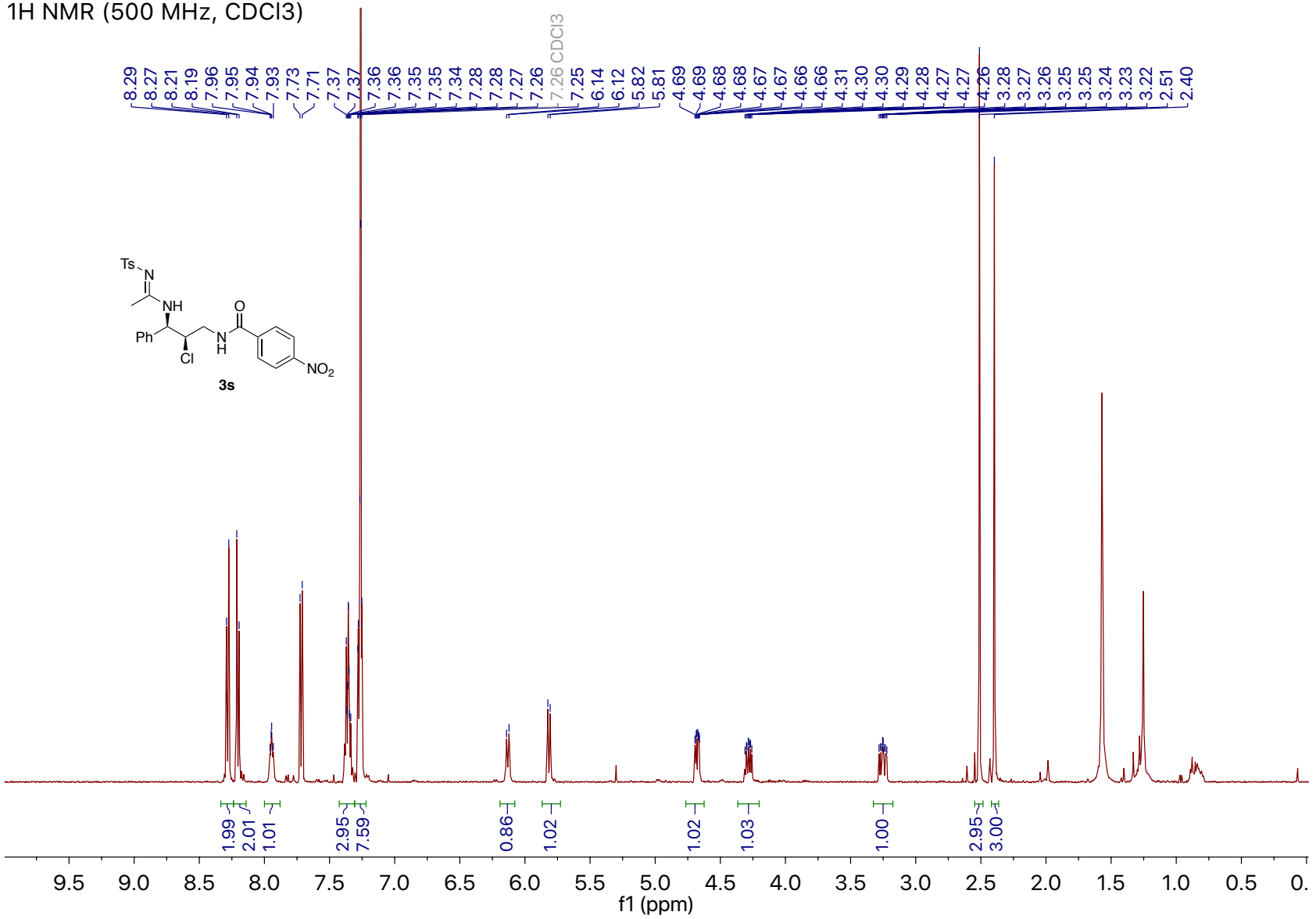
1H NMR (500 MHz, CDCl3)



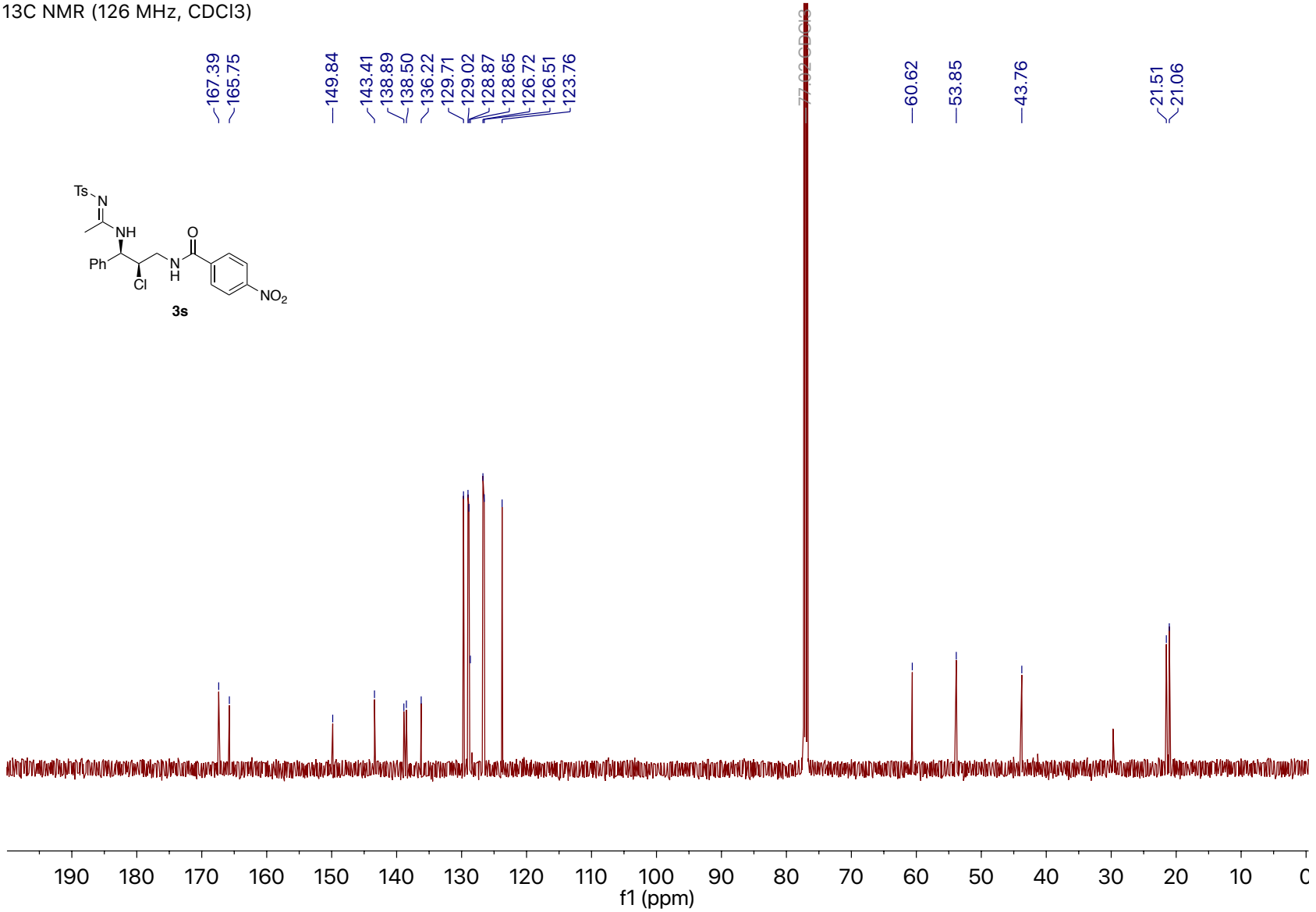
13C NMR (126 MHz, CDCl3)

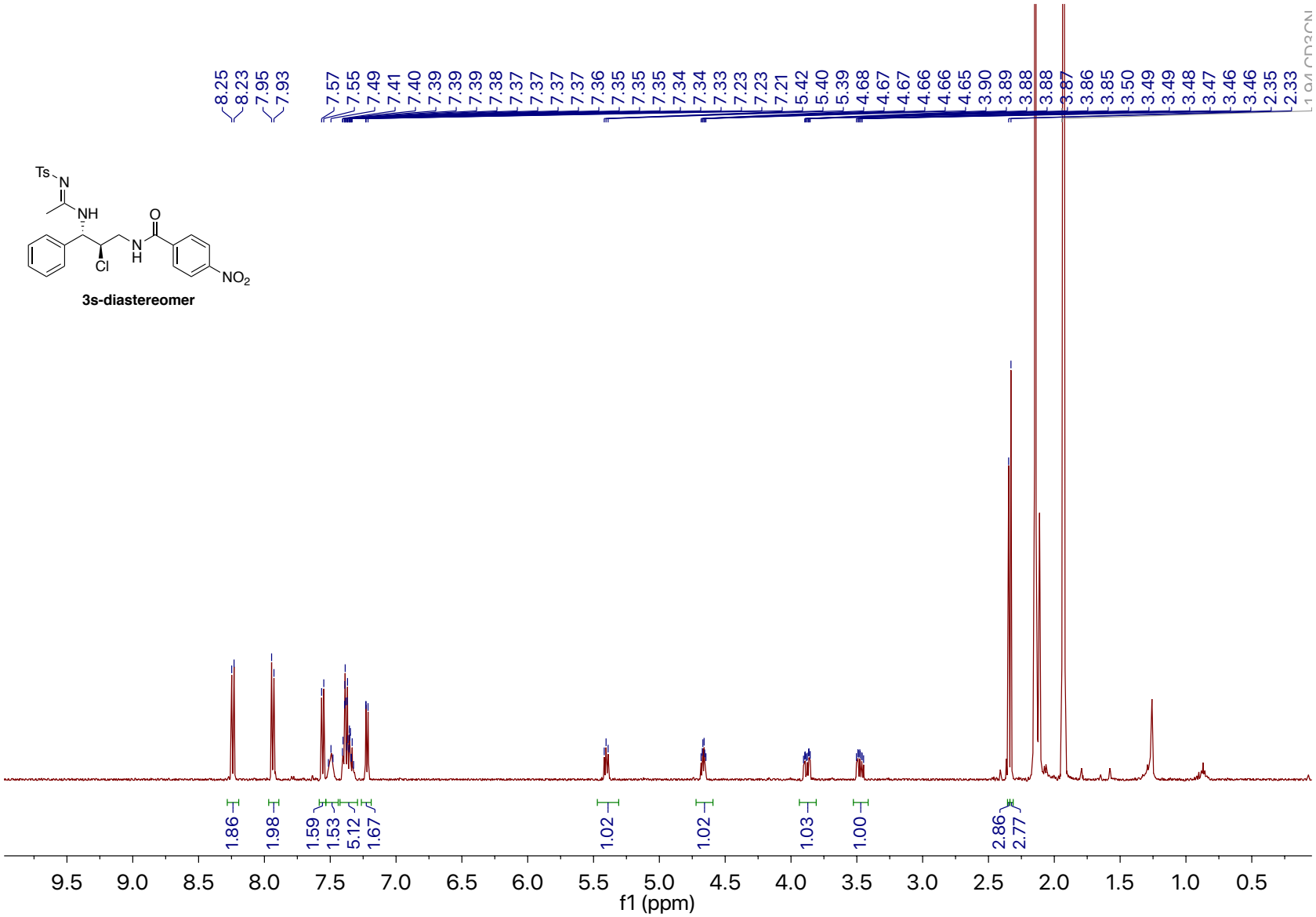


1H NMR (500 MHz, CDCl3)

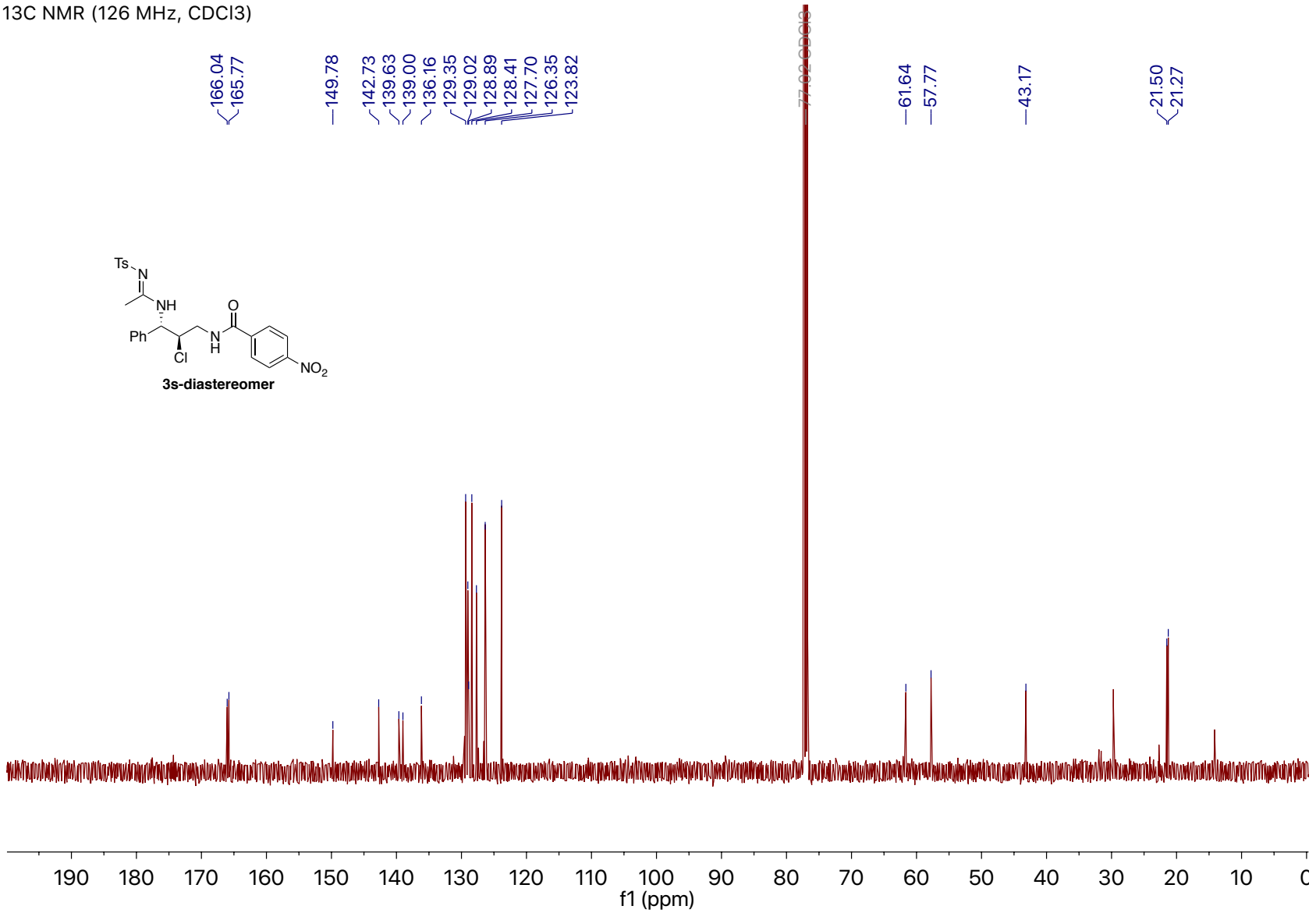


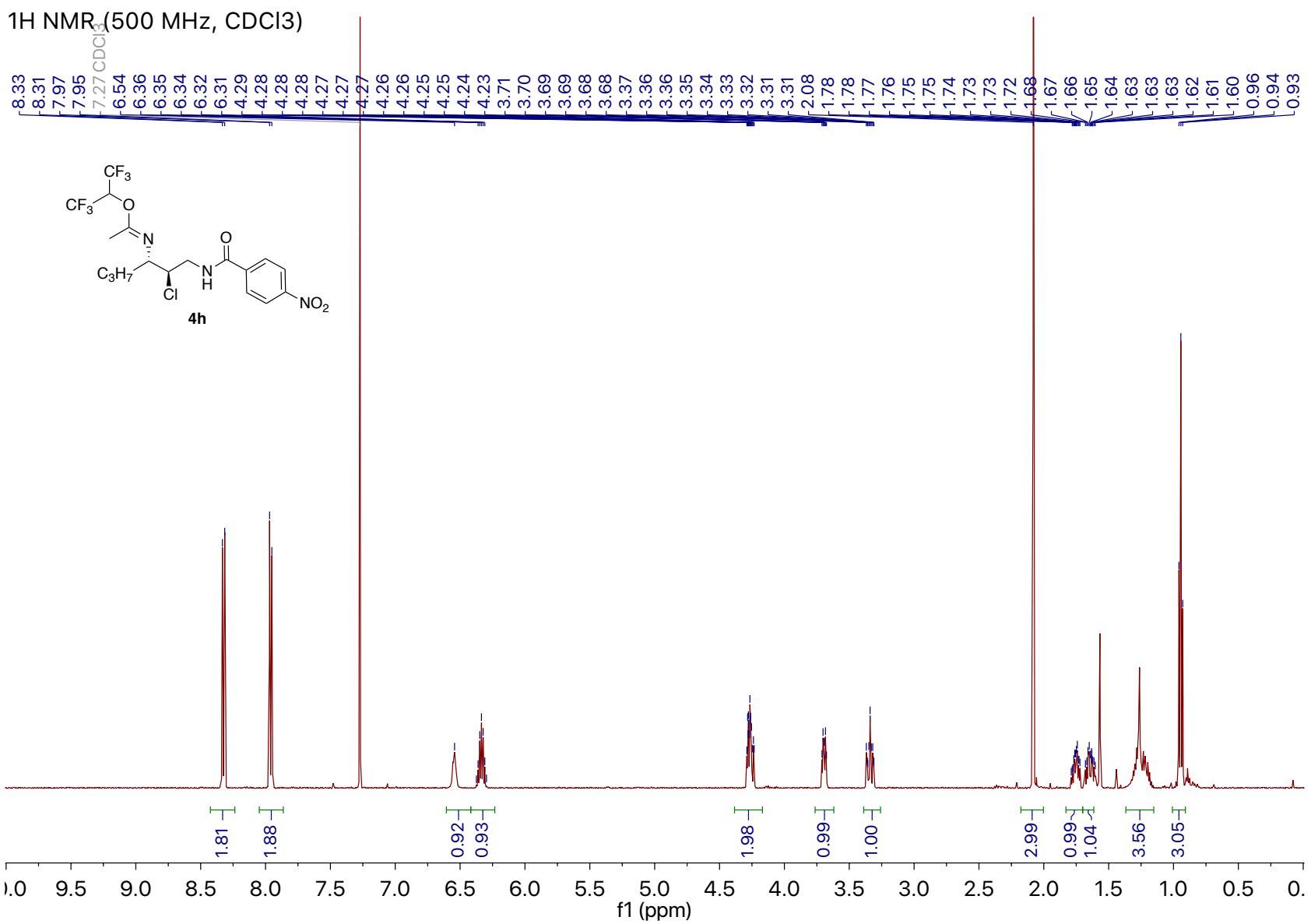
13C NMR (126 MHz, CDCl3)



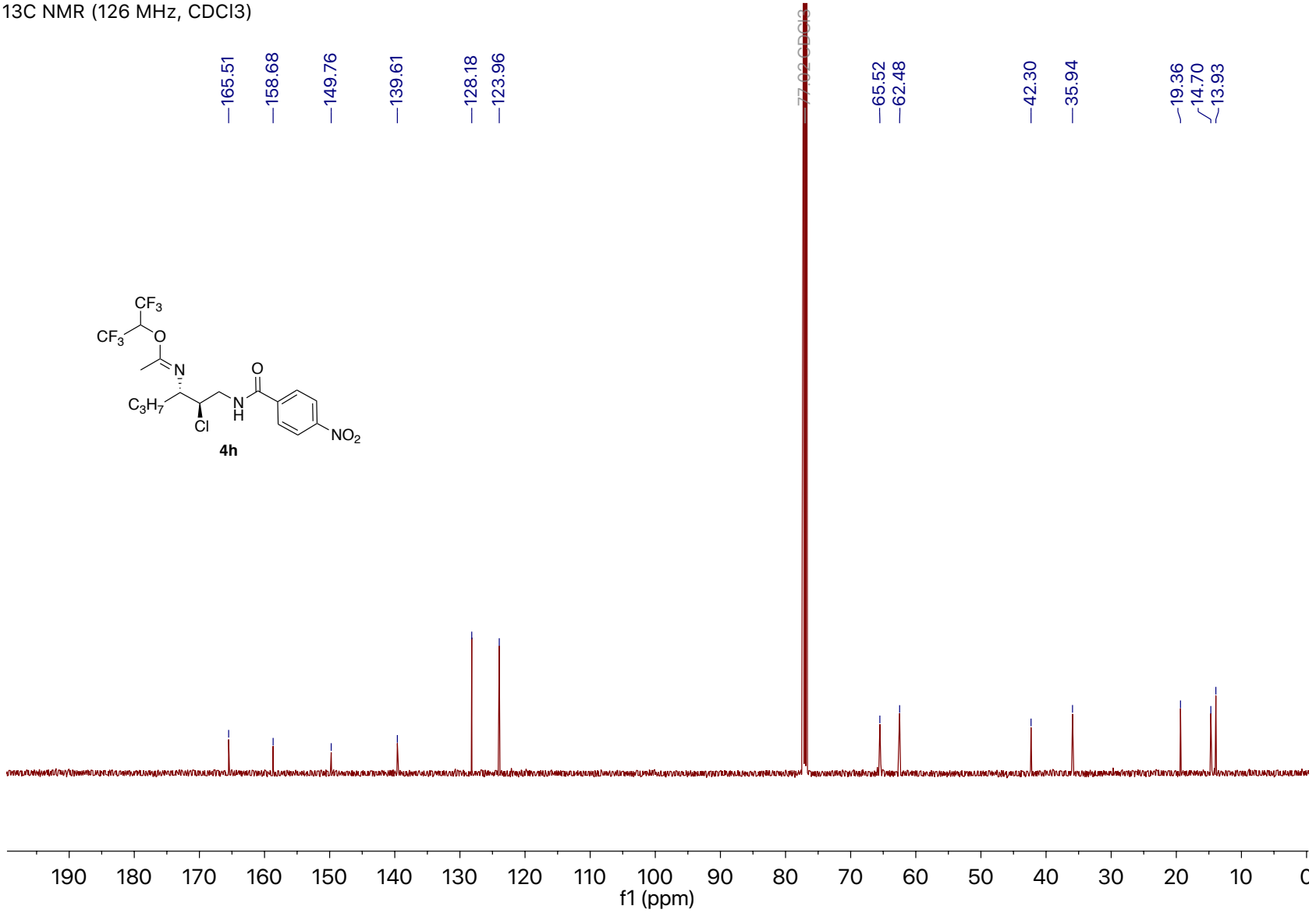

Ts
N
NH
O
N
H
Cl
NO2
3s-diastereomer
8.25
8.23
7.95
7.93
7.57
7.55
7.49
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.23
7.23
7.21
5.42
5.40
5.39
4.68
4.67
4.67
4.66
4.66
4.65
3.90
3.89
3.88
3.88
3.87
3.86
3.85
3.50
3.49
3.49
3.48
3.47
3.46
3.46
2.35
2.33
1.86
1.98
1.59
1.53
5.12
1.67
1.02
1.02
1.03
1.00
2.86
2.77
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

13C NMR (126 MHz, CDCl3)

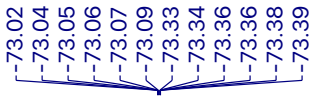


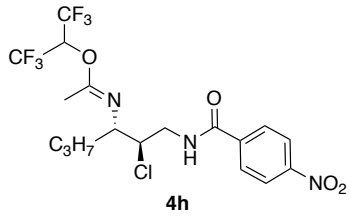

1H NMR (500 MHz, CDCl3)
7.27 CDCl3
8.33 8.31 7.97 7.95 6.54 6.36 6.35 6.34 6.32 6.31 4.29 4.28 4.28 4.28 4.27 4.27 4.27 4.26 4.26 4.25 4.25 4.24 4.23 3.71 3.70 3.69 3.69 3.68 3.68 3.37 3.36 3.36 3.35 3.34 3.33 3.32 3.31 3.31 2.08 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.68 1.67 1.66 1.65 1.64 1.63 1.63 1.62 1.61 1.60 0.96 0.94 0.93
CF3
CF3
O
N
O
C3H7
N
H
Cl
NO2
4h
1.81 1.88 0.92 0.93 1.98 0.99 1.00 2.99 0.99 1.04 3.56 3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

13C NMR (126 MHz, CDCl3)

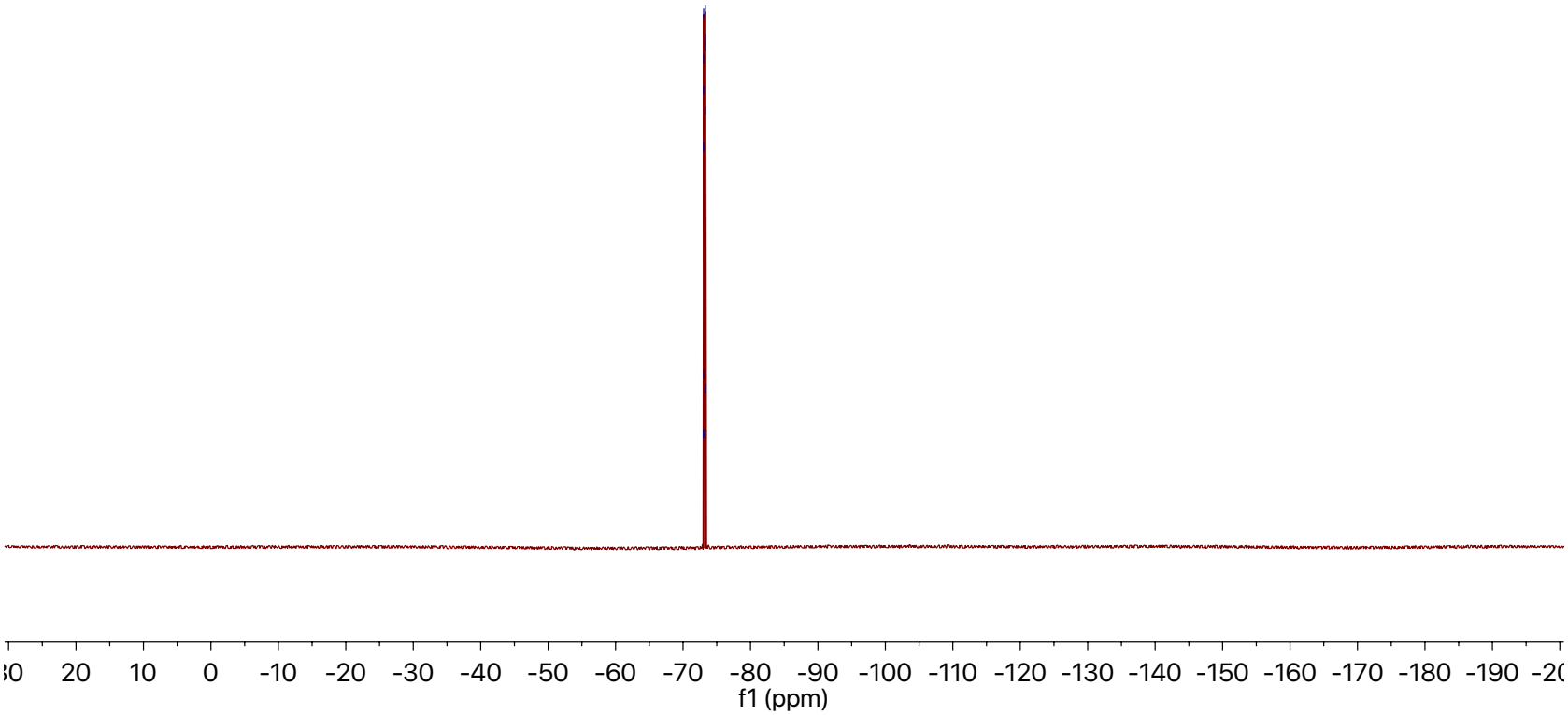


19F NMR (470 MHz, CDCl3)

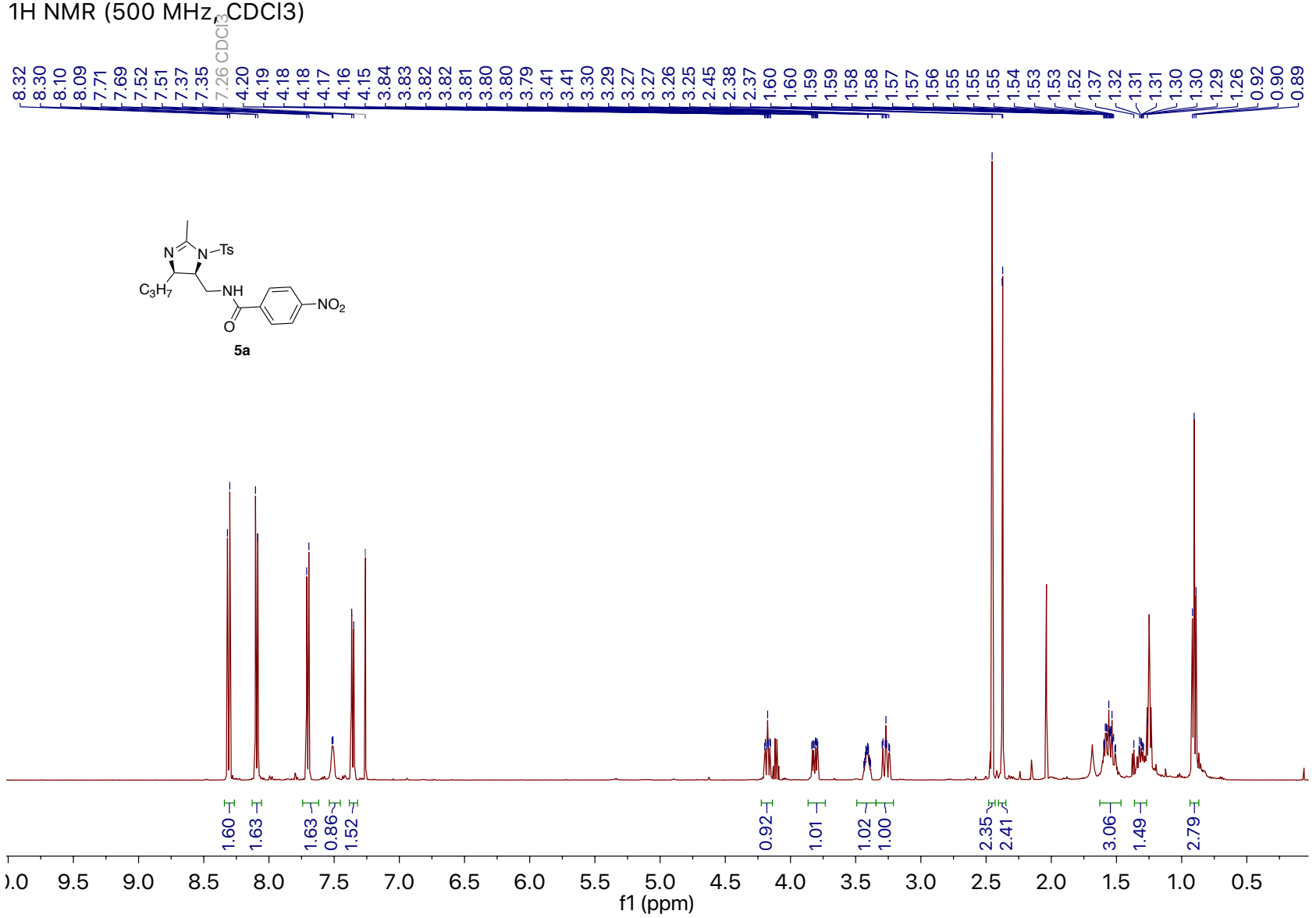




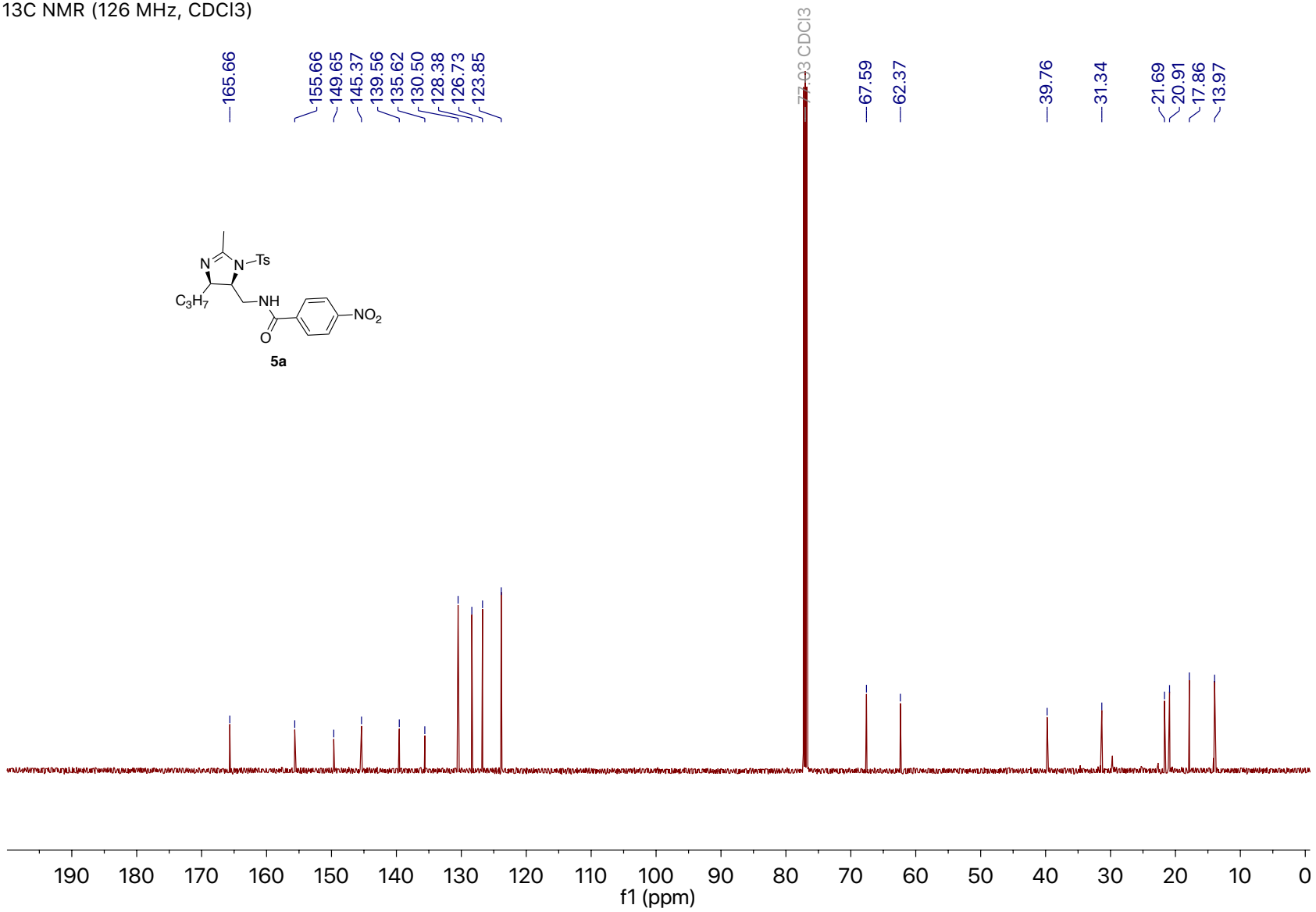
4h

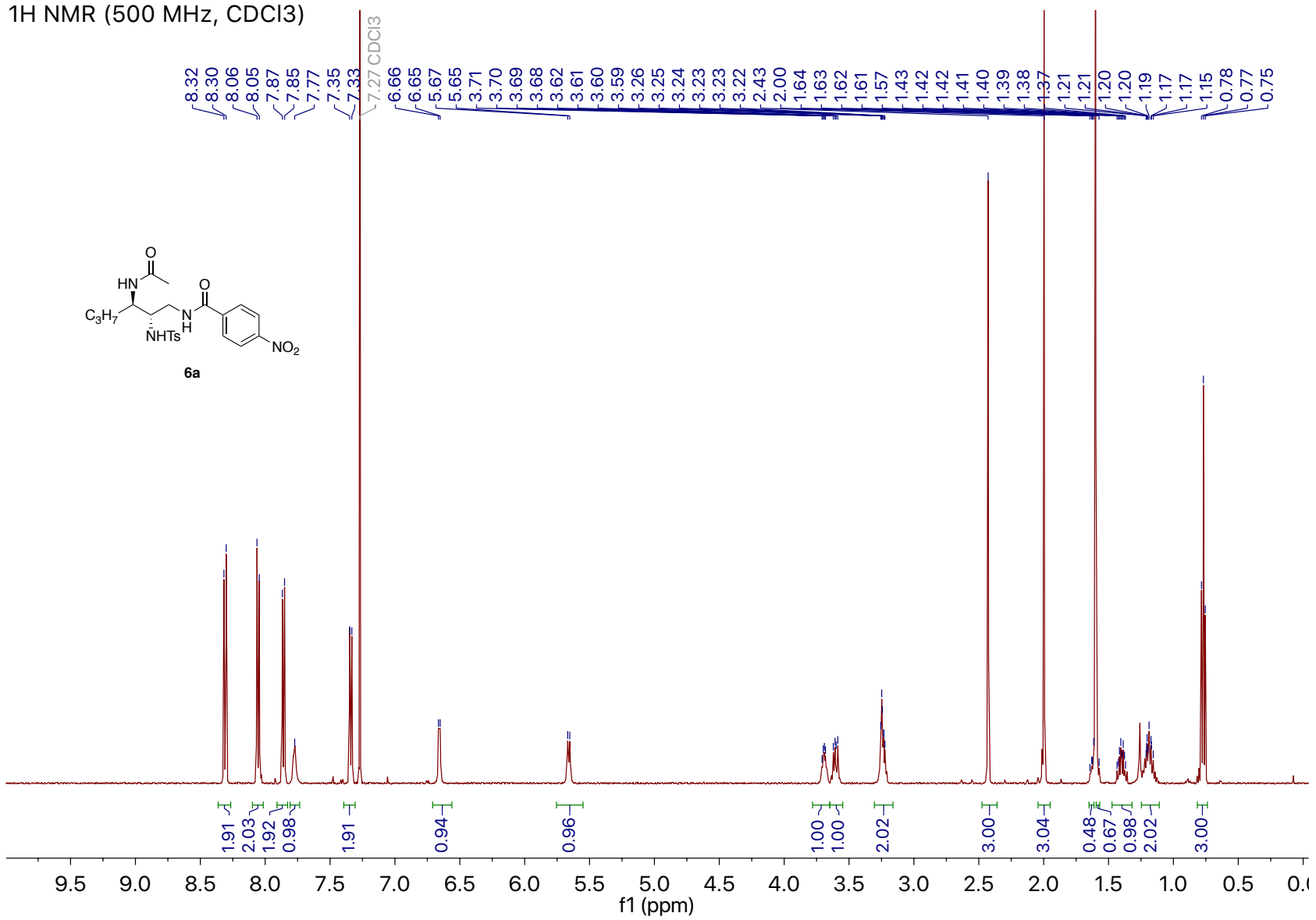


1H NMR (500 MHz, CDCl3)

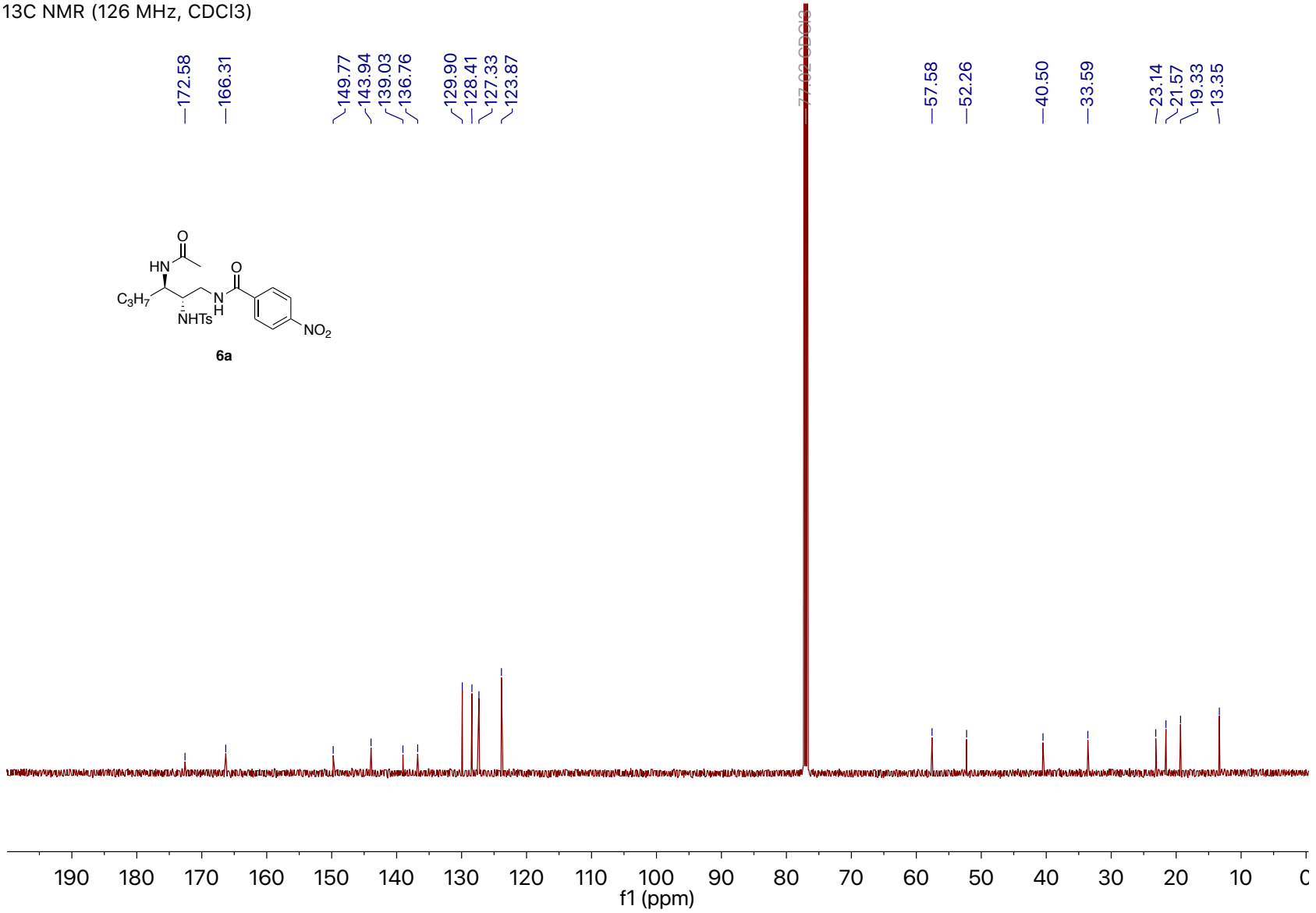


13C NMR (126 MHz, CDCl3)

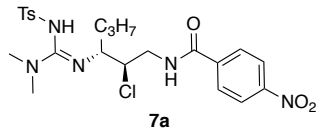



1H NMR (500 MHz, CDCl3)
7.27 CDCl3
f1 (ppm)
6a

13C NMR (126 MHz, CDCl3)

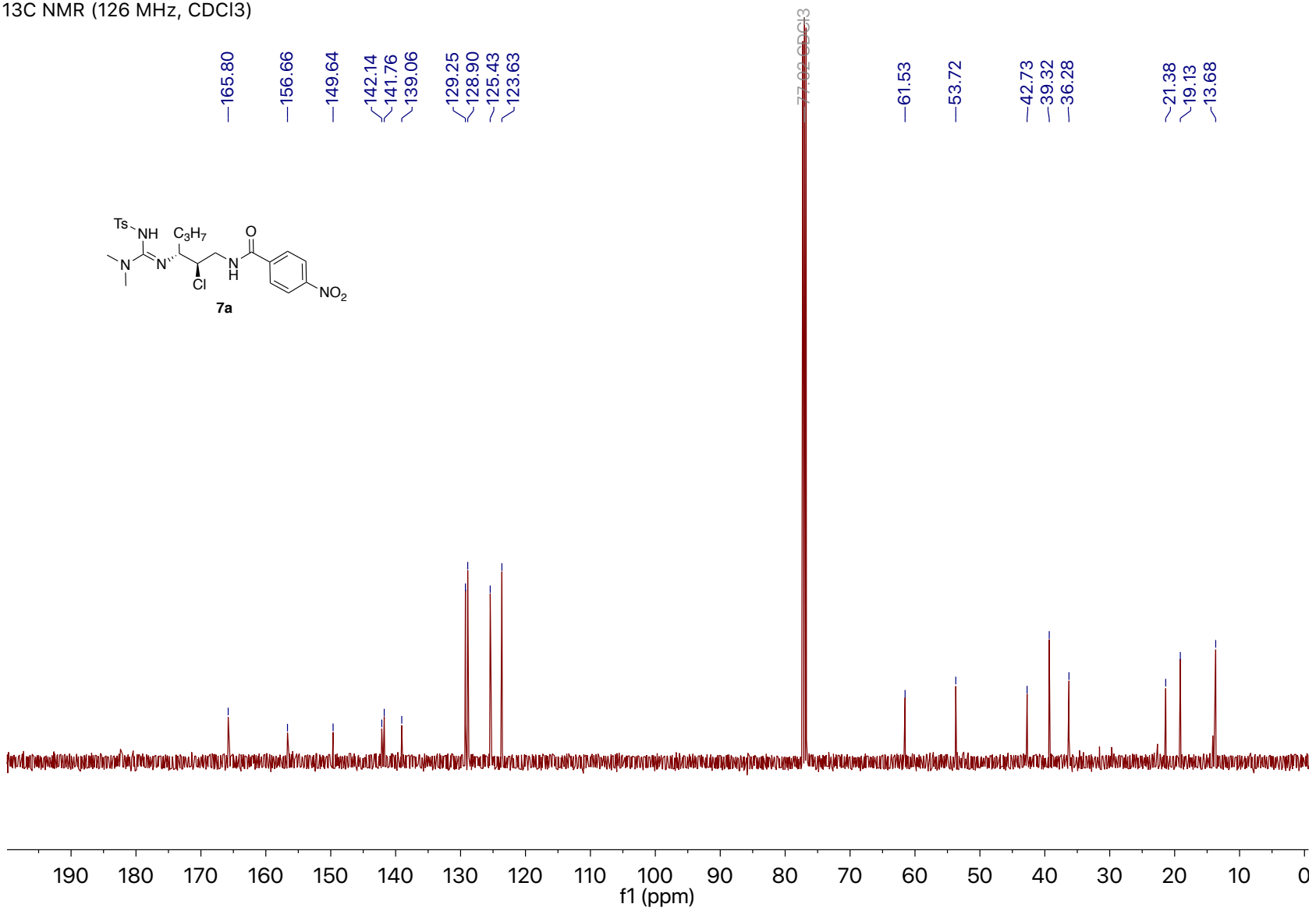


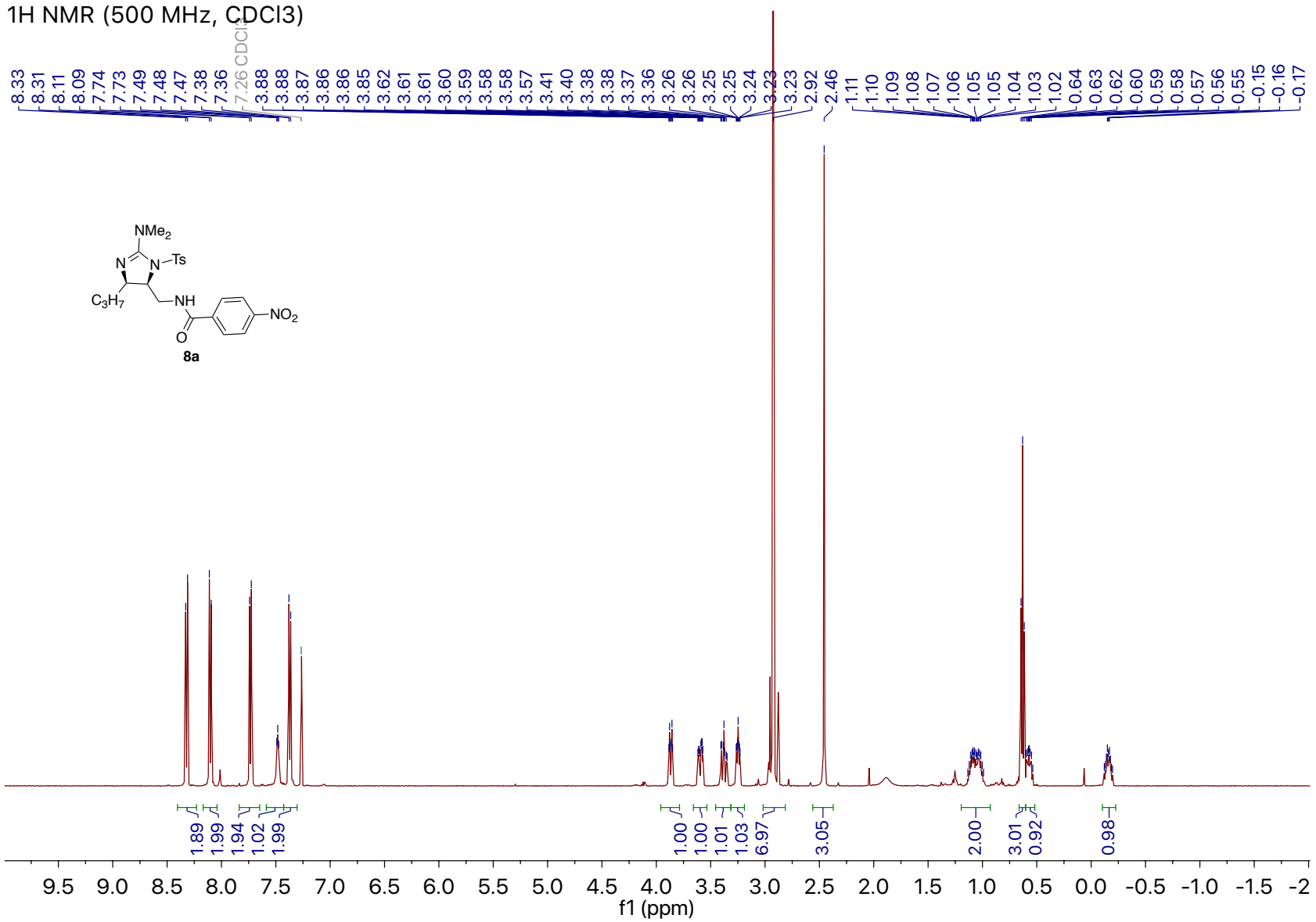
1H NMR (500 MHz, CDCl3)

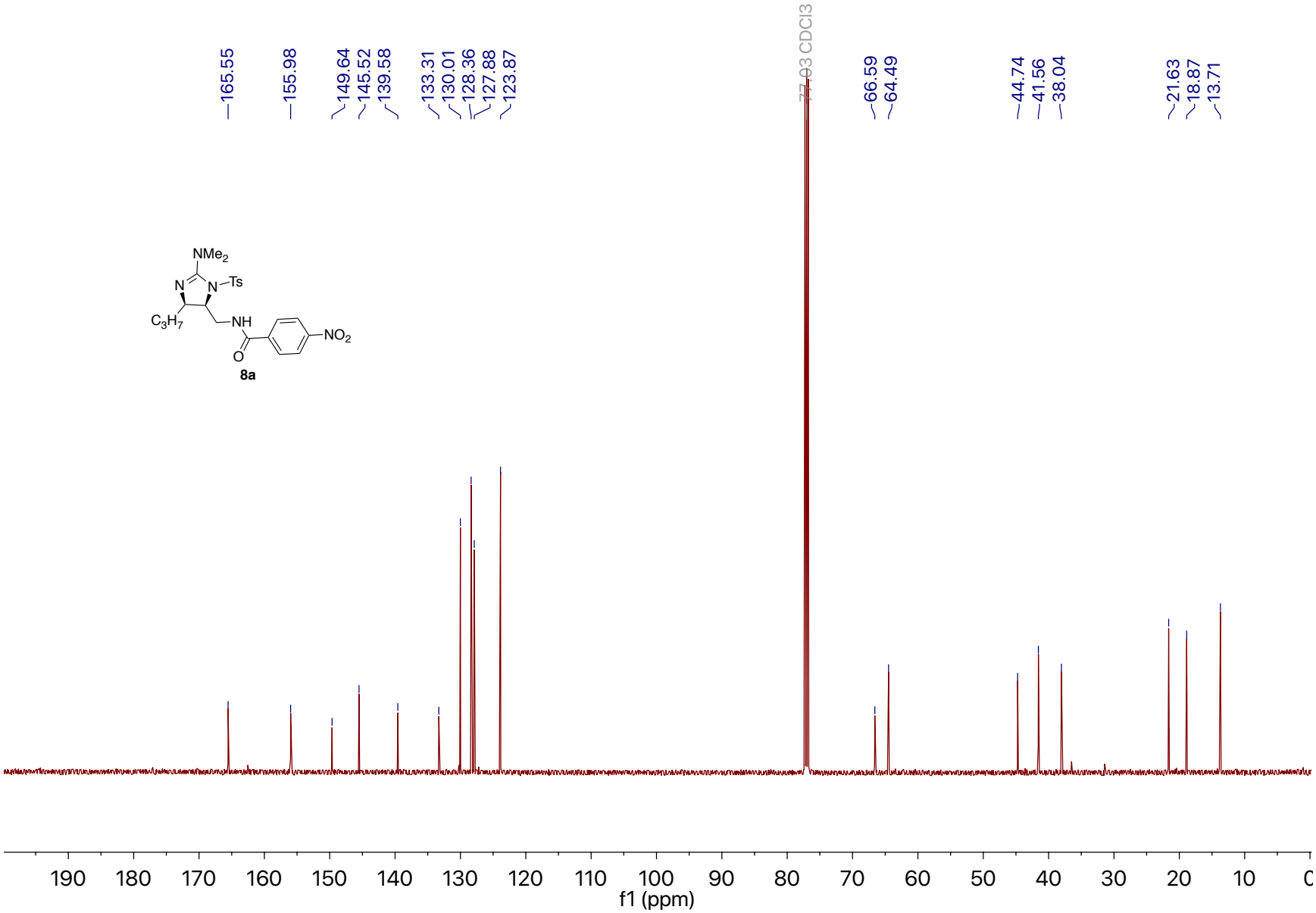


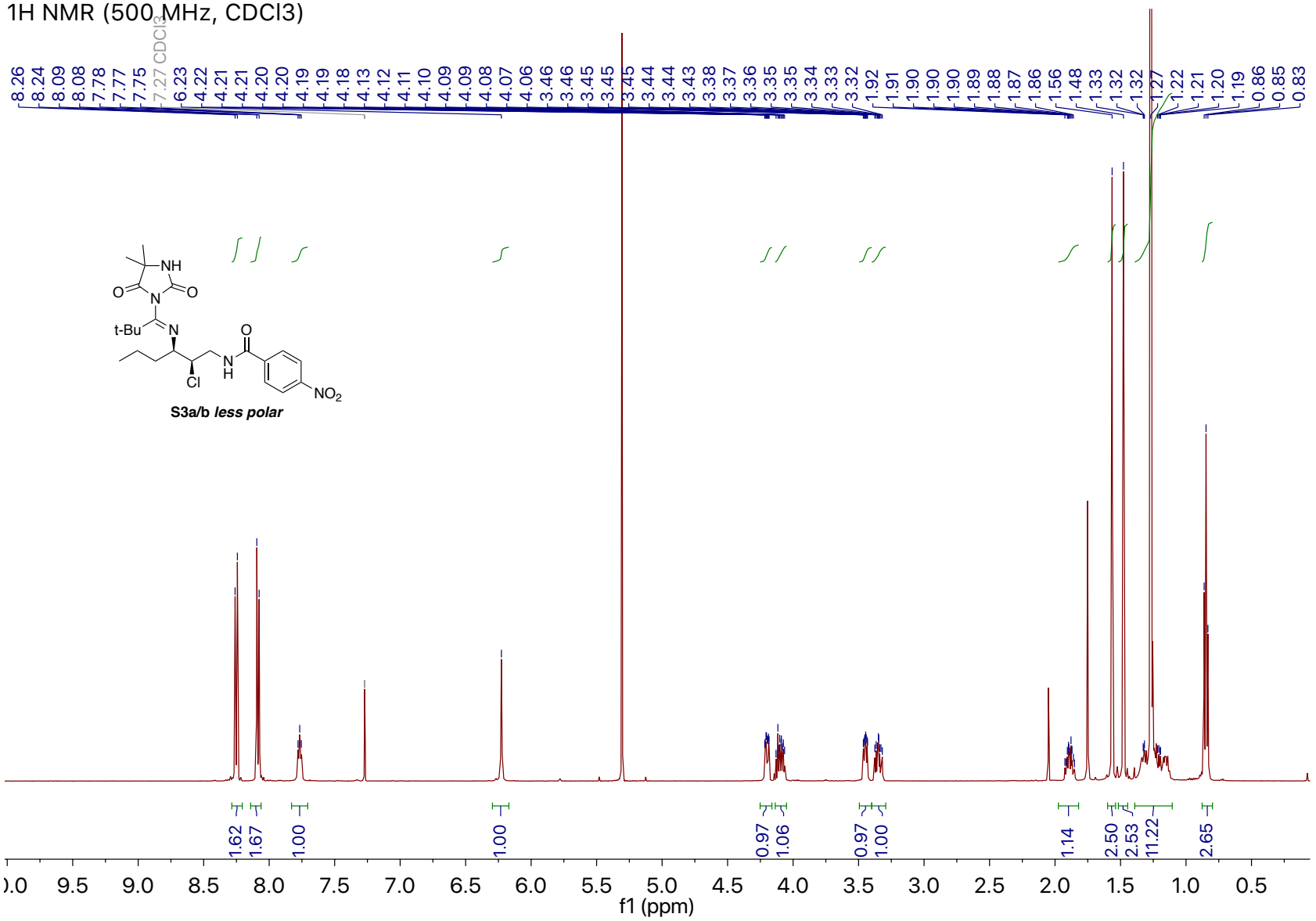
7a

13C NMR (126 MHz, CDCl3)

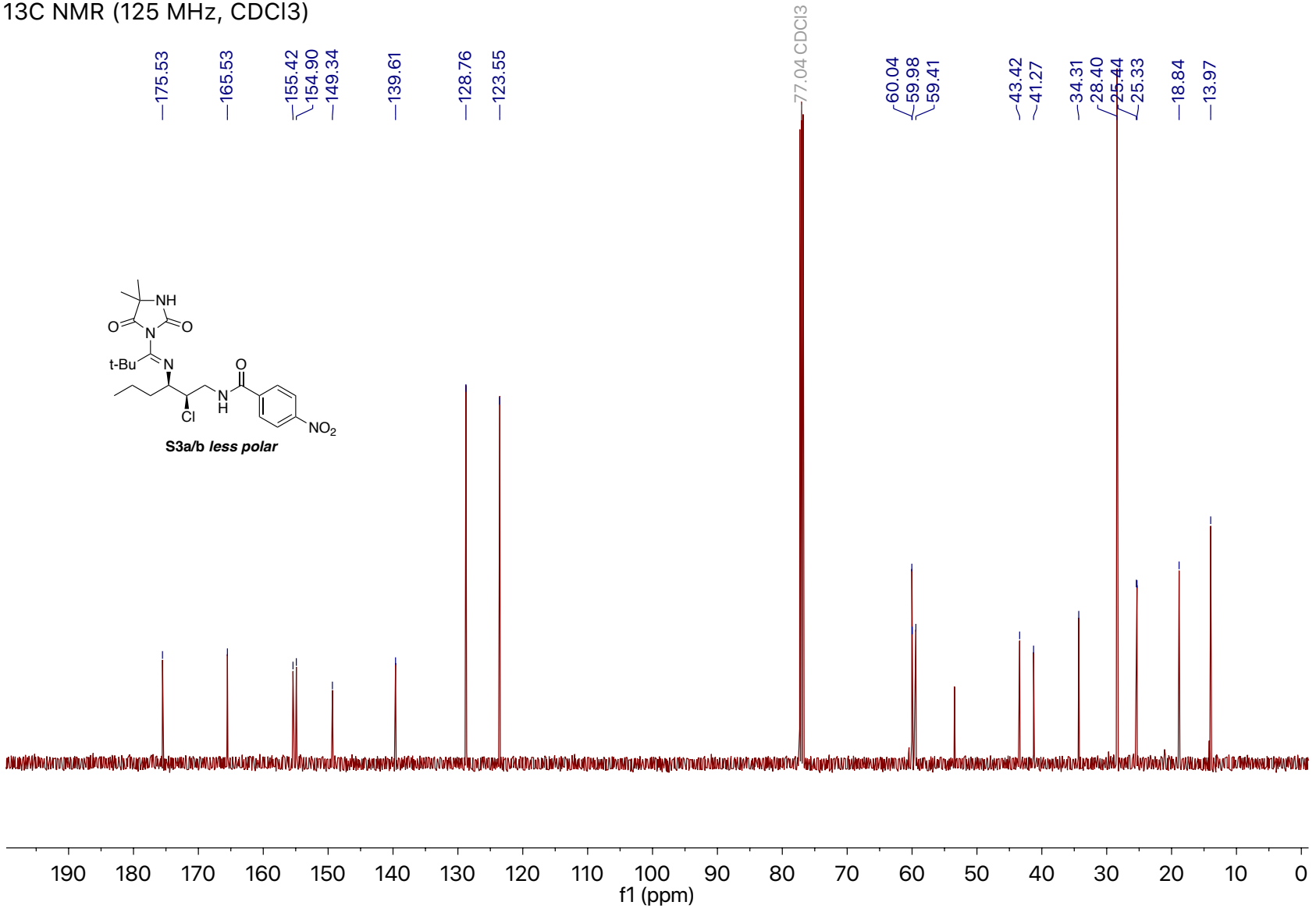



1H NMR (500 MHz, CDCl3)
8.33 8.31 8.11 8.09 7.74 7.73 7.49 7.48 7.47 7.38 7.36 7.26 CDCl3 3.88 3.88 3.87 3.86 3.86 3.85 3.62 3.61 3.61 3.60 3.59 3.58 3.58 3.57 3.41 3.40 3.38 3.38 3.37 3.36 3.26 3.26 3.25 3.25 3.24 3.23 3.23 2.92 2.46 1.11 1.10 1.09 1.08 1.07 1.06 1.05 1.05 1.04 1.03 1.02 0.64 0.63 0.62 0.60 0.59 0.58 0.57 0.56 0.55 -0.15 -0.16 -0.17
NMe2
N
N
Ts
C3H7
NH
NO2
O
8a
1.89 1.99 1.94 1.02 1.99 1.00 1.00 1.01 1.03 6.97 3.05 2.00 3.01 0.92 0.98
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 -0.5 -1.0 -1.5 -2
f1 (ppm)

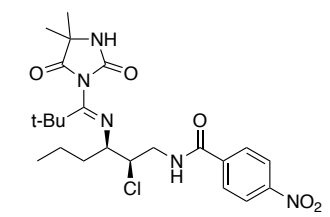

165.55
155.98
149.64
145.52
139.58
133.31
130.01
128.36
127.88
123.87
77.03 CDCl3
66.59
64.49
44.74
41.56
38.04
21.63
18.87
13.71
NMe2
N
N
Ts
C3H7
NH
O
NO2
8a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR (500 MHz, CDCl3)
S3a/b less polar
f1 (ppm)

13C NMR (125 MHz, CDCl3)



COSY

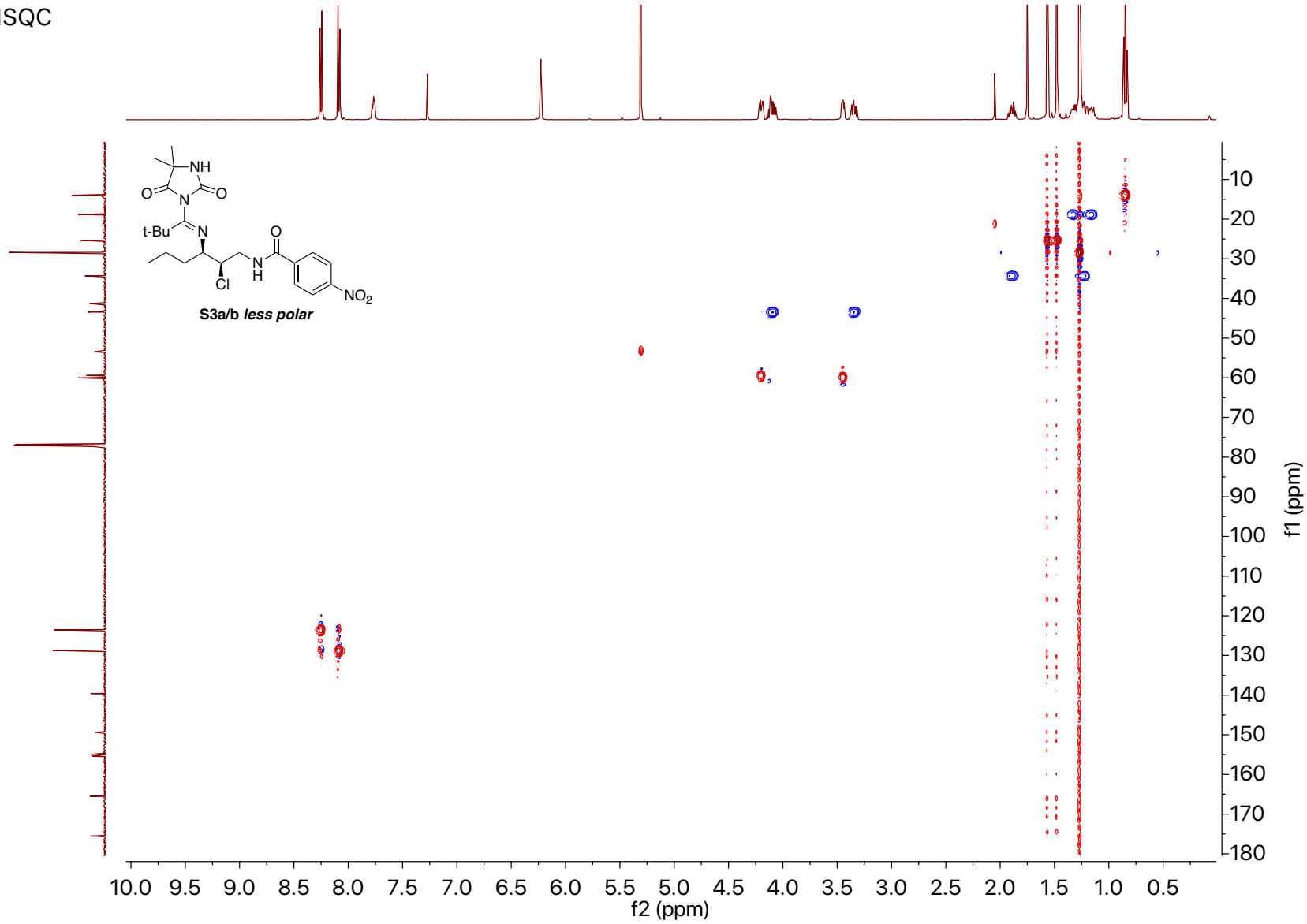


S3a/b *less polar*

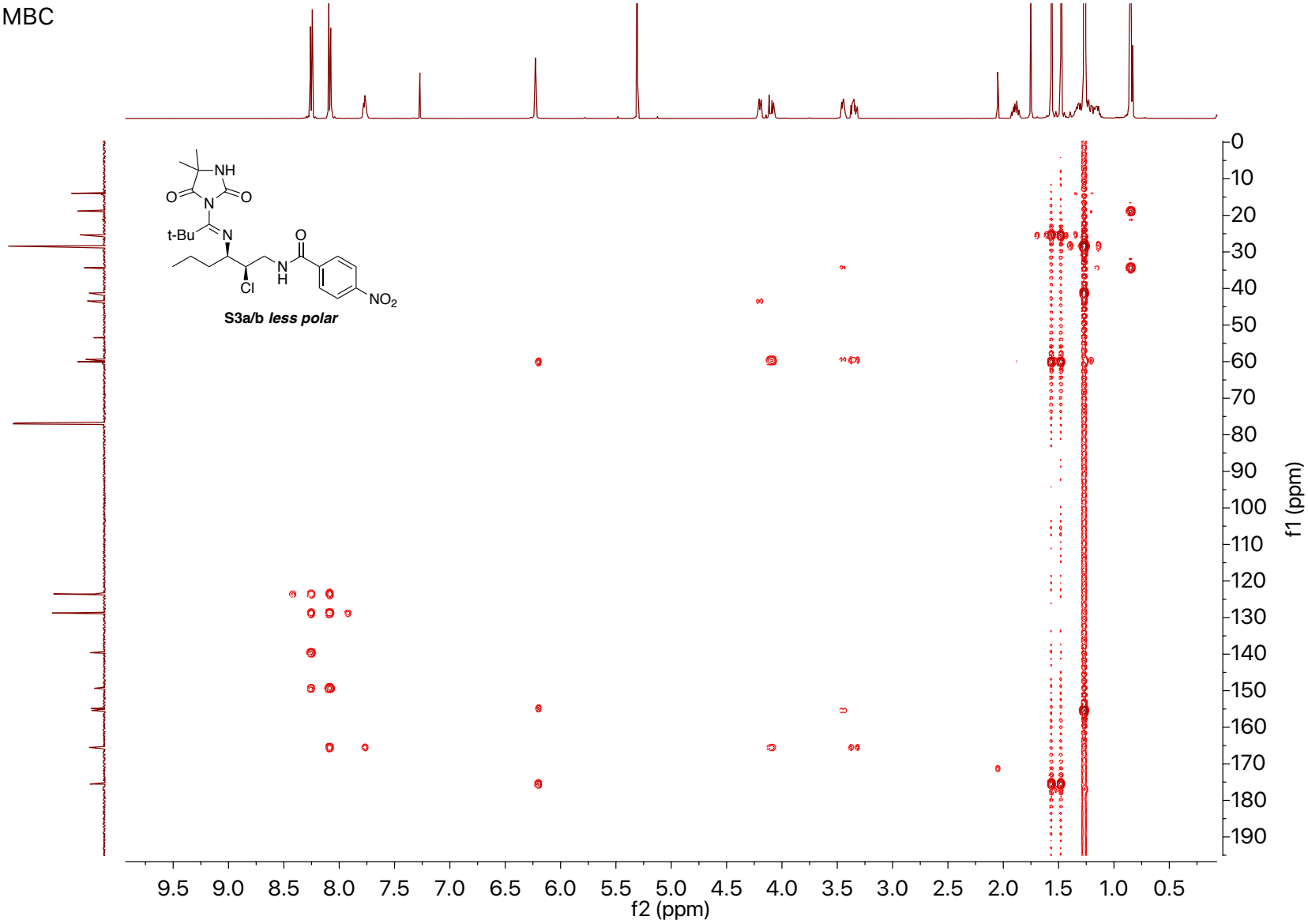
f2 (ppm)

f1 (ppm)

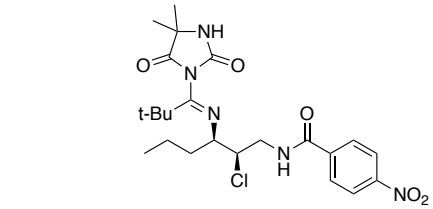
HSQC


NH
O
O
N
t-Bu
N
O
N
H
Cl
NO2
S3a/b less polar
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
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
f1 (ppm)

HMBC

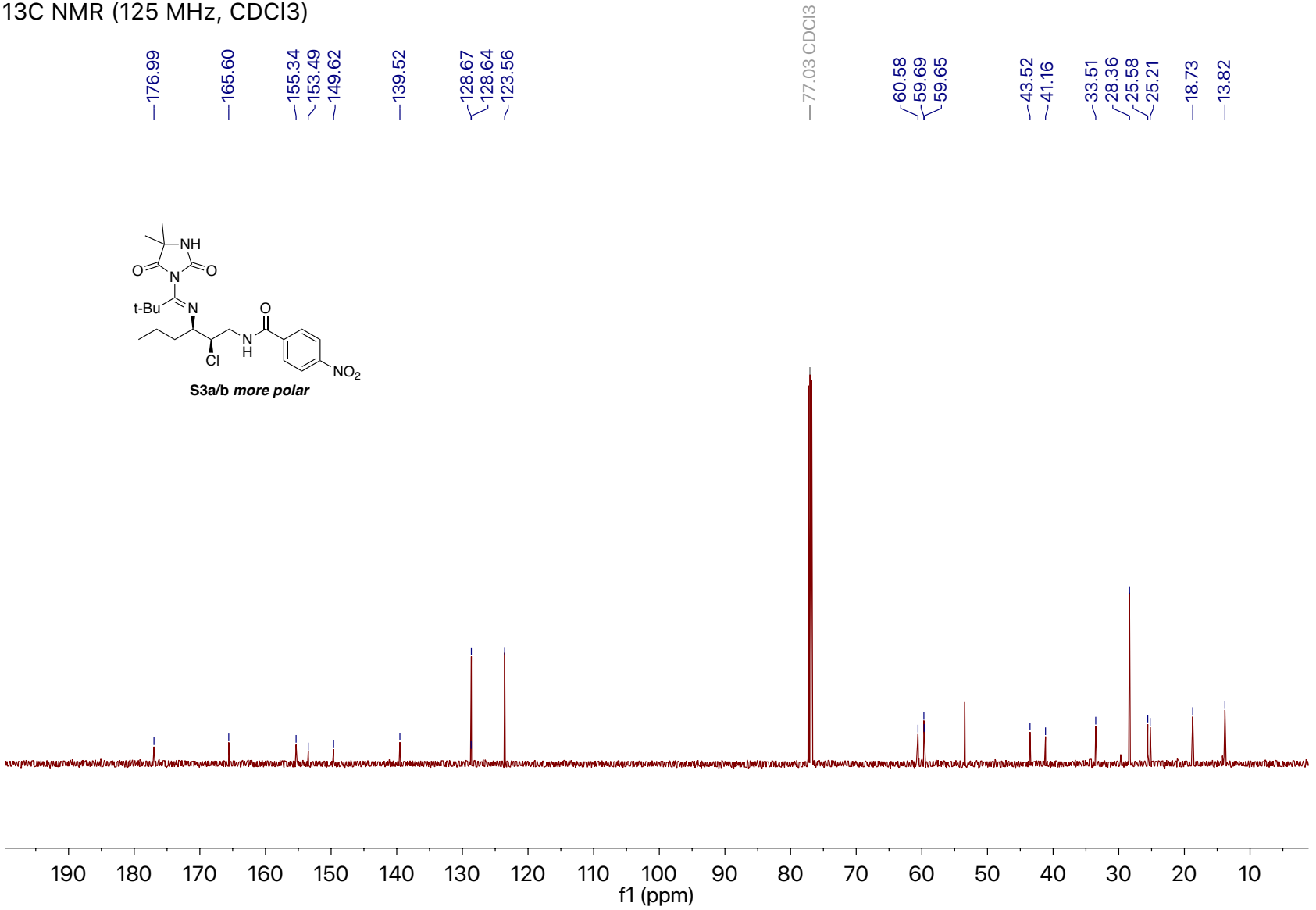

NH
O
O
N
t-Bu
N
O
N
H
Cl
NO2
S3a/b less polar
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

1H NMR (500 MHz, CDCl3)



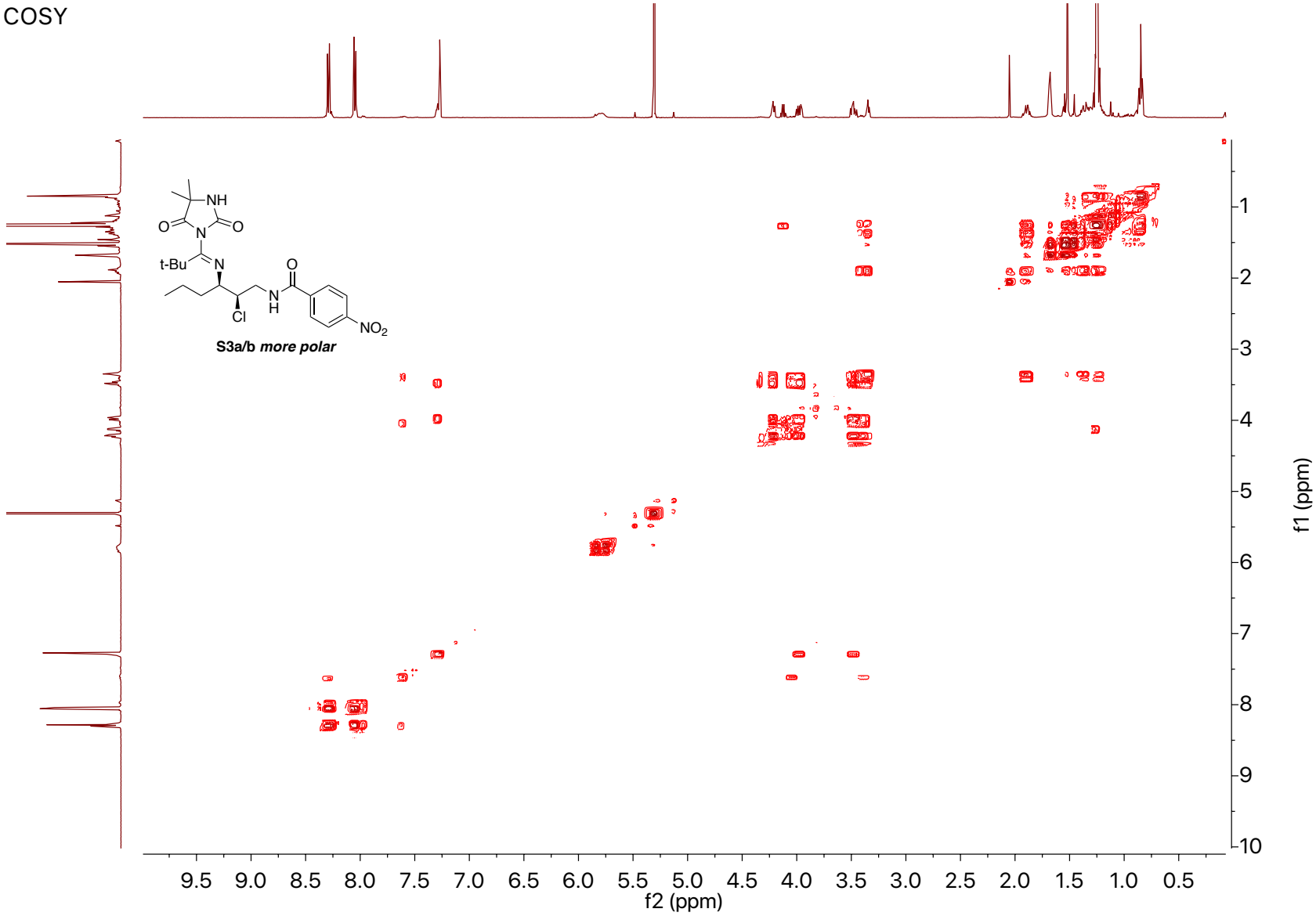
S3a/b *more polar*

13C NMR (125 MHz, CDCl3)

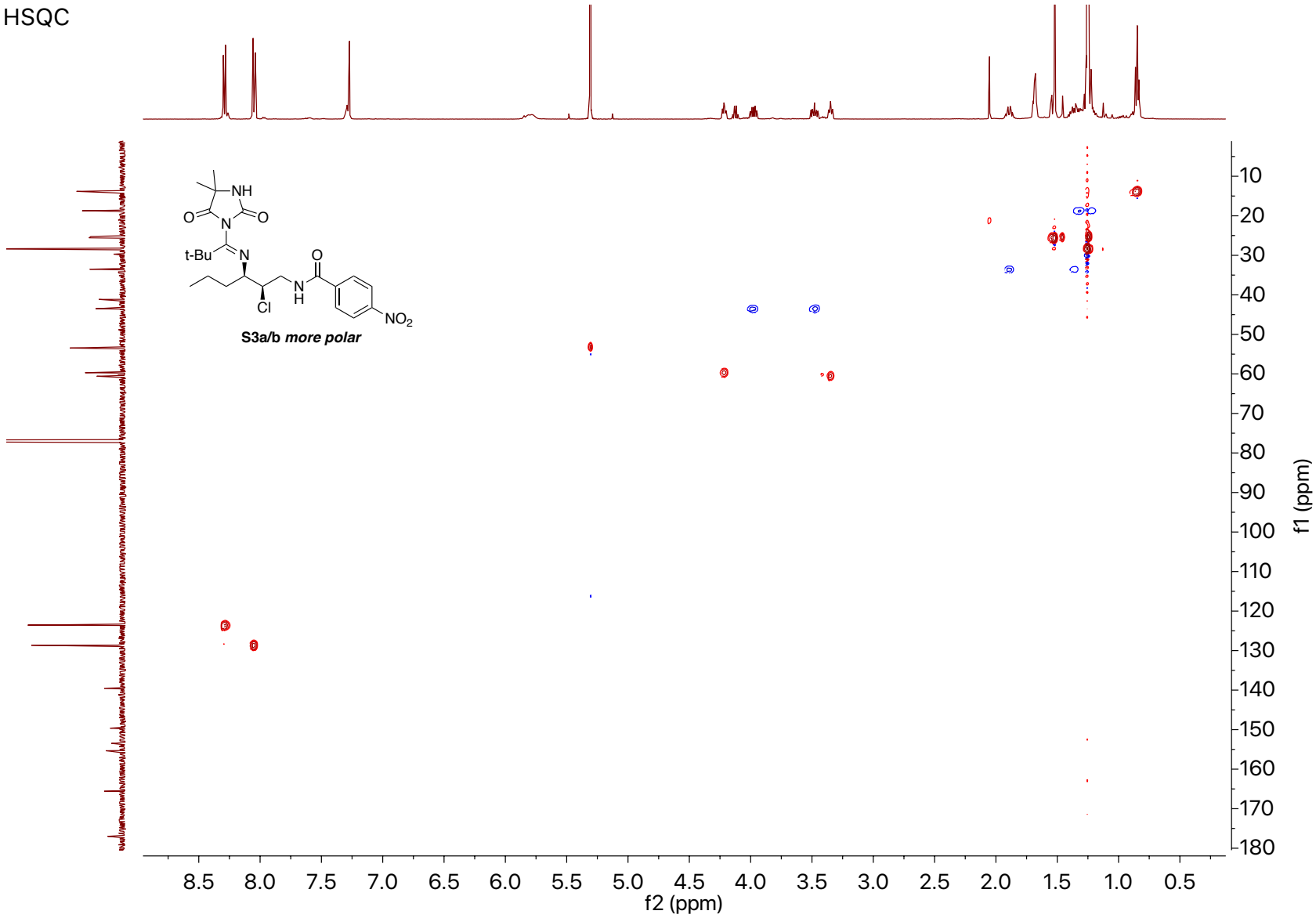


S3a/b *more polar*

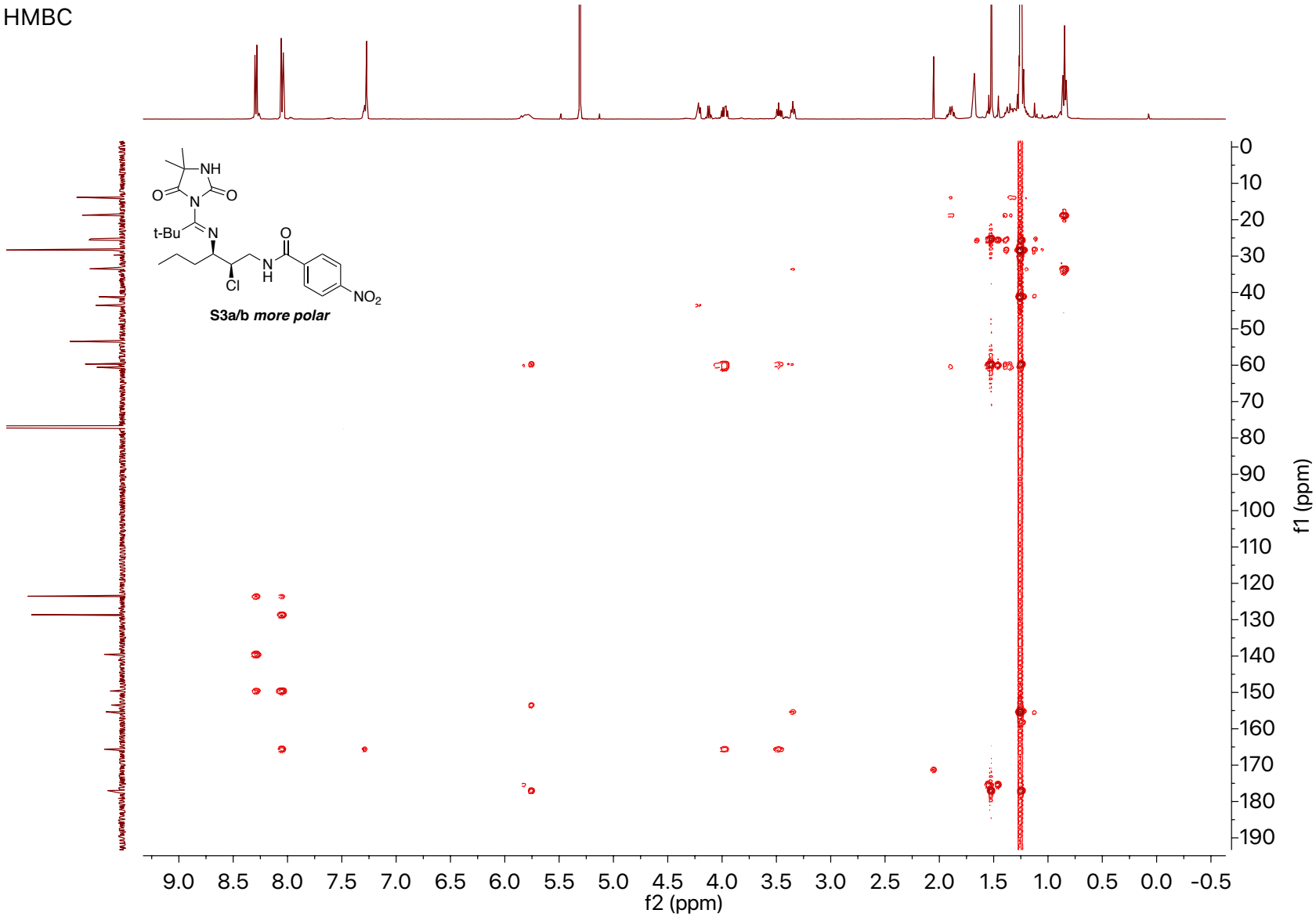
COSY


NH
O
O
N
t-Bu
N
O
N
H
Cl
NO2
S3a/b more polar
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
f2 (ppm)
1 2 3 4 5 6 7 8 9 10
f1 (ppm)

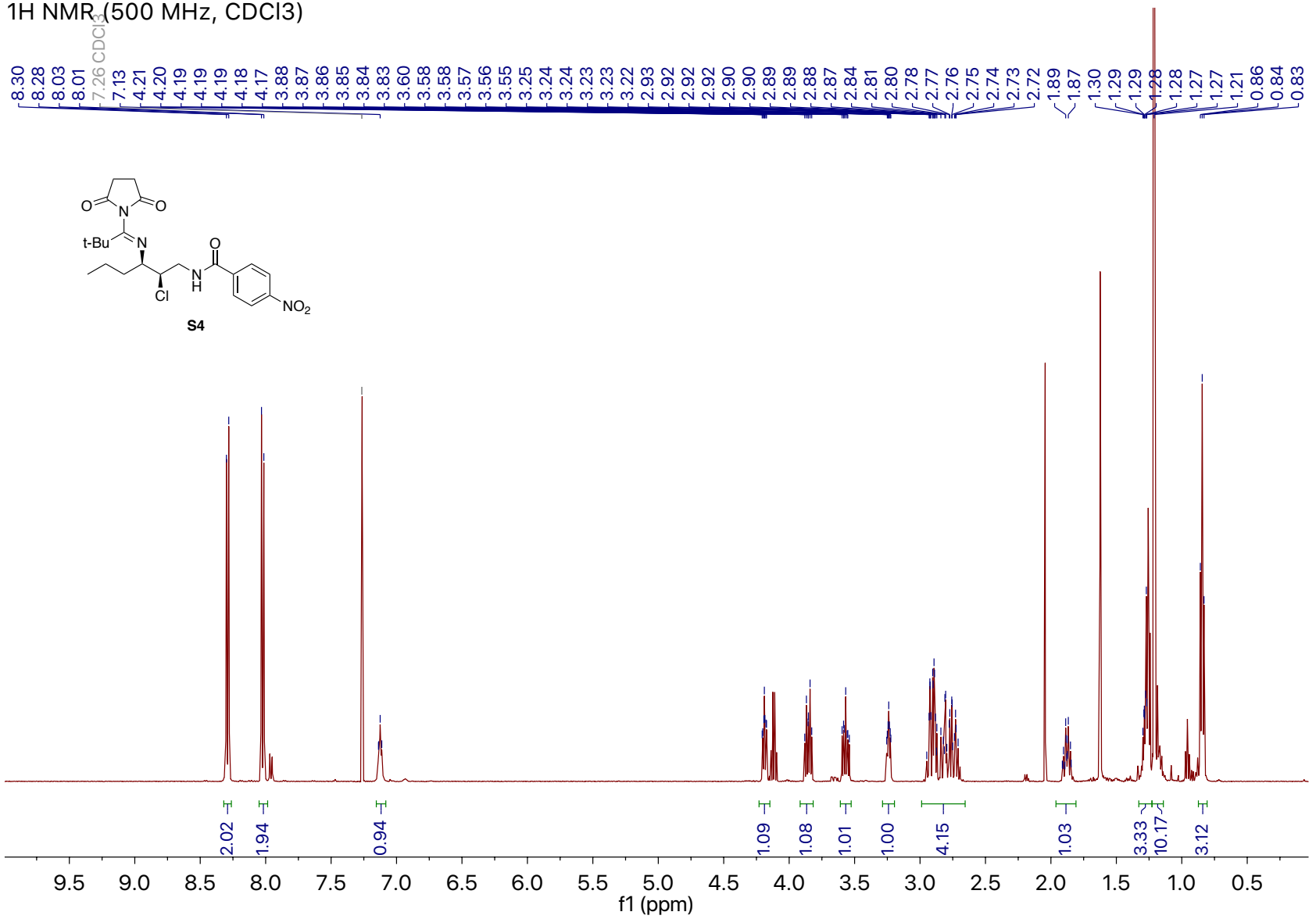
HSQC


NH
O
O
N
t-Bu
N
O
N
H
Cl
NO2
S3a/b more polar
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
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

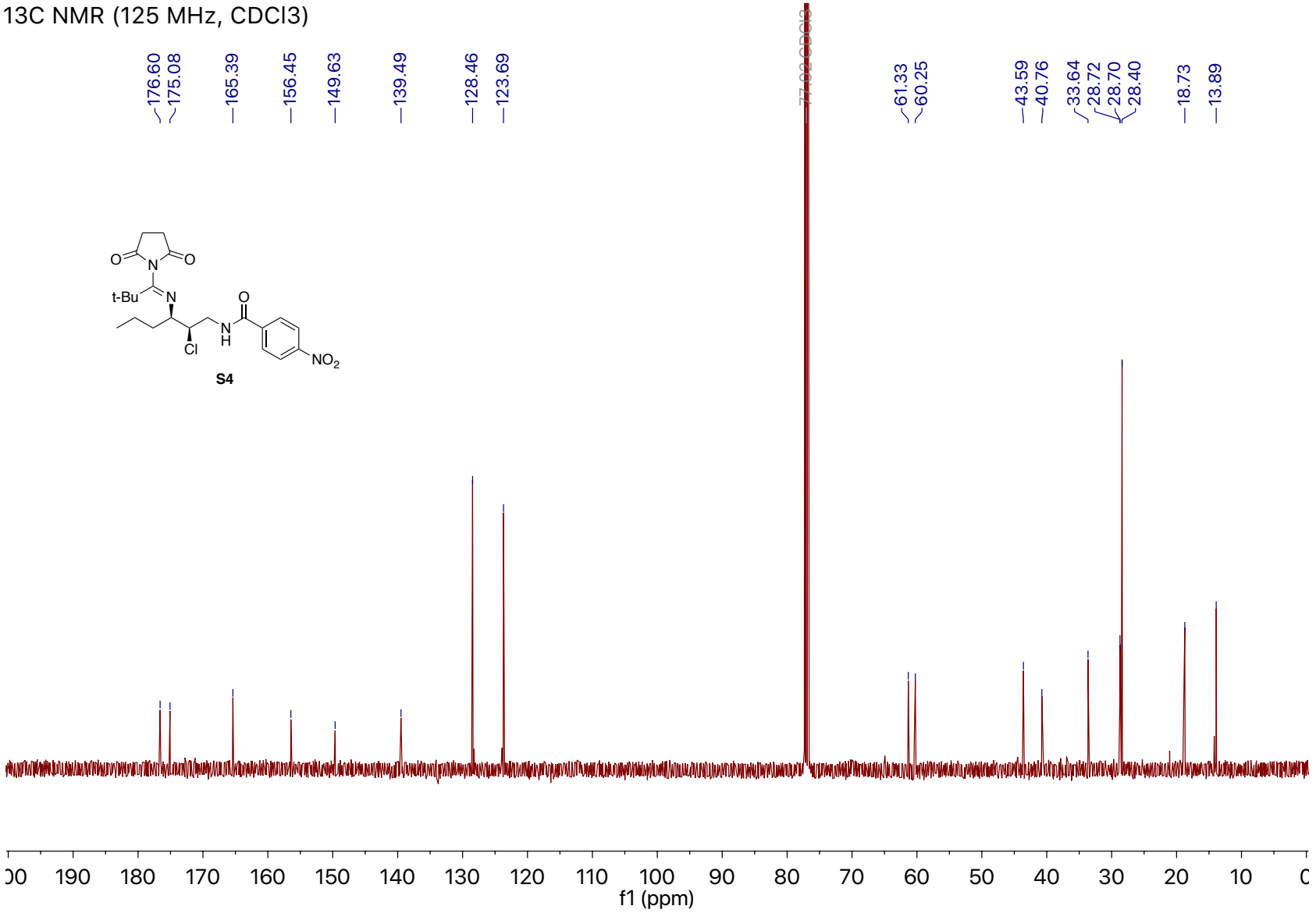
HMBC


NH
O
O
N
t-Bu
N
O
N
H
Cl
NO2
S3a/b more polar
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
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
0.0
-0.5
f2 (ppm)

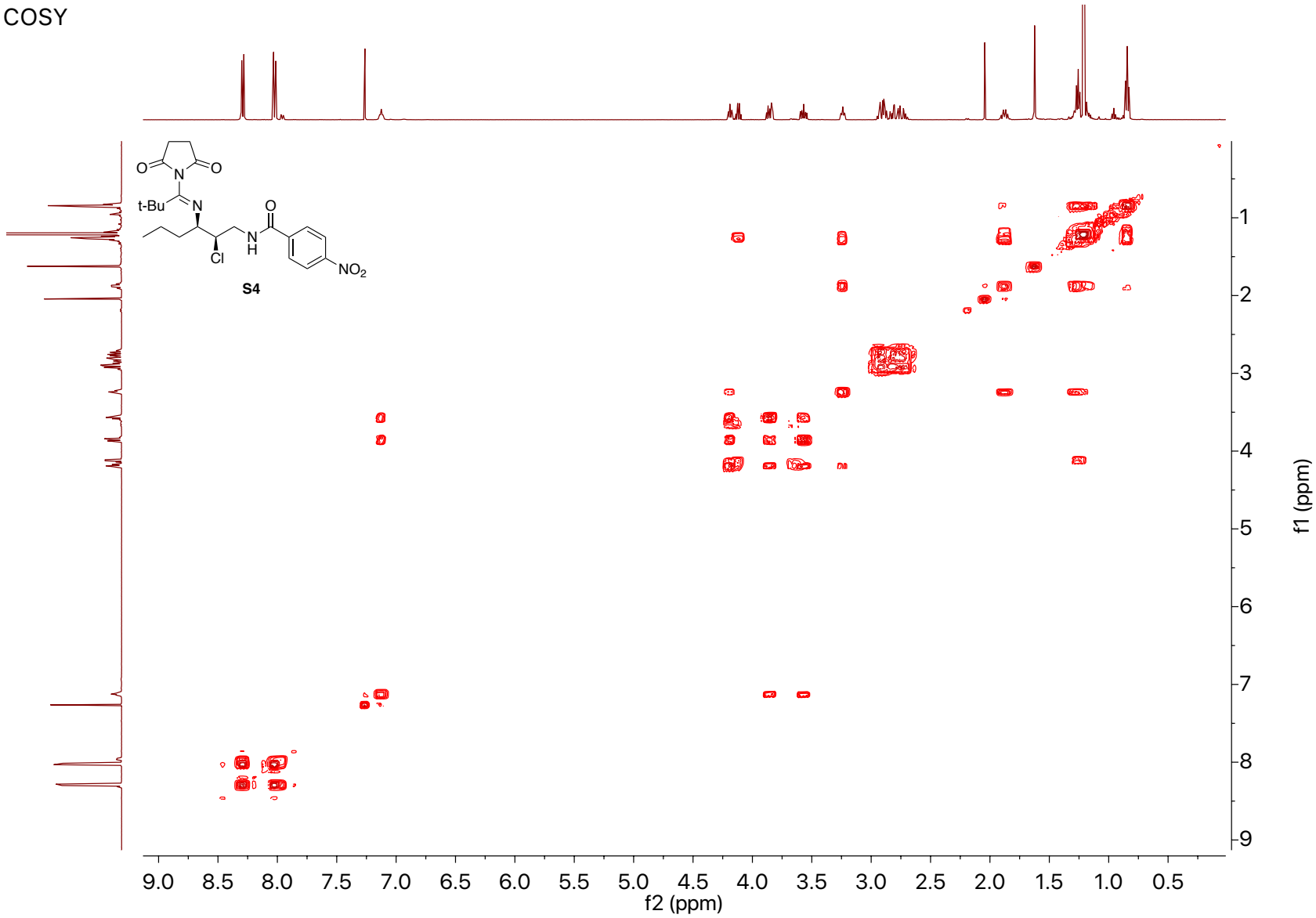
1H NMR (500 MHz, CDCl3)



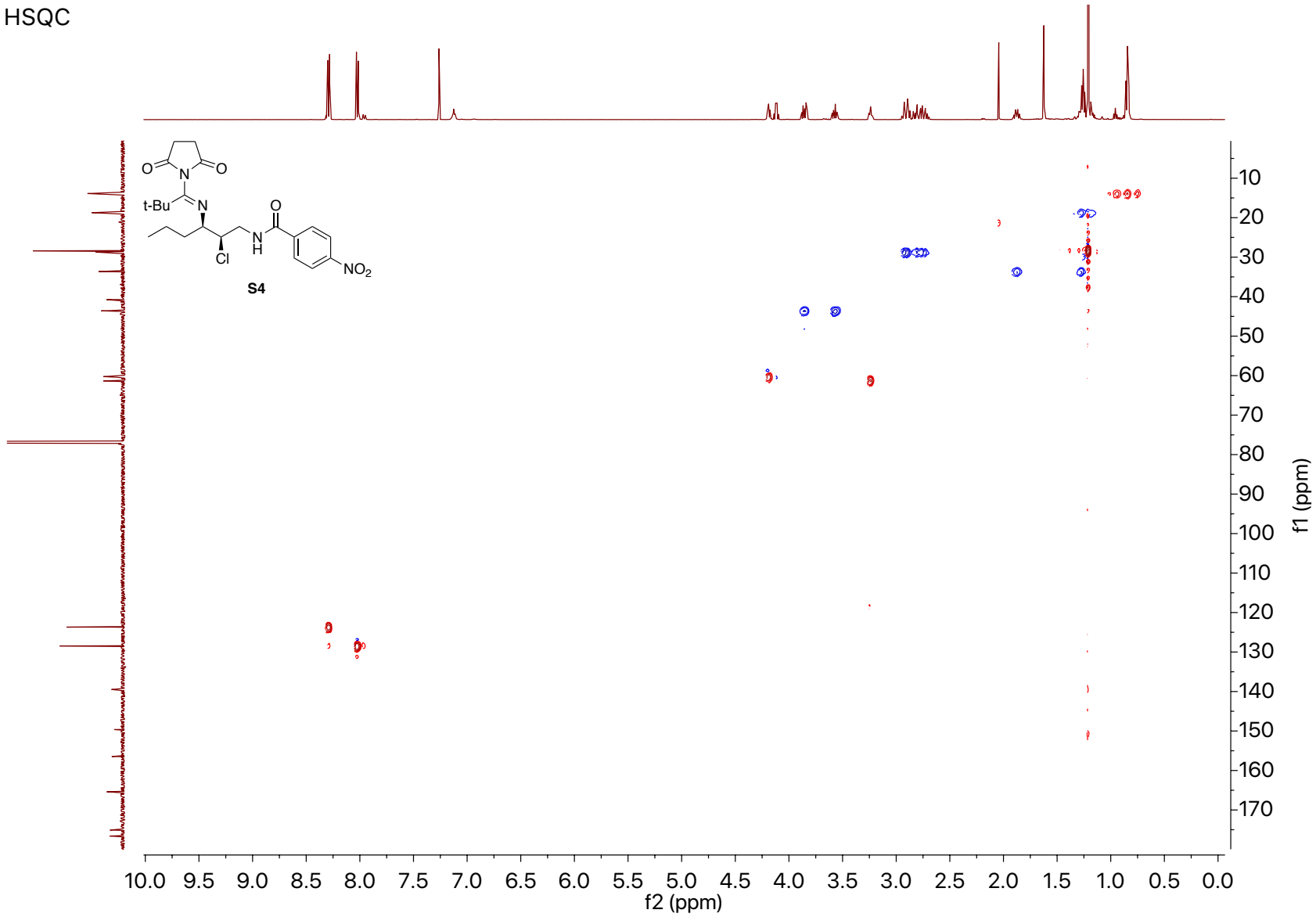
13C NMR (125 MHz, CDCl3)



COSY



HSQC


O
N
O
t-Bu
N
O
N
H
Cl
NO2
S4
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
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)

HMBC