Supporting Information

O-Cyclopropyl Hydroxylamines: Gram-Scale Synthesis and Utility as Precursors for *N*-Heterocycles

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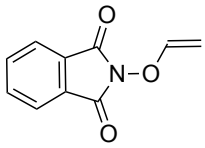
General Remarks

All starting material syntheses were performed in oven-dried 50 mL or 100 mL round-bottomed flasks. Commercially available solvents and reagents were used without further purification. All arylation reactions were carried out in oven-dried 8 mL scintillation vials, while rearrangement reactions were carried out in oven-dried 20 mL scintillation vials. All reactions were monitored by thin-layer chromatography (TLC) with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was carried out using a Biotage Isolera One system with 10g KP-Sil cartridges utilizing ethyl acetate (EA) and hexane (hex) as eluents. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX-600 NMR spectrometer. Chemical shifts are documented in parts per million (δ, ppm). ^{1}H NMR spectra are referenced to 7.26 ($CDCl_3$) and ^{13}C NMR spectra are referenced to 77.16 ($CDCl_3$). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, p = pentet, br s = broad singlet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, dt = doublet of triplets, td = triplet of doublets, dtd = doublet of triplet of doublets, tt = triplet of triplets, dp = doublet of pentets, ddt = doublet of doublet of triplets, dtdd = doublet of triplet of doublet of doublets, tddd = triplet of doublet of doublet of doublets, dqt = doublet of quartet of triplets, qd = quartet of doublets, dtt = doublet of triplet of triplets, qt = quartet of triplets, dq = doublet of quartets, tq = triplet of quartets. High Resolution Mass Spectrometry was performed on an Agilent 1290/6230 LCMS-TOF under electrospray ionization (ESI) conditions in both positive and negative mode. Melting points were recorded on a Mettler Toledo MP50 melting point system.

Preparation of *N*-enoxyphthalimides

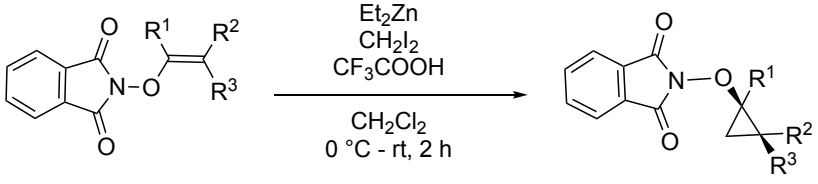
The preparation of the *N*-enoxyphthalimides was carried out following literature reported protocols. *N*-enoxyphthalimide **15a** was synthesized following protocol A[1] and the *N*-enoxyphthalimides (**15b-15g**) (i.e those used to synthesize 2-cyclopropoxyisoindolin-1,3diones (**16b-16g**) were synthesized following the copper promoted protocol B[2]. The ^{1}H and ^{13}C NMR spectra of the obtained *N*-enoxyphthalimides were consistent with those reported in the literature.[1-3]

2-(vinyloxy)isoindoline-1,3-dione (15a)



The ^{1}H and ^{13}C NMR spectra for 2-(vinyloxy)isoindoline-1,3-dione were consistent with those reported in the literature.[1]

Preparation of 2-cyclopropoxyisoindoline-1,3-diones

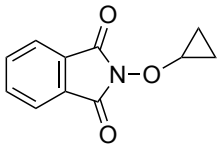


Neat diethylzinc (20.5 mL, 200 mmol, 2.0 equiv) was added to 250 mL of dry DCM under inert atmosphere in a glove box. The diethylzinc solution was removed from the glove box and kept under inert gas. A

solution of trifluoroacetic acid (15.3 mL, 200 mmol, 2.0 equiv) in DCM (125 mL) was slowly added to the diethylzinc solution at 0 °C and stirred until gas evolution ceased. After stirring at 0 °C for about 20 minutes, a solution of diiodomethane (16.13 mL, 200 mmol, 2.0 equiv) in DCM (125 mL) was added. The mixture was stirred for an additional 20 minutes. Upon further stirring, a solution of *N*-enoxyphthalimide **15a** (22.7 g, 120 mmol, 1.0 equiv) in DCM (100 mL) was added. Then the reaction was removed from the ice bath, allowed to warm to rt and stirred for 2 h or until the reaction was complete by TLC analysis. Once the starting material was consumed, the reaction mixture was decanted into a separatory funnel and carefully quenched with 0.1 N HCl (500 mL). The organic layer was separated and washed with saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated.[4] The crude mixture was purified via flash chromatography (30% EA in hexanes) to give 2-cyclopropoxyisoindoline-1,3-dione **16a** as a white solid. The same procedure was used to synthesize **16b**-**16g** from the corresponding *N*-enoxyphthalimides.

Characterization of 2-cyclopropoxyisoindoline-1,3-diones

2-cyclopropoxyisoindoline-1,3-dione (16a)



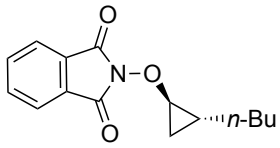
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.40 (tt, *J* = 6.1, 2.7 Hz, 1H), 1.18 – 1.14 (m, 2H), 0.70 – 0.66 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.70 (2C), 134.61 (2C), 129.12 (2C), 123.71 (2C), 61.57, 6.90 (2C).

Yield: 2.16 g, 94%. White solid (m.p. 76.0 °C).

HRMS (ESI): m/z calcd for $[C_{11}H_9NO_3]^+$ ($[M+H]^+$): 204.0655, found 204.0655

2-((1*R*,2*R*)-2-butylcyclopropoxy)isoindoline-1,3-dione (16b)



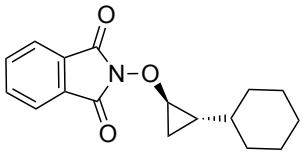
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (td, *J* = 5.2, 3.5 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.11 (dt, *J* = 6.5, 2.4 Hz, 1H), 1.50 (dtd, *J* = 12.9, 9.3, 8.3, 6.0 Hz, 1H), 1.32 – 1.23 (m, 5H), 1.17 (dq, *J* = 17.6, 6.9 Hz, 2H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.49 (q, *J* = 6.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.68 (2C), 134.57 (2C), 129.10 (2C), 123.66 (2C), 67.20, 30.98, 30.62, 22.34, 20.41, 14.05, 13.67.

Yield: 1.23 g, 95%. Tan solid (m.p. 79.9 °C).

HRMS (ESI): m/z calcd for $[C_{15}H_{17}NO_3K]^+$ ($[M+K]^+$): 298.0840, found 298.0858

2-((1*R*,2*S*)-2-cyclohexylcyclopropoxy)isoindoline-1,3-dione (16c)



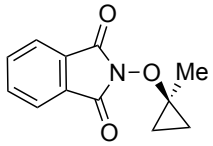
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.16 (dt, *J* = 6.3, 2.5 Hz, 1H), 1.69 – 1.57 (m, 5H), 1.37 (dddd, *J* = 11.3, 9.2, 6.7, 2.3 Hz, 1H), 1.22 (ddd, *J* = 10.6, 6.1, 2.6 Hz, 1H), 1.16 – 1.08 (m, 3H), 1.01 (dddd, *J* = 15.5, 11.6, 7.5, 4.3 Hz, 2H), 0.62 – 0.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.68 (2C), 134.58 (2C), 129.09 (2C), 123.69 (2C), 66.24, 39.40, 32.49, 31.83, 26.92, 26.41, 26.12, 26.08, 12.47.

Yield: 262.5 mg, 92%. White solid (m.p. 109.8 °C).

HRMS (ESI): m/z calcd for $[C_{17}H_{20}NO_3]^+$ ($[M+H]^+$): 286.1438, found 286.1441

2-(1-methylcyclopropoxy)isoindoline-1,3-dione (16d)



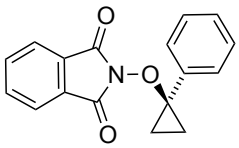
^{1}H NMR (600 MHz, $CDCl_3$) δ.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 1.59 (s, 3H), 1.43 – 1.40 (m, 2H), 0.60 – 0.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.73 (2C), 134.60 (2C), 129.29 (2C), 123.66 (2C), 67.80, 21.05, 14.13 (2C).

Yield: 206.3 mg, 95%. White solid (m.p. 93.4 °C).

HRMS (ESI): m/z calcd for $[C_{12}H_{12}NO_3]^+$ ($[M+H]^+$): 218.0812, found 218.0795

2-(1-phenylcyclopropoxy)isoindoline-1,3-dione (16e)

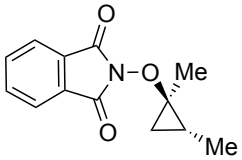


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (ddt, *J* = 19.1, 5.5, 3.2 Hz, 4H), 7.57 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.32 (p, *J* = 3.5 Hz, 3H), 1.85 – 1.80 (m, 2H), 1.14 – 1.10 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.90 (2C), 137.30, 134.43 (4C), 130.27 (2C), 129.05, 128.24 (2C), 123.52 (2C), 72.57, 13.55 (2C).

Yield: 252.0 mg, 90%. White solid.

2-((1*R*,2*R*)-1,2-dimethylcyclopropoxy)isoindoline-1,3-dione (16f)



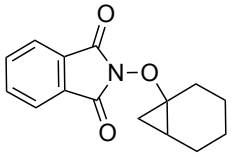
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 1.70 (dp, *J* = 10.5, 6.5 Hz, 1H), 1.55 (s, 3H), 1.55 – 1.52 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.19 (dd, *J* = 7.0, 5.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.90 (2C), 134.59 (2C), 129.37 (2C), 123.67 (2C), 71.26, 20.72, 19.04, 16.55, 13.93.

Yield: 208.1 mg, 90%. White solid (m.p. 111.0 °C).

HRMS (ESI): m/z calcd for $[C_{13}H_{13}NO_3]^+$ ($[M+H]^+$): 254.0788, found 254.0774

2-(bicyclo[4.1.0]heptan-1-yloxy)isoindoline-1,3-dione (16g)



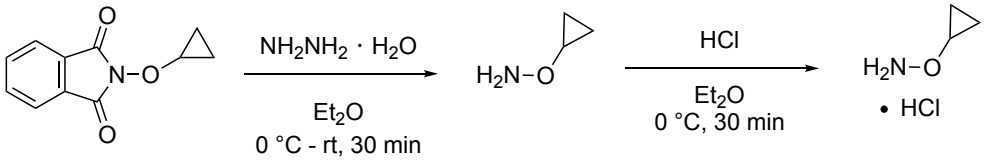
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 2.39 (dddd, *J* = 13.4, 9.5, 5.9, 1.6 Hz, 1H), 2.17 (dt, *J* = 13.4, 5.4 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.85 – 1.73 (m, 1H), 1.56 – 1.47 (m, 2H), 1.42 (dddd, *J* = 14.4, 8.1, 5.9, 1.8 Hz, 1H), 1.24 (dtdd, *J* = 25.6, 13.2, 6.5, 2.9 Hz, 2H), 1.08 (tddd, *J* = 12.8, 9.7, 6.5, 3.9 Hz, 1H), 0.46 (t, *J* = 6.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.91 (2C), 134.57 (2C), 129.31 (2C), 123.64 (2C), 70.70, 28.02, 24.16, 21.60, 21.27, 19.27, 18.46.

Yield: 190.3mg, 74%. Yellow solid (m.p. 75.3 °C).

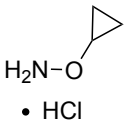
HRMS (ESI): m/z calcd for $[C_{15}H_{16}NO_3]^+$ ($[M+H]^+$): 258.1125, found 258.1110

Preparation and Characterization of Ring-unsubstituted *O*-cyclopropyl Hydroxylamine Hydrochloride Salt



Hydrazine hydrate (50-60 %, 7.5 ml, 118 mmol, 2.8 equiv) was added dropwise (over 3 minutes) to a solution of 2-cyclopropoxyisoindoline-1,3-dione **16a** (8.5 g, 42 mmol, 1.0 equiv) in diethyl ether (167 ml, 0.25 M) at 0 °C. The reaction mixture was allowed to warm to rt and stirred for 30 minutes. The turbid mixture turned clear with a white precipitate. The precipitated diazine byproduct was filtered and washed with diethyl ether (60 ml). The combined ether filtrate was re-cooled to 0 °C and 2M HCl in ether (31.5 ml, 63 mmol, 1.5 equiv) was added over 3 minutes. The flask was stirred at 0 °C for an additional 30 minutes. The mixture was filtered, and the white solid was collected and dried to give the desired O-cyclopropyl hydroxylamine hydrochloride salt **17a** as a white solid.

***O*-cyclopropylhydroxylamine hydrochloride salt (17a)**



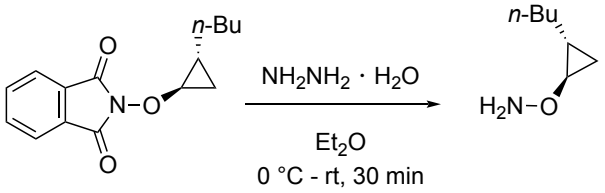
^{1}H NMR (600 MHz, DMSO-*d6*) δ 11.21 (br s, 2H), 4.13 (tt, *J* = 5.8, 2.6 Hz, 1H), 0.88 (q, *J* = 4.6, 3.5 Hz, 2H), 0.67 (qd, *J* = 6.4, 1.4 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-*d6*) δ 57.26, 6.62 (2C).

Yield: 8.55 g, 73%. White solid (m.p. 57.1 °C).

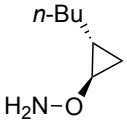
HRMS (CI): m/z calcd for $[C_3H_8NO]^+$ ($[M]^+$): 74.0600, found 74.0607

Preparation and Characterization of Ring-substituted *O*-cyclopropyl Hydroxylamine



Hydrazine hydrate (50-60 %, 0.60 ml, 9.5 mmol, 2.8 equiv) was added dropwise (over 2 minutes) to a solution of 2-((1*R*,2*R*)-2-butylcyclopropoxy)isoindoline-1,3-dione **16b** (877 mg, 3.38 mmol, 1.0 equiv) in diethyl ether (16.9 ml, 0.2 M) at 0 °C. The reaction mixture was removed from the ice bath and allowed to warm to rt. After stirring for 30 minutes, the turbid mixture turned clear with a white precipitate. The precipitated diazine byproduct was filtered and washed with diethyl ether (4.8 ml). The combined filtrate was concentrated and yielded the desired *O*-((1*R*,2*R*)-2-butylcyclopropyl)hydroxylamine product **17b** as a colorless oil.

***O*-((1*R*,2*R*)-2-butylcyclopropyl)hydroxylamine (17b)**



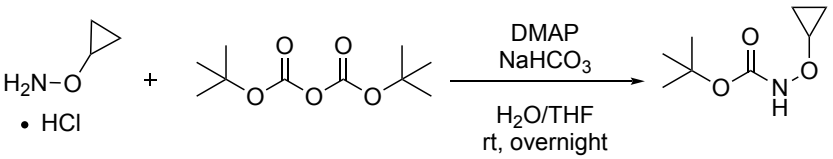
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.33 (br s, 2H), 3.32 (dt, *J* = 5.7, 2.6 Hz, 1H), 1.40 – 1.29 (m, 4H), 1.17 (dh, *J* = 28.7, 7.2 Hz, 2H), 0.98 (dtd, *J* = 16.6, 7.0, 2.3 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.76 (ddd, *J* = 10.0, 5.7, 2.8 Hz, 1H), 0.34 (q, *J* = 6.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 64.42, 31.29, 31.18, 22.53, 19.66, 14.18, 12.90.

Yield: 792 mg, 78%. Colorless oil.

HRMS (CI): m/z calcd for $[C_7H_{16}NO]^+$ ($[M+H]^+$): 130.1226, found 130.1234

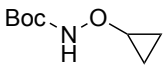
Preparation and Characterization of Unsubstituted *O*-cyclopropyl Hydroxamates



To a suspension of O-cyclopropyl hydroxylamine hydrochloride salt **17a** (3.87 g, 35.3 mmol, 1.0 equiv) in H_2O/THF (3:4, 140 mL, 0.25 M) was slowly added $NaHCO_3$ (2.52g, 30 mmol, 0.85 equiv) at rt. Once the solution became clear, DMAP (43 mg, 0.353 mmol, 1 mol %) was added. Boc_2O (8.08 g, 37.07 mmol, 1.05 equiv) was dissolved in THF (24 mL) and added dropwise to the solution via syringe. The reaction mixture was left stirring at rt overnight. Upon completion via TLC, the reaction mixture was concentrated and re-dissolved in EA (140 mL). The organic layer was separated and washed with $NaHSO_4$, H_2O and brine. The organic layer was then dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue

was purified using flash chromatography (30% EA in hexanes) on a Biotage Isolera system to give the corresponding *tert*-butyl cyclopropoxycarbamate **18a** as a colorless oil.

***tert*-butyl cyclopropoxycarbamate (18a)**

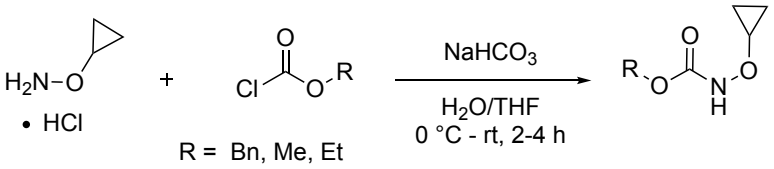


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (br s, 1H), 3.88 (tt, *J* = 5.9, 2.7 Hz, 1H), 1.45 (s, 9H), 0.77 (d, *J* = 7.5 Hz, 2H), 0.56 – 0.47 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 81.6, 58.7, 28.1 (3C), 5.7 (2C).

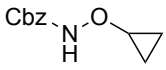
Yield: 4.57 g, 75%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_8H_{15}NO_3]^+$ ($[M+Na]^+$): 196.0944; found 196.0917



A suspension of O-cyclopropyl hydroxylamine hydrochloride salt **17a** (1.1g, 10 mmol) in H_2O/THF (3:4, 40 mL, 0.25 M) was cooled to 0 °C and stirred for 5 min. Then, $NaHCO_3$ (2.52g, 30 mmol, 3.0 equiv) followed by the corresponding chloroformate (i.e. benzyl chloroformate, methyl chloroformate, ethyl chloroformate, 15 mmol, 1.5 equiv) were added at 0 °C. The reaction mixture was removed from the ice bath and allowed to warm to rt. Reaction progress was monitored via TLC. Once the reaction was complete, the mixture was diluted with EA (20 mL). The layers were separated, and the organic layer was washed twice with H_2O, followed by NH_4Cl, and brine. The solution was dried with Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified using flash chromatography (30% EA in hexanes) on a Biotage Isolera system to give the corresponding *N*-protected-*O*-cyclopropyl hydroxamates (**18b-18d**).

benzyl cyclopropoxycarbamate (18b)



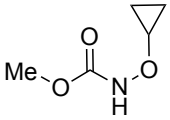
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 6H), 5.19 (s, 2H), 3.96 (tt, *J* = 5.9, 2.8 Hz, 1H), 0.85 – 0.80 (m, 2H), 0.60 – 0.55 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.51, 135.72, 128.75 (2C), 128.60, 128.48 (2C), 67.76, 59.37, 6.03 (2C).

Yield: 497 mg, 78%. White solid (m.p. 56.3 °C).

HRMS (ESI): m/z calcd for $[C_{11}H_{13}NO_3Na]^+$ ($[M+Na]^+$): 230.0788, found 230.0783

methyl cyclopropoxycarbamate (18c)



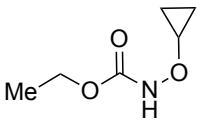
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (br s, 1H), 3.92 (tt, *J* = 5.9, 2.7 Hz, 1H), 3.76 (s, 3H), 0.80 (pd, *J* = 4.5, 3.6, 2.1 Hz, 2H), 0.56 (dddd, *J* = 8.1, 6.8, 5.4, 1.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.21, 59.22, 52.97, 5.91 (2C).

Yield: 233.6 mg, 59%. Colorless liquid.

HRMS (ESI): m/z calcd for $[C_5H_9NO_3K]^+$ ($[M+K]^+$): 170.0214, found 170.0113

ethyl cyclopropoxycarbamate (18d)



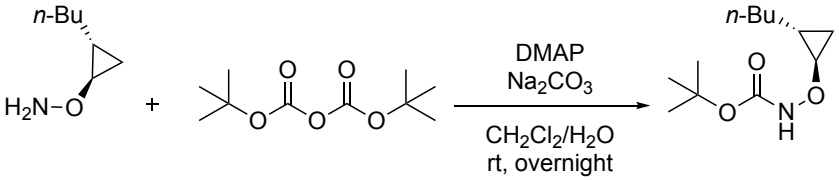
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (br s, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 3.91 (tt, *J* = 6.0, 2.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.83 – 0.78 (m, 2H), 0.57 – 0.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.81, 62.07, 59.14, 14.53, 5.91 (2C).

Yield: 275 mg, 52%. Colorless liquid.

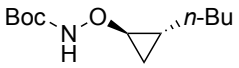
HRMS (ESI): m/z calcd for $[C_6H_{11}NO_3Na]^+$ ($[M+Na]^+$): 168.0631, found 168.0612

Preparation and Characterization of Substituted *O*-cyclopropyl Hydroxamate



To a solution of *O*-((1*R*,2*R*)-2-butylcyclopropyl)hydroxylamine **17b** (370 mg, 2.87 mmol, 1.0 equiv) in CH_2Cl_2/H_2O (4:3, 11.5 mL, 0.25 M) was slowly added $NaHCO_3$ (253 mg, 3.0 mmol, 1.05 equiv) at rt. Once the solution became clear, DMAP (3.5 mg, 28.7 μmol, 1 mol %) was added. Boc_2O (657 mg, 3.0 mmol, 1.05 equiv) was dissolved in THF (2 mL) and added dropwise to the solution via syringe. The reaction mixture was left stirring at rt overnight. Upon completion via TLC, the reaction mixture was concentrated and re-dissolved in EA (11.5 mL). The organic layer was separated and washed with $NaHSO_4$, H_2O and brine. The organic layer was then dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue was purified using flash chromatography (30% EA in hexanes) on a Biotage Isolera system to give the corresponding *tert*-butyl ((2*R*)-2-butylcyclopropoxy)carbamate **18e** as a colorless oil.

***tert*-butyl ((2*R*)-2-butylcyclopropoxy)carbamate (18e)**



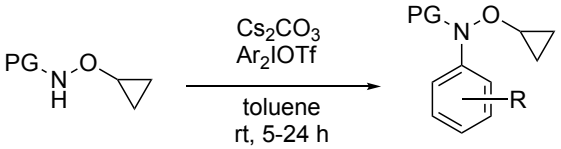
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (br s, 1H), 3.62 (dt, *J* = 6.5, 2.1 Hz, 1H), 1.48 (s, 9H), 1.38 – 1.28 (m, 4H), 1.16 (dqt, *J* = 11.7, 5.9, 3.8 Hz, 3H), 0.91 (ddt, *J* = 8.6, 6.0, 2.7 Hz, 1H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.37 (q, *J* = 5.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.94, 81.82, 64.90, 31.17, 30.94, 28.33 (3C), 22.43, 19.53, 14.15, 12.87.

Yield: 132.0 mg, 72%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{12}H_{23}NO_3Na]^+$ ($[M+Na]^+$): 252.1570, found 252.1559

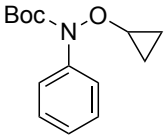
Preparation of *N*-arylated-*O*-cyclopropyl Hydroxamates



In an oven-dried 8 mL vial, *O*-cyclopropyl hydroxamate (0.3 mmol, 1.0 equiv) and cesium carbonate (196mg, 0.6 mmol, 2.0 equiv) were suspended in dry toluene (1.5 mL, 0.1 M). The desired diaryliodonium salt (0.45 mmol, 1.5 equiv) was added at room temperature in one portion. The mixture was stirred for 5-24 hours at room temperature, until TLC indicated complete consumption of the *O*-cyclopropyl hydroxamate starting material. Upon reaction completion, the mixture was filtered through celite. The celite was washed four times with ethyl acetate (5 ml each), the filtrate was collected, and the solvent was removed in vacuo. The crude product was purified using flash chromatography (10% EA in hexanes) on a Biotage Isolera system to give the desired *N*-arylated-*O*-cylcopropyl hydroxamate products.

Characterization of *N*-arylated-*O*-cyclopropyl Hydroxamates

***tert*-butyl cyclopropoxy(phenyl)carbamate (19a)**



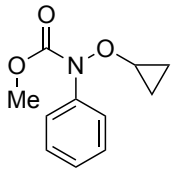
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 15.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.00 (tt, *J* = 6.1, 2.8 Hz, 1H), 1.53 (s, 9H), 0.87 (dp, *J* = 6.2, 3.2 Hz, 2H), 0.53 (qd, *J* = 6.3, 1.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.08, 141.53, 128.49 (2C), 125.63, 122.75 (2C), 82.23, 58.04, 28.33 (3C), 5.68 (2C).

Yield: 510 mg, 63%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{14}H_{19}NO_3Na]^+$ ($[M+Na]^+$): 272.1257, found 272.1268

methyl cyclopropoxy(phenyl)carbamate (19b)



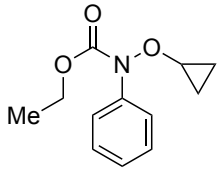
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.02 (tt, *J* = 6.0, 2.8 Hz, 1H), 3.82 (s, 3H), 0.85 (dtt, *J* = 4.8, 3.2, 2.1 Hz, 2H), 0.56 – 0.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.68, 141.02, 128.77 (2C), 126.41, 123.31 (2C), 58.38, 53.55, 5.71 (2C).

Yield: 241 mg, 55%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{11}H_{13}NO_3+H]^+$ [-H_2O]([M]): 190.0868, found 190.0857

ethyl cyclopropoxy(phenyl)carbamate (19c)



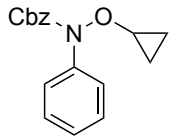
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.9 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.02 (dt, *J* = 6.3, 3.3 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.88 – 0.84 (m, 2H), 0.56 – 0.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.21, 141.16, 128.73 (2C), 126.16, 123.07 (2C), 62.70, 58.35, 14.65, 5.74 (2C).

Yield: 254 mg, 57%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{12}H_{15}NO_3Na]^+$ ($[M+Na]^+$): 244.0944, found 244.0926

benzyl cyclopropoxy(phenyl)carbamate (19d)



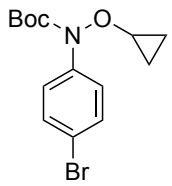
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.39 – 7.31 (m, 4H), 7.23 – 7.19 (m, 1H), 5.26 (s, 1H), 4.02 (tt, *J* = 6.0, 2.9 Hz, 1H), 0.86 – 0.82 (m, 1H), 0.52 (ddd, *J* = 5.4, 4.1, 2.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.03, 140.96, 136.00, 128.75 (3C), 128.66 (2C), 128.35, 128.17 (2C), 126.34, 123.21, 68.11, 58.40, 5.76 (2C).

Yield: 35 mg, 62%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{17}H_{17}NO_3Na]^+$ ($[M+Na]^+$): 306.1101, found 306.1105

***tert*-butyl (4-bromophenyl)(cyclopropoxy)carbamate (19e)**



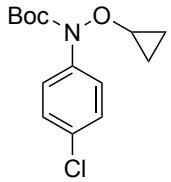
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 3.98 (tq, *J* = 6.8, 4.0, 3.4 Hz, 1H), 1.52 (s, 9H), 0.91 – 0.83 (m, 2H), 0.58 – 0.51 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 140.6, 131.4, 123.8, 118.5, 82.7, 58.2, 28.2, 5.6.

Yield: 13 mg, 12%. Colorless liquid.

HRMS (ESI): m/z calcd for $[C_{14}H_{18}BrNO_3Na]^+$ ($[M+Na]^+$): 350.0362; found 350.0381

***tert*-butyl (4-chlorophenyl)(cyclopropoxy)carbamate (19f)**



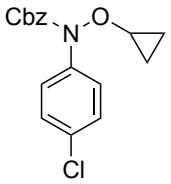
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.31 – 7.28 (m, 2H), 4.00 – 3.96 (m, 1H), 1.52 (s, 9H), 0.85 (th, *J* = 2.8, 1.5 Hz, 2H), 0.54 (dq, *J* = 6.1, 1.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.86, 140.24, 130.87, 128.63 (2C), 123.74 (2C), 82.75, 58.31, 28.36 (3C), 5.76 (2C).

Yield: 18 mg, 21%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{14}H_{18}ClNO_3Na]^+$ ($[M+Na]^+$): 306.0867, found 306.0856

benzyl (4-chlorophenyl)(cyclopropoxy)carbamate (19g)



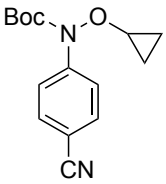
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 7H), 7.33 – 7.30 (m, 2H), 5.26 (s, 2H), 4.01 (dt, *J* = 6.2, 3.2 Hz, 1H), 0.83 (tt, *J* = 5.2, 3.1 Hz, 2H), 0.55 – 0.50 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.79, 154.80, 139.61, 135.77, 131.56, 128.85 (2C), 128.73 (2C), 128.50, 128.27 (2C), 124.07, 68.36, 58.64, 5.80 (2C).

Yield: 35.2 mg, 38%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{17}H_{16}ClNO_3Na]^+$ ($[M+Na]^+$): 340.0711, found 340.0697

***tert*-butyl (4-cyanophenyl)(cyclopropoxy)carbamate (19h)**

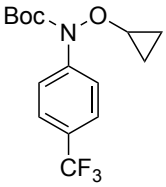


^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 4.02 (tt, *J* = 6.0, 2.8 Hz, 1H), 1.56 (s, 9H), 0.94 – 0.89 (m, 2H), 0.61 – 0.56 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.8, 145.2, 132.5, 120.5, 118.8, 107.5, 83.6, 58.7, 28.2, 5.7.

Yield: 23 mg, 27%. Colorless oil.

***tert*-butyl cyclopropoxy(4-(trifluoromethyl)phenyl)carbamate (19i)**



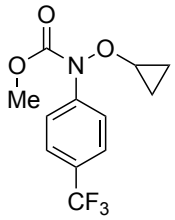
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (q, *J* = 8.9 Hz, 4H), 4.02 (s, 1H), 1.55 (s, 9H), 0.90 (s, 2H), 0.57 (q, *J* = 6.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 153.3, 144.5, 126.6 (q, *J* = 32.7 Hz), 125.58 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.6 Hz), 120.9, 83.1, 58.5, 28.2, 5.7.

Yield: 39 mg, 41%. Colorless liquid.

HRMS (ESI): m/z calcd for $[C_{15}H_{18}F_3NO_3Na]^+$ ($[M+Na]^+$): 340.1131; found 340.1150

methyl cyclopropoxy(4-(trifluoromethyl)phenyl)carbamate (19j)



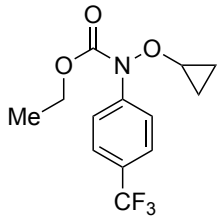
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (q, *J* = 9.1 Hz, 4H), 4.05 (tt, *J* = 6.1, 2.8 Hz, 1H), 3.87 (s, 3H), 0.88 (qt, *J* = 3.9, 2.2 Hz, 2H), 0.57 (dq, *J* = 6.2, 1.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.06, 144.08, 127.34 (q, *J* = 32.8 Hz), 125.91 (2C, q, *J* = 3.8 Hz), 125.04 (q, *J* = 286.9 Hz), 121.31 (2C), 58.99, 53.83, 5.79 (2C).

Yield: 165.6 mg, 60%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{12}H_{13}F_3NO_3]^+$ ($[M+H]^+$): 276.0842, found 276.0859

ethyl cyclopropoxy(4-(trifluoromethyl)phenyl)carbamate (19k)



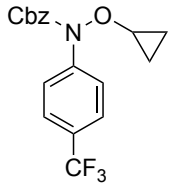
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.05 (tt, *J* = 6.0, 2.8 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.90 (q, *J* = 5.8, 5.2 Hz, 2H), 0.60 – 0.54 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.57, 144.19, 127.15 (q, *J* = 32.7 Hz), 125.87 (2C, q, *J* = 3.7 Hz), 124.18 (q, *J* = 271.8 Hz), 121.14 (2C), 63.16, 58.92, 14.56, 5.82 (2C).

Yield: 39.0 mg, 67%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{13}H_{15}F_3NO_3]^+$ ($[M+H]^+$): 290.0999, found 290.1002

benzyl cyclopropoxy(4-(trifluoromethyl)phenyl)carbamate (19l)



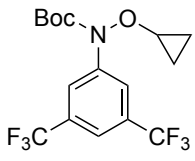
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.45 – 7.34 (m, 5H), 5.30 (s, 2H), 4.06 (tt, *J* = 6.1, 2.8 Hz, 1H), 0.92 – 0.86 (m, 2H), 0.56 (h, *J* = 5.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.33, 143.93, 135.45, 128.68 (2C), 128.53, 128.29 (2C), 127.18 (q, *J* = 32.7 Hz), 125.79 (2C, q, *J* = 3.7 Hz), 124.04 (q, *J* = 271.8 Hz), 121.14 (2C), 68.50, 58.90, 5.74 (2C).

Yield: 69.2 mg, 66%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{18}H_{16}F_3NO_3Na]^+$ ($[M+Na]^+$): 374.0974, found 374.0985

***tert*-butyl (3,5-bis(trifluoromethyl)phenyl)(cyclopropoxy)carbamate (19m)**



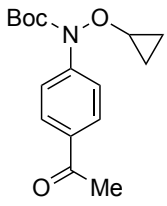
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.62 (s, 1H), 4.03 (tt, *J* = 6.0, 2.8 Hz, 1H), 1.56 (s, 9H), 0.99 – 0.88 (m, 2H), 0.61 (q, *J* = 6.7, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.8, 143.0, 131.8 (q, *J* = 33.5 Hz), 123.2 (q, *J* = 272.7 Hz), 120.6 (q, *J* = 3.8 Hz), 117.9 (pent, *J* = 3.8 Hz), 83.9, 58.9, 28.1, 5.8.

Yield: 72 mg, 62%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{17}F_6NO_3Na]^+$ ($[M+Na]^+$): 408.1005; found 408.1018

***tert*-butyl (3-acetylphenyl)(cyclopropoxy)carbamate (19n)**



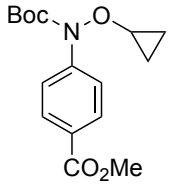
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 4.03 (tt, *J* = 6.0, 2.8 Hz, 1H), 2.57 (s, 3H), 1.55 (s, 9H), 0.96 – 0.87 (m, 2H), 0.56 (tt, *J* = 6.7, 3.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.9, 152.9, 145.4, 133.2, 128.8, 120.2, 83.0, 58.5, 28.1, 26.4, 5.6.

Yield: 41 mg, 47%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{21}NO_4Na]^+$ ($[M+Na]^+$): 314.1363; found 314.1379

***tert*-butyl cyclopropoxy(4-(trifluoromethyl)phenyl)carbamate (19o)**



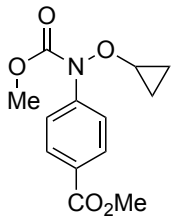
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 4.02 (tt, *J* = 5.9, 2.7 Hz, 1H), 3.90 (s, 3H), 1.55 (s, 9H), 0.91 (d, *J* = 7.6 Hz, 2H), 0.55 (q, *J* = 6.1 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 153.1, 145.4, 130.0, 126.1, 120.3, 82.9, 58.5, 52.0, 28.2, 5.6.

Yield: 42 mg, 45%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{21}NO_5Na]^+$ ($[M+Na]^+$): 330.1312; found 330.1333

methyl 4-(cyclopropoxy(methoxycarbonyl)amino)benzoate (19p)



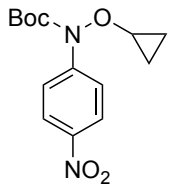
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.8, 2.9 Hz, 2H), 7.52 (dd, *J* = 8.8, 2.8 Hz, 2H), 4.04 (tq, *J* = 6.1, 3.0 Hz, 1H), 3.89 (d, *J* = 3.1 Hz, 3H), 3.85 (d, *J* = 3.0 Hz, 3H), 0.90 – 0.85 (m, 2H), 0.57 – 0.52 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.57, 154.86, 144.94, 130.28 (2C), 126.79, 120.60 (2C), 58.94, 53.75, 52.16, 5.74 (2C).

Yield: 46.3 mg, 56%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{13}H_{15}NO_5Na]^+$ ($[M+Na]^+$): 288.0842, found 288.0838

***tert*-butyl cyclopropoxy(4-nitrophenyl)carbamate (19q)**



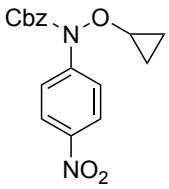
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 2H), 4.08 – 4.03 (m, 1H), 1.58 (s, 9H), 0.94 (tq, *J* = 5.4, 3.2 Hz, 2H), 0.63 – 0.58 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.77, 147.06, 143.95, 124.41 (2C), 120.03 (2C), 83.99, 59.06, 28.32 (3C), 5.92 (2C).

Yield: 195.0 mg, 66%. Yellow solid (m.p. 58.2 °C).

HRMS (ESI): m/z calcd for $[C_{14}H_{18}N_2O_5Na]^+$ ($[M+Na]^+$): 317.1108, found 317.1080

benzyl cyclopropoxy(4-nitrophenyl)carbamate (19r)



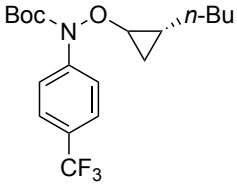
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.2 Hz, 2H), 7.66 (d, *J* = 9.2 Hz, 2H), 7.45 – 7.35 (m, 5H), 5.31 (s, 2H), 4.07 (tt, *J* = 6.1, 2.9 Hz, 1H), 0.94 – 0.87 (m, 2H), 0.61 – 0.55 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.96, 146.49, 144.32, 135.22, 128.89 (2C), 128.85, 128.55 (2C), 124.53 (2C), 120.21 (2C), 69.02, 59.49, 5.98 (2C).

Yield: 283.4 mg, 86%. Yellow solid (m.p. 86.6 °C).

HRMS (ESI): m/z calcd for $[C_{17}H_{16}N_2O_5Na]^+$ ($[M+Na]^+$): 351.0951, found 351.0939

***tert*-butyl ((2*R*)-2-butylcyclopropoxy)(4-(trifluoromethyl)phenyl)carbamate (19s)**



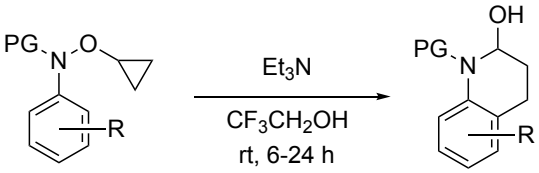
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 3.71 (dt, *J* = 6.2, 2.3 Hz, 1H), 1.55 (s, 9H), 1.31 – 1.19 (m, 6H), 1.07 – 0.98 (m, 2H), 0.88 – 0.84 (m, 3H), 0.39 (q, *J* = 6.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.2, 144.4, 126.6 (q, *J* = 32.7 Hz, 2C), 125.6 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.6 Hz), 120.9 (2C), 83.0, 64.4, 31.0, 30.8, 28.2 (3C), 22.2, 19.1, 14.0, 12.7.

Yield: 50 mg, 45%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{19}H_{26}F_3NO_3Na]^+$ ($[M+Na]^+$): 396.1757; found 396.1736

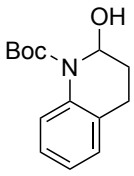
Preparation of 2-Hydroxy-tetrahydroquinolines via *[3,3]*-Rearrangement of *N*-arylated-O-cyclopropyl Hydroxamates



N-arylated-*O*-cyclopropyl hydroxamate (50 mg, 0.2 mmol, 1.0 equiv) was added to an 8 mL oven-dried vial equipped with a stir bar. The vial was capped, placed under argon atmosphere and trifluoroethanol (2.0 mL, 0.1M) was added. Triethylamine (55.8 µL, 0.4 mmol, 2.0 equiv) was then added to the solution via syringe. The reaction mixture was stirred at rt for 6-24 hours. After complete consumption of the starting material was confirmed via TLC, the reaction mixture was concentrated under reduced pressure. The crude mixture was then purified using flash chromatography (12 % EA in hexanes) on a Biotage Isolera system to give the desired tetrahydroquinoline products.

Characterization of 2-hydroxy-tetrahydroquinolines

tert-butyl 2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20a)



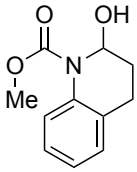
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 6.0 Hz, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 5.80 (ddd, *J* = 7.3, 5.9, 3.3 Hz, 1H), 3.92 (br s, 1H), 2.67 (ddd, *J* = 14.8, 6.6, 3.8 Hz, 1H), 2.54 (ddd, *J* = 14.7, 10.9, 3.6 Hz, 1H), 2.24 (dtd, *J* = 12.8, 6.2, 3.6 Hz, 1H), 1.79 (dddd, *J* = 13.3, 11.0, 7.3, 3.8 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.79, 136.48, 132.13, 127.34, 126.37, 123.94, 123.65, 82.21, 79.15, 31.16, 28.53 (3C), 24.75.

Yield: 276 mg, 60%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{14}H_{20}NO_3]^+$ ($[M+H]^+$): 250.1438; found 250.1440

methyl 2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20b)



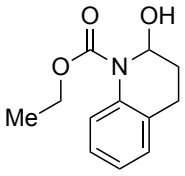
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.87 (dq, *J* = 6.8, 2.2 Hz, 1H), 4.04 (br s, 1H), 3.83 (s, 3H), 2.68 (ddd, *J* = 14.9, 6.7, 3.9 Hz, 1H), 2.54 (ddd, *J* = 14.8, 10.8, 3.8 Hz, 1H), 2.25 (dtd, *J* = 12.9, 6.3, 3.8 Hz, 1H), 1.80 (dddd, *J* = 13.4, 10.9, 7.1, 3.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.12, 135.91, 132.20, 127.39, 126.54, 124.13, 123.84, 79.09, 53.18, 31.08, 24.52.

Yield: 65 mg, 46%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{11}H_{14}NO_3]^+$ ($[M+H]^+$): 208.0968, found 208.0961

ethyl 2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20c)



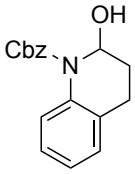
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 6.5 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.86 (td, *J* = 6.5, 2.8 Hz, 1H), 4.34 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.26 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.01 (br s, 1H), 2.69 (ddd, *J* = 14.9, 6.7, 3.9 Hz, 1H), 2.55 (ddd, *J* = 14.8, 10.7, 3.8 Hz, 1H), 2.25 (dtd, *J* = 12.9, 6.3, 3.7 Hz, 1H), 1.80 (dddd, *J* = 14.0, 10.9, 7.1, 3.9 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.69, 136.04, 132.14, 127.39, 126.50, 123.97, 123.85, 79.06, 62.39, 31.05, 24.56, 14.55.

Yield: 25.2 mg, 57%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{12}H_{15}NO_3Na]^+$ ($[M+Na]^+$): 244.0944, found 244.0924

benzyl 2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20d)



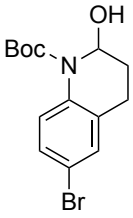
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.17 (td, *J* = 7.8, 1.7 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.03 (td, *J* = 7.4, 1.2 Hz, 1H), 5.89 (ddd, *J* = 7.1, 5.9, 3.5 Hz, 1H), 5.34 (d, *J* = 12.3 Hz, 1H), 5.25 (d, *J* = 12.3 Hz, 1H), 3.83 (br s, 1H), 2.70 (ddd, *J* = 14.9, 6.7, 3.9 Hz, 1H), 2.55 (ddd, *J* = 14.7, 10.7, 3.7 Hz, 1H), 2.25 (dtd, *J* = 12.9, 6.3, 3.7 Hz, 1H), 1.81 (dddd, *J* = 13.4, 10.9, 7.1, 3.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.50, 135.94, 135.87, 132.19, 128.80 (2C), 128.52, 128.31(2C), 127.45, 126.61, 124.16, 123.91, 79.29, 68.08, 31.06, 24.57.

Yield: 18.6 mg, 53%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{17}H_{17}NO_3Na]^+$ ($[M+Na]^+$): 306.1101, found 306.1107

***tert*-butyl 6-bromo-2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20e)**



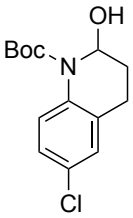
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.26 (s, 1H), 5.84 – 5.77 (m, 1H), 3.95 (br s, 1H), 2.68 (ddd, *J* = 15.0, 6.9, 3.9 Hz, 1H), 2.54 (ddd, *J* = 14.5, 10.4, 3.4 Hz, 1H), 2.20 (dtd, *J* = 13.1, 6.4, 3.8 Hz, 1H), 1.82 (dddd, *J* = 13.8, 10.6, 6.9, 3.9 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.32, 135.62, 134.05, 130.13, 129.26, 125.41, 116.37, 82.60, 76.95, 30.70, 28.48 (3C), 24.41.

Yield: 76.8 mg, 52%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{14}H_{19}BrNO_3]^+$ ($[M+H]^+$): 328.0543; found 328.0534

***tert*-butyl 6-chloro-2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20f)**



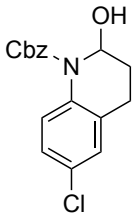
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 1H), 7.12 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.10 – 7.08 (m, 1H), 5.78 (ddd, *J* = 7.0, 5.8, 3.2 Hz, 1H), 3.88 (br s, 1H), 2.66 (ddd, *J* = 15.0, 6.9, 3.8 Hz, 1H), 2.52 (ddd, *J* = 14.7, 10.5, 3.7 Hz, 1H), 2.23 – 2.16 (m, 1H), 1.80 (dddd, *J* = 13.4, 10.7, 7.0, 3.9 Hz, 1H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.42, 135.09, 133.69, 128.62, 127.22, 126.35, 125.06, 82.60, 78.87, 30.75, 28.51 (3C), 24.52.

Yield: 27 mg, 60%. White solid (m.p. 108.4 °C).

HRMS (ESI): m/z calcd for $[C_{14}H_{18}ClNO_3Na]^+$ ($[M+Na]^+$): 306.0867, found 306.0857

benzyl 6-chloro-2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20g)



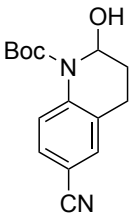
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.41 – 7.37 (m, 4H), 7.37 – 7.34 (m, 1H), 7.14 – 7.09 (m, 2H), 5.87 (ddd, *J* = 6.8, 5.7, 3.5 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 3.76 (br s, 1H), 2.69 (ddd, *J* = 15.0, 7.1, 3.9 Hz, 1H), 2.53 (ddd, *J* = 14.7, 10.2, 3.7 Hz, 1H), 2.20 (dddd, *J* = 13.1, 7.0, 5.7, 3.8 Hz, 1H), 1.82 (dddd, *J* = 13.8, 10.5, 6.8, 3.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) 155.16, 135.64, 134.57, 133.69, 129.16, 128.89 (2C), 128.69, 128.39 (2C), 127.37, 126.62, 125.00, 79.02, 68.29, 30.61, 24.34.

Yield: 15.4 mg, 22%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{17}H_{16}ClNO_3Na]^+$ ($[M+Na]^+$): 340.0711, found 340.0693

***tert*-butyl 6-cyano-2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20h)**



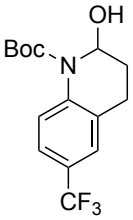
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.40 (s, 1H), 5.81 (td, *J* = 5.9, 3.5 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 2.78 (ddd, *J* = 15.0, 7.9, 3.9 Hz, 1H), 2.58 (ddd, *J* = 14.7, 9.5, 3.7 Hz, 1H), 2.14 (ddt, *J* = 13.2, 8.5, 4.6 Hz, 1H), 1.89 (tdd, *J* = 13.4, 6.4, 3.9 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 153.8, 140.7, 132.1, 131.2, 130.3, 123.7, 119.0, 106.3, 83.3, 78.6, 29.9, 28.3 (3C), 23.9.

Yield: 54 mg, 66%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{15}H_{19}N_2O_3]^+$ ($[M+H]^+$): 275.1390; found 275.1379

***tert*-butyl 2-hydroxy-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (20i)**



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 1H), 5.82 (q, *J* = 6.0 Hz, 1H), 3.92 (s, 1H), 2.77 (ddd, *J* = 14.5, 6.9, 3.6 Hz, 1H), 2.65 – 2.53 (m, 1H), 2.25 – 2.12 (m, 1H), 1.86 (dtt, *J* = 13.5, 6.9, 3.9 Hz, 1H), 1.57 (s, 9H).

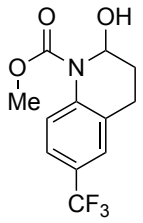
^{13}C NMR (151 MHz, $CDCl_3$): δ 154.2, 139.6, 131.9, 125.2 (q, *J* = 32.6 Hz), 124.4 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 242.3 Hz), 123.5, 123.3 (q, *J* = 3.7 Hz), 82.9, 78.8, 30.3, 28.4 (3C), 24.3.

^{19}F NMR (471 MHz, $CDCl_3$) −62.03 (s).

Yield: 74 mg, 78%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{15}H_{18}F_3NO_3Na]^+$ ($[M+Na]^+$): 340.1131; found 340.1101

methyl 2-hydroxy-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (20j)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.38 (s, 1H), 5.88 (t, *J* = 6.0 Hz, 1H), 3.90 (br s, 1H), 3.87 (s, 3H), 2.80 (ddd, *J* = 15.2, 7.7, 4.0 Hz, 1H), 2.60 (ddd, *J* = 14.6, 9.7, 3.8 Hz, 1H), 2.20 (dddd, *J* = 13.3, 7.7, 5.5, 3.9 Hz, 1H), 1.89 (dddd, *J* = 13.6, 10.2, 6.6, 4.0 Hz, 1H).

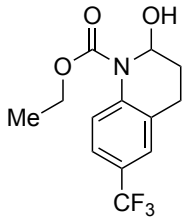
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.74, 139.18, 132.03, 125.83 (q, *J* = 32.6 Hz), 124.67 (q, *J* = 3.9 Hz), 124.26 (q, *J* = 271.6 Hz), 123.75 (q, *J* = 3.7 Hz), 123.58, 78.95, 53.55, 30.33, 24.27.

^{19}F NMR (471 MHz, $CDCl_3$) −62.12 (s).

Yield: 25.3 mg, 52%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{12}H_{12}F_3NO_3K]^+$ ($[M+K]^+$): 314.0401, found 314.0296

ethyl 2-hydroxy-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (20k)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.38 (s, 1H), 5.88 (ddd, *J* = 6.5, 5.4, 3.4 Hz, 1H), 4.40 – 4.28 (m, 2H), 3.89 (br s, 1H), 2.80 (ddd, *J* = 15.1, 7.6, 3.9 Hz, 1H), 2.61 (ddd, *J* = 14.6, 9.8, 3.8 Hz, 1H), 2.20 (dddd, *J* = 13.2, 7.6, 5.5, 3.8 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

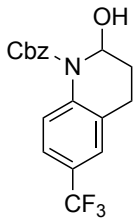
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.30, 139.30, 132.01, 125.69 (q, *J* = 32.6 Hz), 124.64 (q, *J* = 3.8 Hz), 124.30 (q, *J* = 271.6 Hz), 123.57, 123.70 (q, *J* = 3.7 Hz), 78.92, 62.89, 30.33, 24.32, 14.57.

^{19}F NMR (471 MHz, $CDCl_3$) −62.09 (s).

Yield: 20.0 mg, 51%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{13}H_{14}F_3NO_3Na]^+$ ($[M+Na]^+$): 312.0818, found 312.0808

benzyl 2-hydroxy-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (20l)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.33 (m, 7H), 5.91 (td, *J* = 6.0, 3.4 Hz, 1H), 5.34 (d, *J* = 12.2 Hz, 1H), 5.28 (d, *J* = 12.2 Hz, 1H), 3.85 (br s, 1H), 2.80 (ddd, *J* = 15.2, 7.8, 3.9 Hz, 1H), 2.61 (ddd, *J* = 14.6, 9.7, 3.8 Hz, 1H), 2.19 (dp, *J* = 13.2, 4.3 Hz, 1H), 1.89 (dddd, *J* = 13.6, 10.0, 6.5, 3.9 Hz, 1H).

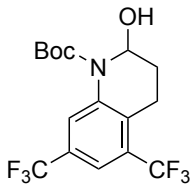
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.06, 139.15, 135.46, 132.00, 128.93 (2C), 128.79, 128.48 (2C), 125.81 (q, *J* = 32.6 Hz), 124.68 (q, *J* = 3.8 Hz), 124.27 (q, *J* = 271.7 Hz), 123.72 (q, *J* = 3.8 Hz), 123.61, 78.95, 68.50, 30.29, 24.22.

^{19}F NMR (471 MHz, $CDCl_3$) −62.10 (s).

Yield: 69.2 mg, 65%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{18}H_{16}F_3NO_3Na]^+$ ($[M+Na]^+$): 374.0974, found 374.0969

***tert*-butyl 2-hydroxy-5,7-bis(trifluoromethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (20m)**



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.60 (s, 1H), 5.85 (td, *J* = 6.8, 3.4 Hz, 1H), 3.96 (s, 1H), 3.03 (d, *J* = 15.5 Hz, 1H), 2.61 (t, *J* = 12.7 Hz, 1H), 2.28 (dtd, *J* = 13.0, 6.3, 3.6 Hz, 1H), 1.79 (dddd, *J* = 14.0, 11.0, 7.3, 3.3 Hz, 1H), 1.55 (s, 9H);

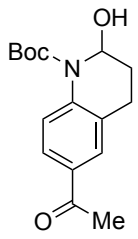
^{13}C NMR (151 MHz, $CDCl_3$): δ 153.9, 138.6, 135.2, 128.37 (p, *J* = 32.1, 30.8 Hz), 126.15 (d, *J* = 7.0 Hz), 124.74 (q, *J* = 3.9 Hz), 124.33 (d, *J* = 5.4 Hz), 122.52 (d, *J* = 3.7 Hz), 117.68 – 117.41 (m), 83.5, 78.4, 30.1, 28.2 (3C), 20.8.

^{19}F NMR (471 MHz, $CDCl_3$) −60.39 (s), -62.96 (s).

Yield: 60 mg, 52%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{18}F_6NO_3]^+$ ($[M+H]^+$): 386.1185; found 386.1190

***tert*-butyl 7-acetyl-2-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (20n)**



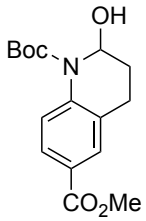
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.72 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 5.81 (q, *J* = 6.1 Hz, 1H), 4.00 – 3.96 (m, 1H), 2.79 (ddd, *J* = 14.5, 7.2, 3.6 Hz, 1H), 2.61 (ddd, *J* = 14.3, 10.2, 3.2 Hz, 1H), 2.56 (s, 3H), 2.17 (dt, *J* = 12.4, 6.2 Hz, 1H), 1.87 (dtt, *J* = 13.5, 6.9, 3.9 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 197.2, 154.1, 140.9, 132.1, 131.3, 127.6, 126.8, 123.0, 82.9, 78.8, 30.3, 28.3 (3C), 26.4, 24.3.

Yield: 58 mg, 67%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{22}NO_4]^+$ ($[M+H]^+$): 292.1543; found 292.1542

1-(*tert*-butyl) 6-methyl 2-hydroxy-3,4-dihydroquinoline-1,6(2*H*)-dicarboxylate (20o)



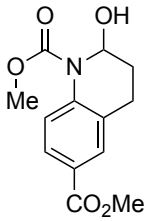
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 10.3 Hz, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 5.80 (td, *J* = 6.3, 3.4 Hz, 1H), 3.98 (s, 1H), 3.89 (s, 3H), 2.77 (ddd, *J* = 14.8, 7.3, 3.8 Hz, 1H), 2.59 (ddd, *J* = 14.4, 10.1, 3.4 Hz, 1H), 2.17 (dq, *J* = 13.0, 7.5, 5.5 Hz, 1H), 1.85 (dddd, *J* = 13.6, 10.3, 6.8, 3.8 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 154.2, 140.7, 131.3, 128.8, 127.8, 124.7, 123.1, 82.8, 78.9, 51.9, 30.3, 28.3 (3C), 24.2.

Yield: 63 mg, 68%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{16}H_{22}NO_5]^+$ ($[M+H]^+$): 308.1492; found 308.1480

dimethyl 2-hydroxy-3,4-dihydroquinoline-1,6(2*H*)-dicarboxylate (20p)



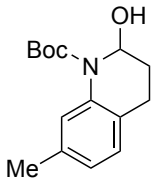
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 1H), 7.80 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 5.87 (td, *J* = 6.1, 3.0 Hz, 1H), 3.97 (br s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.79 (ddd, *J* = 15.1, 7.7, 4.0 Hz, 1H), 2.59 (ddd, *J* = 14.5, 9.7, 3.8 Hz, 1H), 2.18 (dddd, *J* = 13.3, 7.7, 5.4, 3.8 Hz, 1H), 1.90 – 1.83 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 155.79, 140.33, 131.42, 129.08, 128.24, 125.37, 123.11, 79.12, 53.53, 52.14, 30.36, 24.20.

Yield: 35 mg, 45%. Yellow oil.

HRMS (ESI): m/z calcd for $[C_{13}H_{15}NO_5Na]^+$ ($[M+Na]^+$): 288.0842, found 288.0838

***tert*-butyl 2-hydroxy-7-methyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (20q)**



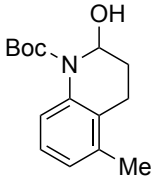
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.78 (td, *J* = 7.2, 3.2 Hz, 1H), 3.88 (s, 1H), 2.63 (ddd, *J* = 14.7, 6.4, 3.9 Hz, 1H), 2.50 (ddd, *J* = 14.6, 11.0, 3.4 Hz, 1H), 2.31 (s, 3H), 2.22 (dtd, *J* = 12.7, 6.2, 3.7 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.56 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.6, 136.1, 135.8, 128.9, 126.9, 124.4, 124.2, 81.9, 78.9, 31.1, 28.4 (3C), 24.1, 21.3.

Yield: 16 mg, 20%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{15}H_{22}NO_3]^+$ ($[M+H]^+$): 264.1594; found 264.1577

***tert*-butyl 2-hydroxy-5-methyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (20r)**



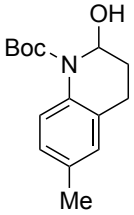
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.2 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 5.83 (td, *J* = 7.0, 3.2 Hz, 1H), 3.74 (s, 1H), 2.74 (ddd, *J* = 15.3, 6.6, 4.2 Hz, 1H), 2.40 (ddd, *J* = 14.9, 10.6, 3.8 Hz, 1H), 2.28 (s, 3H), 2.24 (dtd, *J* = 13.0, 6.2, 4.1 Hz, 1H), 1.76 (dddd, *J* = 13.4, 11.0, 7.2, 4.1 Hz, 1H), 1.54 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.7, 136.1, 134.5, 130.6, 125.4, 125.3, 122.1, 81.9, 78.5, 30.6, 28.4 (3C), 20.5, 19. 6.

Yield: 18 mg, 22%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{15}H_{21}NO_3Na]^+$ ($[M+Na]^+$): 286.1414; found 286.1418

***tert*-butyl 2-hydroxy-6-methyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (20s)**



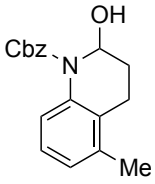
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.91 (s, 1H), 5.78 (td, *J* = 7.2, 3.3 Hz, 1H), 3.90 (s, 1H), 2.62 (ddd, *J* = 14.7, 6.3, 3.9 Hz, 1H), 2.51 (ddd, *J* = 14.6, 11.1, 3.4 Hz, 1H), 2.29 (s, 3H), 2.26 – 2.18 (m, 1H), 1.77 (dddd, *J* = 13.3, 11.1, 7.3, 3.8 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.7, 133.8, 133.0, 131.8, 127.8, 126.8, 123.6, 81.9, 79.0, 31.1, 28.4 (3C), 24.6, 20.7.

Yield: 30 mg, 38%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{15}H_{21}NO_3Na]^+$ ($[M+Na]^+$): 286.1414, found 286.1404

benzyl 2-hydroxy-5-methyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (20t)



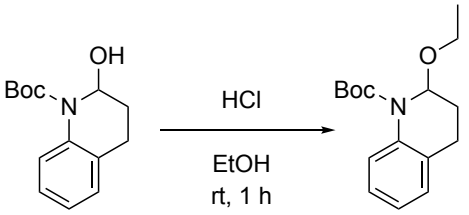
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (q, *J* = 7.6, 7.1 Hz, 4H), 7.37 – 7.33 (m, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 5.89 – 5.84 (m, 1H), 5.36 (d, *J* = 12.3 Hz, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 3.77 (s, 1H), 2.71 – 2.59 (m, 1H), 2.55 – 2.46 (m, 1H), 2.28 (s, 3H), 2.27 – 2.20 (m, 1H), 1.78 (dddd, *J* = 13.6, 11.0, 7.2, 3.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.3, 136.1, 135.7, 135.5, 129.0, 128.6, 128.4, 128.1, 127.0, 124.8, 124.4, 79.2, 67.9, 31.1, 24.0, 21.3.

Yield: 37 mg, 41%. Colorless oil.

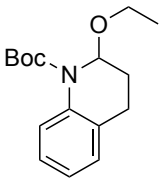
HRMS (ESI): m/z calcd for $[C_{18}H_{19}NO_3Na]^+$ ($[M+Na]^+$): 320.1257; found 320.1243

Preparation of Derivatized 2-hydroxy-tetrahydroquinoline Products



Tert-butyl 2-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate **20a** (50 mg, 0.2 mmol, 1.0 equiv) was dissolved in EtOH (1 mL, 0.2 M). At room temperature, 2M HCl in Et_2O (200 µL, 0.4 mmol, 2.0 equiv) was added in two equal portions (100 µL each). The reaction was left stirring at rt for 1 h. Upon reaction completion the mixture was quenched with aq. $NaHCO_3$ (2 mL). The organic layer was separated, washed with brine, dried over $MgSO_4$ and concentrated. The crude residue was purified using flash chromatography (20% EA in hexanes) on a Biotage Isolera system to give the corresponding *tert*-butyl 2-ethoxy-3,4-dihydroquinoline-1(2*H*)-carboxylate **21** as a colorless liquid.

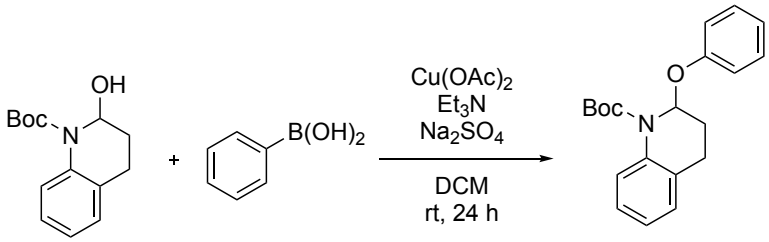
***tert*-butyl 2-ethoxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (21)**



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.83 (t, *J* = 4.1 Hz, 1H), 3.64 – 3.52 (m, 2H), 2.87 (ddd, *J* = 16.3, 9.7, 6.7 Hz, 1H), 2.66 (dt, *J* = 16.2, 6.0 Hz, 1H), 2.14 (tdd, *J* = 9.7, 6.7, 4.9 Hz, 1H), 1.99 (dddd, *J* = 13.5, 6.8, 5.3, 3.8 Hz, 1H), 1.53 (s, 9H), 1.12 (t, *J* = 7.0 Hz, 3H).

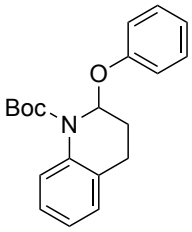
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.81, 136.12, 130.28, 128.28, 125.81, 125.06, 123.92, 81.41, 81.26, 62.79, 29.25, 28.48 (3C), 23.37, 15.15.
Yield: 33.2 mg, 60%. Colorless liquid.

HRMS (ESI): m/z calcd for $[C_{16}H_{23}NO_3Na]^+$ ($[M+Na]^+$): 300.1570, found 300.1568



Tert-butyl 2-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate **20a** (50 mg, 0.2 mmol, 1.0 equiv) was dissolved in DCM (2 mL, 0.1 M). To this solution at rt was added $Cu(OAc)_2$ (36 mg, 0.2 mmol, 1.0 equiv), Et_3N (101 mg, 1 mmol, 5.0 equiv), Na_2SO_4 (142 mg, 1 mmol, 5.0 equiv) and phenylboronic acid (49 mg, 0.4 mmol, 2.0 equiv), in that order. The mixture was stirred at rt for 24 hours.[5] Upon reaction completion, the mixture was then passed through a pad of celite and washed three times with DCM (5 mL). The combined organic washes were concentrated, and the crude residue was purified using flash chromatography (20-30% EA in hexanes) on a Biotage Isolera system to give the corresponding *tert*-butyl 2-phenoxy-3,4-dihydroquinoline-1(2*H*)-carboxylate **22** as a colorless oil.

***tert*-butyl 2-phenoxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (22)**

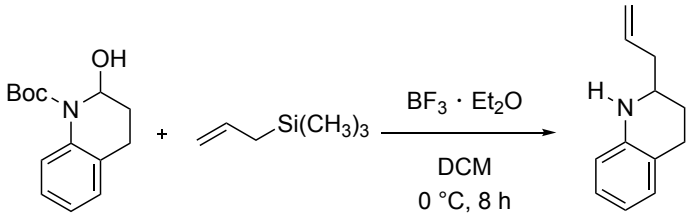


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 14.0, 7.6 Hz, 3H), 6.52 (t, *J* = 3.7 Hz, 1H), 3.05 (dt, *J* = 16.5, 8.5 Hz, 1H), 2.79 (dt, *J* = 16.2, 5.6 Hz, 1H), 2.26 (dq, *J* = 9.4, 4.2 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 56.6, 152.8, 135.7, 129.5, 129.3, 128.2, 125.9, 124.7, 123.9, 122.1, 117.7, 81.6, 81.2, 28.5, 28.1, 23.0.

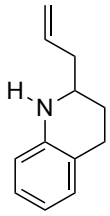
Yield: 98 mg, 39%. Colorless oil.

HRMS (ESI): m/z calcd for $[C_{20}H_{24}NO_3]^+$ ($[M+H]^+$): 326.1751; found 326.1742



Tert-butyl 2-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate **20a** (50 mg, 0.2 mmol, 1.0 equiv) was dissolved in DCM (2 mL, 0.1 M). Then allyltrimethylsilane (39 mg, 0.34 mmol, 1.7 equiv) was added. The solution was cooled to 0 ºC and $BF_3 \bullet Et_2O$ (48 mg, 0.34 mmol, 1.7 equiv) was added to the solution dropwise. After stirring for 8 hours at 0 °C, the reaction was removed from the ice bath and allowed to warm to rt.[6] The mixture was concentrated to give the corresponding *tert*-butyl 2-(allyloxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate **23** as a pure colorless oil.

***tert*-butyl 2-(allyloxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (23)**

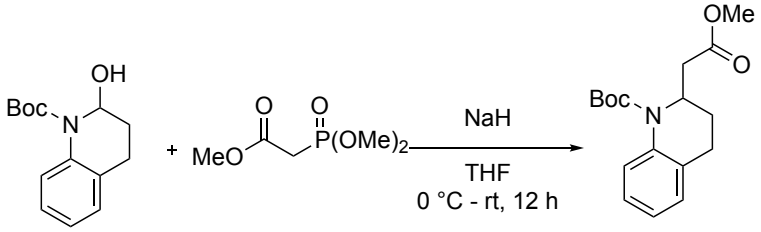


^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (t, *J* = 7.0 Hz, 2H), 6.60 (t, *J* = 7.7 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 5.84 (dddd, *J* = 16.7, 10.2, 8.3, 6.0 Hz, 1H), 5.20 – 5.14 (m, 2H), 3.87 (s, 1H), 3.31 (dddd, *J* = 9.9, 8.0, 4.9, 2.9 Hz, 1H), 2.84 (ddd, *J* = 16.8, 11.4, 5.7 Hz, 1H), 2.74 (dt, *J* = 16.3, 4.6 Hz, 1H), 2.37 – 2.32 (m, 1H), 2.19 (dt, *J* = 13.8, 8.2 Hz, 1H), 1.97 (ddt, *J* = 12.5, 6.0, 3.4 Hz, 1H), 1.68 – 1.61 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 134.9, 129.2, 126.7, 121.2, 117.9, 117.0, 114.0, 50.5, 41.1, 28.2, 26.4.

Yield: 33 mg, 63%. Colorless oil.

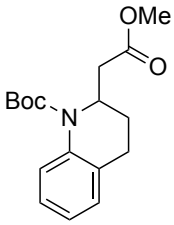
HRMS (ESI): m/z calcd for $[C_{12}H_{16}N]^+$ ($[M+H]^+$): 174.1277; found 174.1289



Methyl 2-(dimethoxyphosphoryl)acetate (109 mg, 0.6 mmol, 2.0 equiv) was dissolved in THF (2 mL) and cooled to 0 °C. NaH (0.6 mmol, 2.0 equiv) was slowly added to the solution. Then a *tert*-butyl 2-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate **20a** (75 mg, 0.3 mmol, 1.0 equiv) solution in THF (1.0 ml, 0.3 M), was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. Upon reaction completion, water was added to quench the reaction. The aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate and

concentrated.[7] The crude mixture was purified using flash chromatography (10-20% EA in hexanes) on a Biotage Isolera system to give the corresponding *tert*-butyl 2-(2-oxopropoxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate **24** as a colorless oil.

***tert*-butyl 2-(2-oxopropoxy)-3,4-dihydroquinoline-1(2*H*)-carboxylate (24)**



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 1H), 7.19 – 7.11 (m, 1H), 7.07 (d, *J* = 5.9 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.93 – 4.82 (m, 1H), 3.64 (s, 3H), 2.70 – 2.61 (m, 3H), 2.38 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.30 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.65 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.5, 153.5, 136.7, 131.3, 127.7, 125.9, 125.6, 123.9, 80.9, 51.6, 50.1, 38.5, 29.1, 28.3, 24. 9.

Yield: 63 mg, 69%. Colorless oil.

HRMS (ESI-TOF): calc'd for $C_{17}H_{24}NO_4$ $[M+H]^+$ 306.1700; found 306.1704.

References

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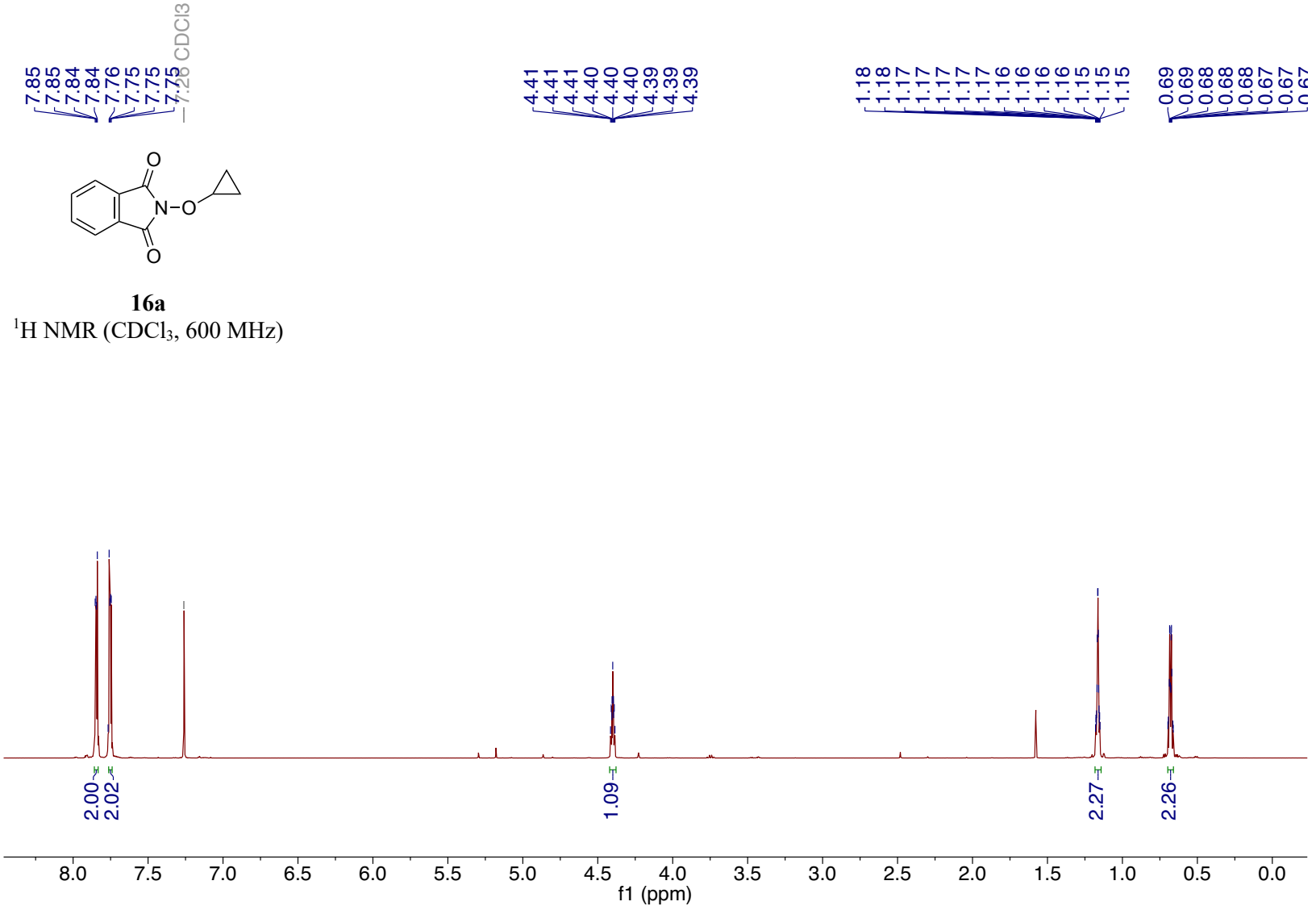
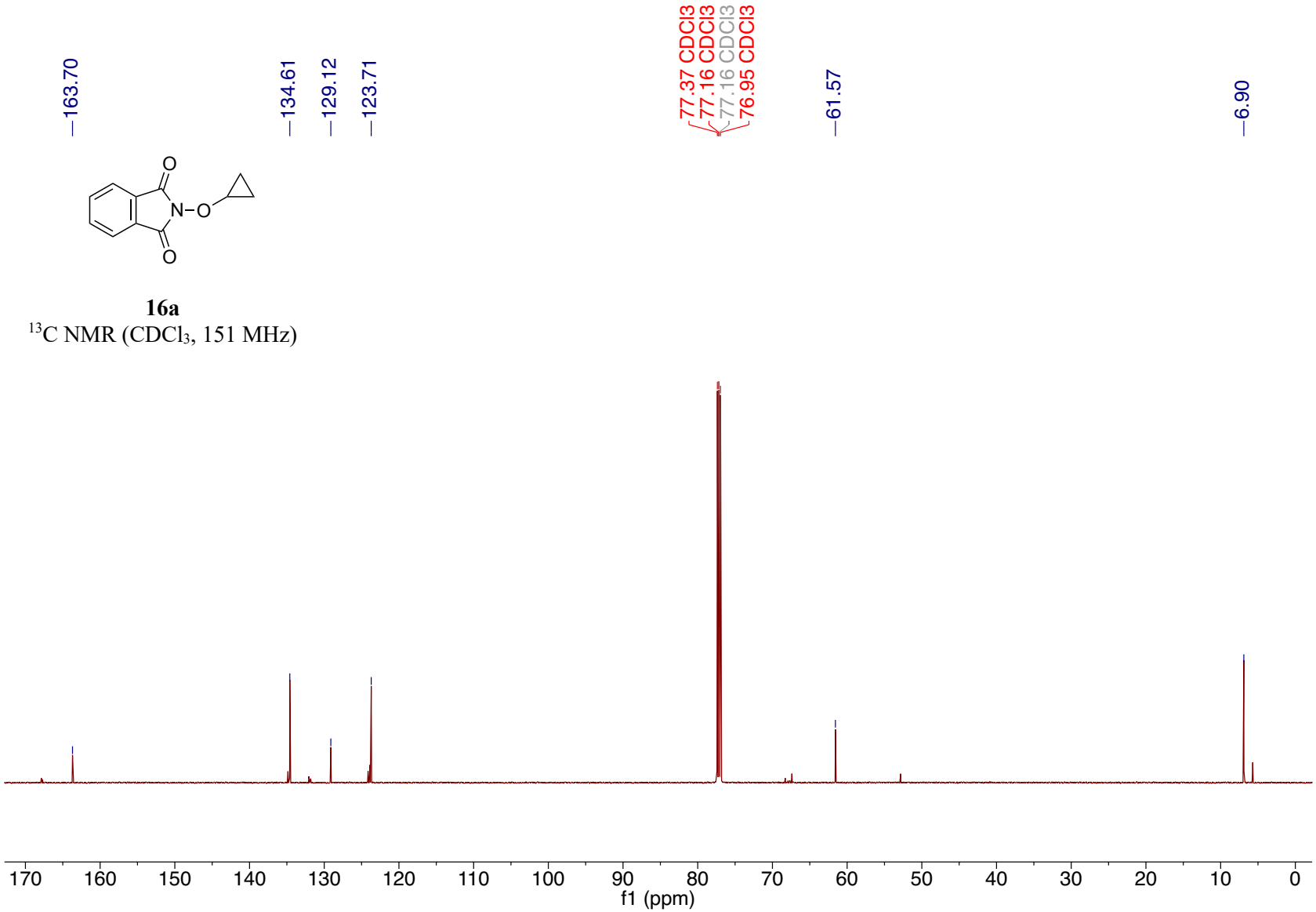


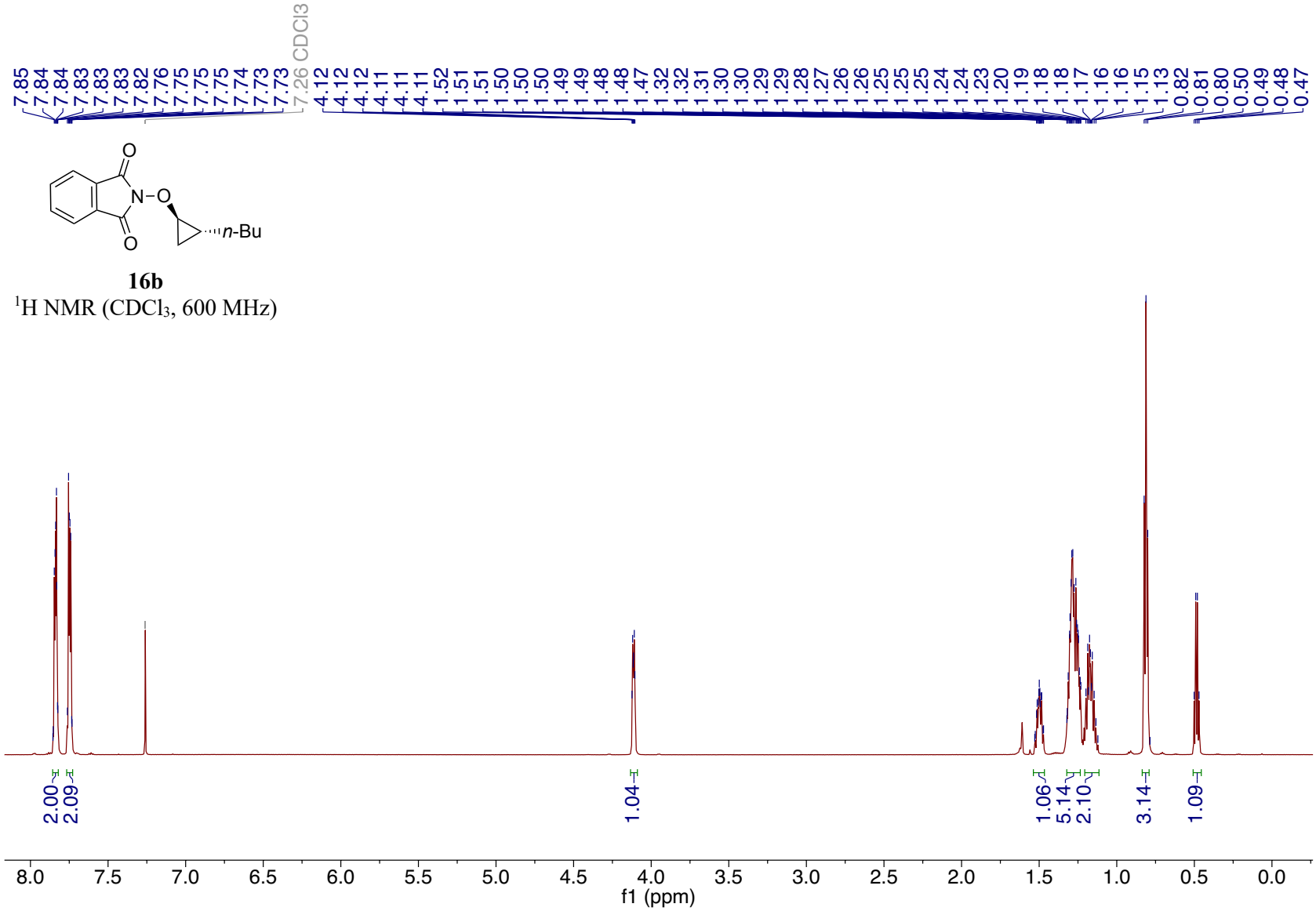
16a

^{1}H NMR ($CDCl_3$, 600 MHz)



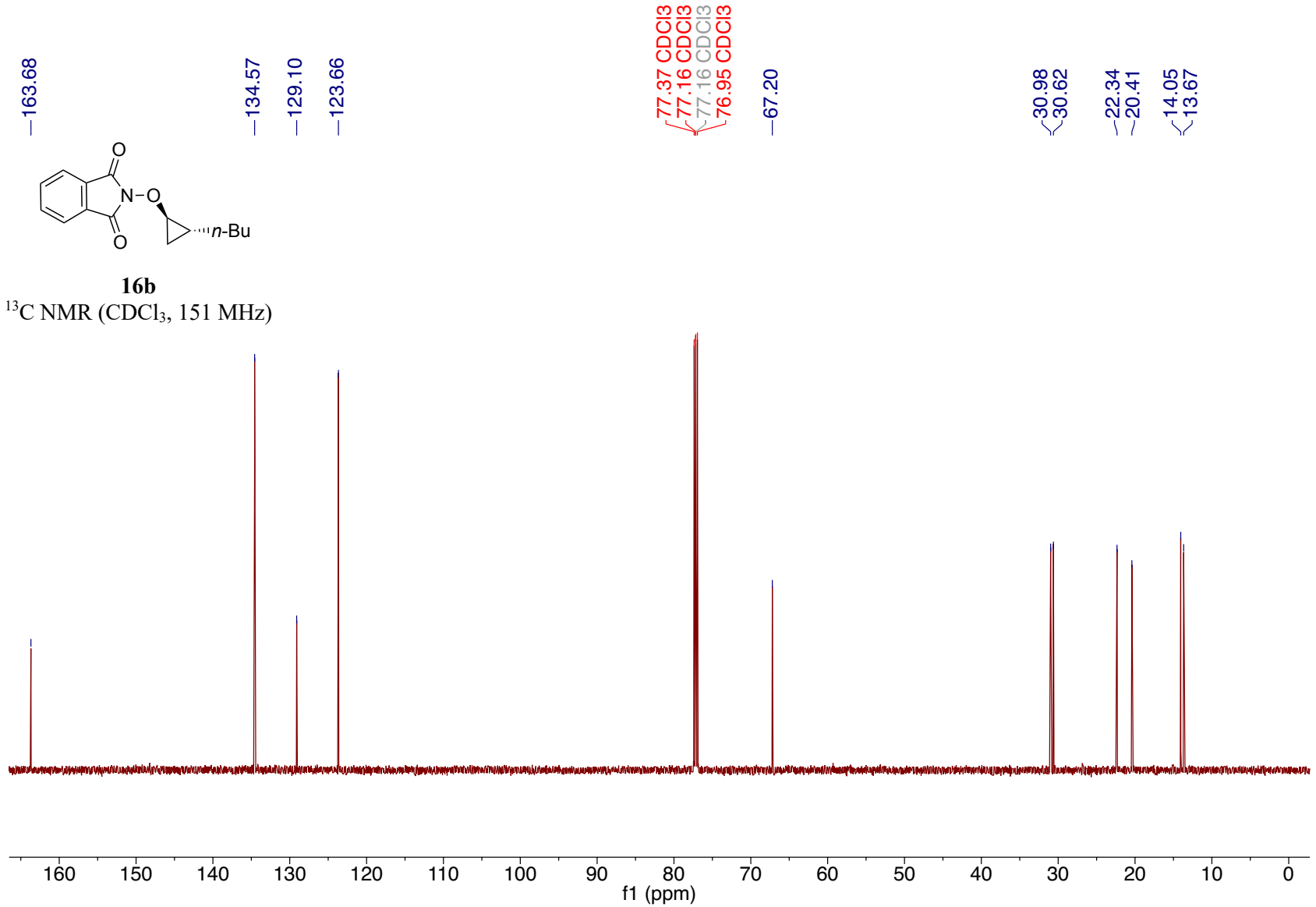
16a

^{13}C NMR ($CDCl_3$, 151 MHz)



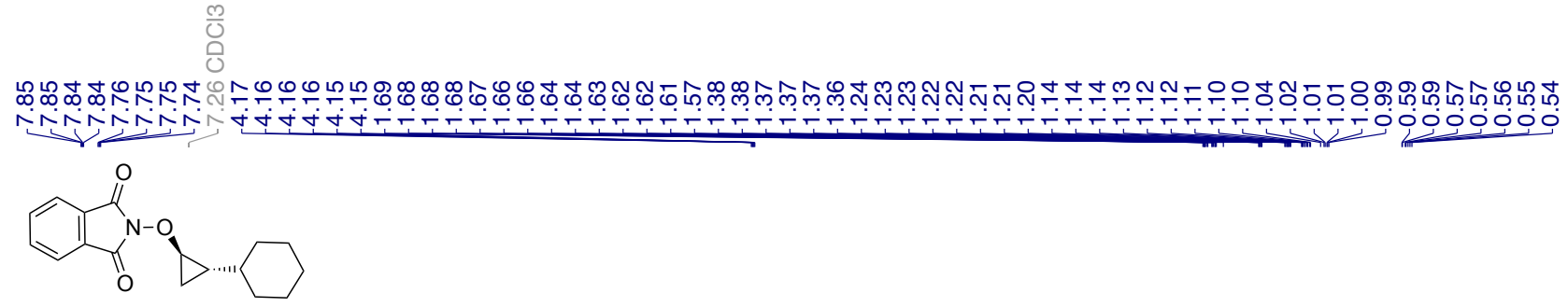
16b

^{1}H NMR ($CDCl_3$, 600 MHz)



16b

^{13}C NMR ($CDCl_3$, 151 MHz)



16c

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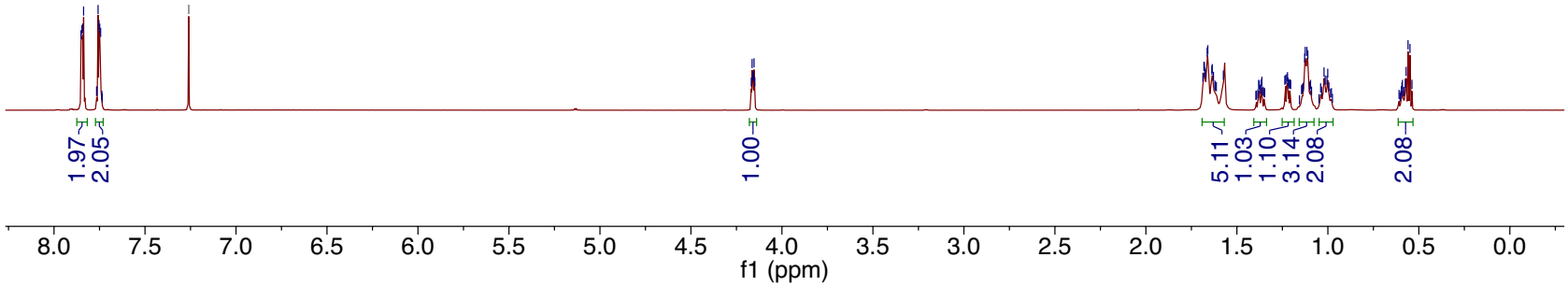

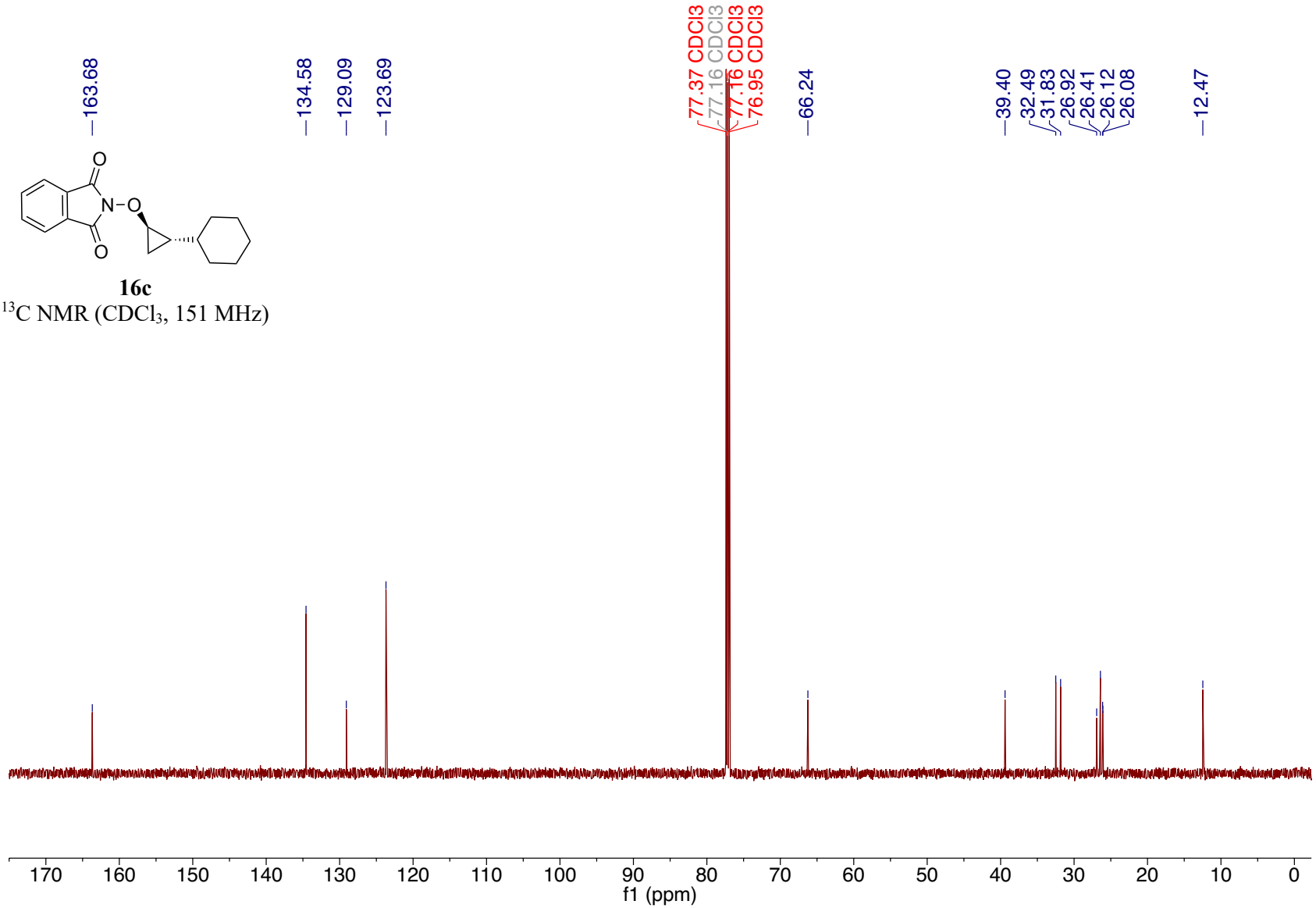

16c

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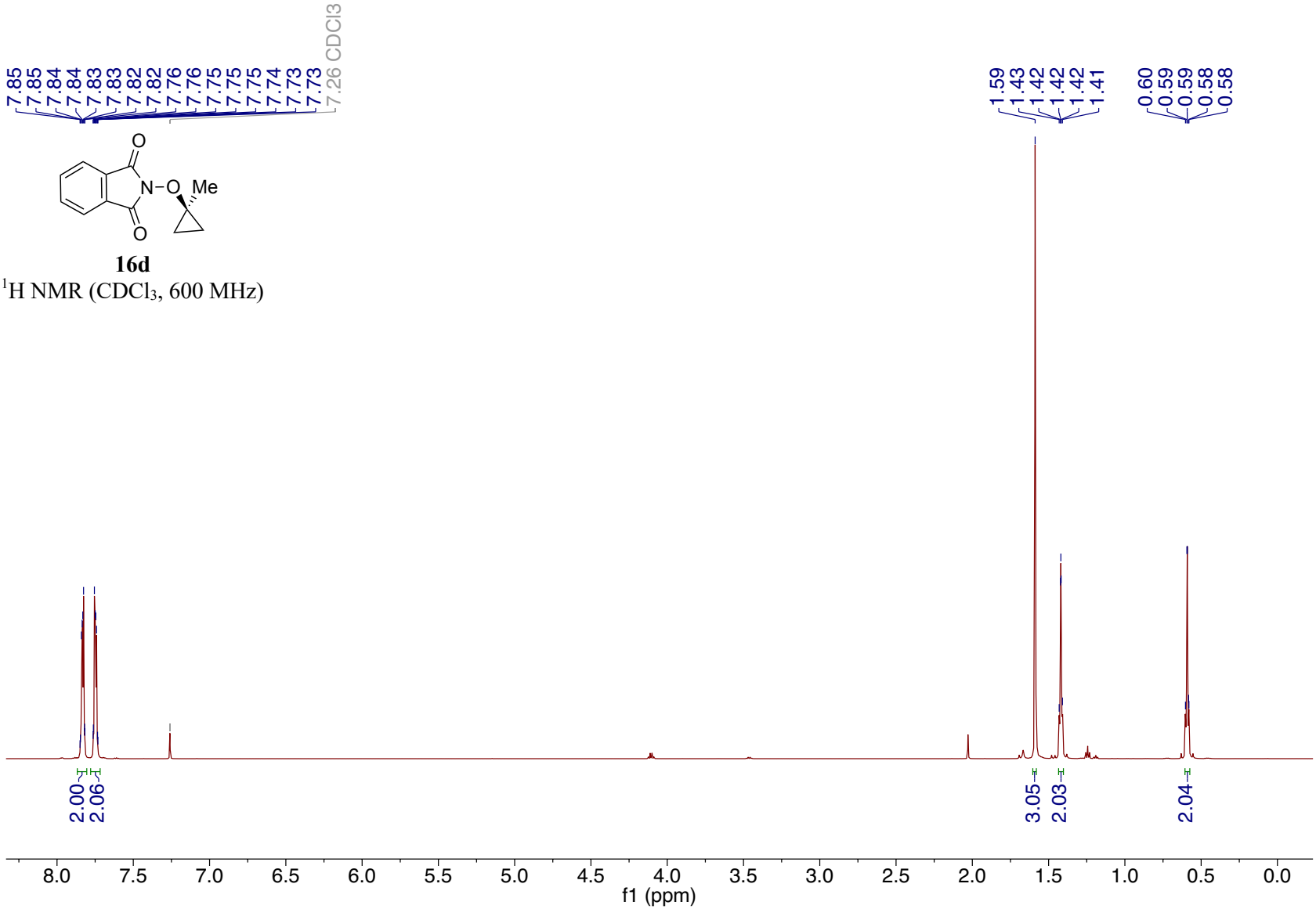

16d

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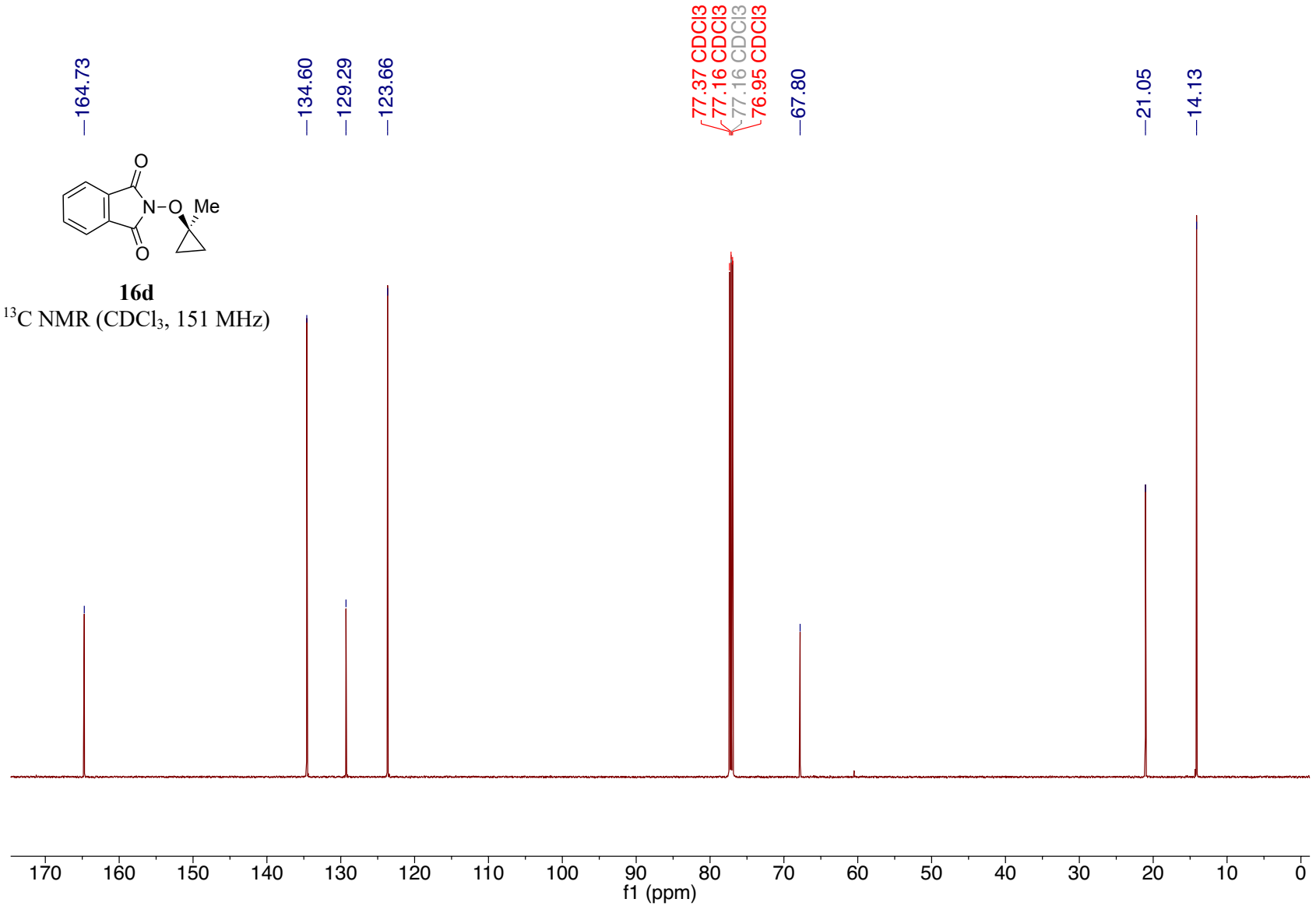
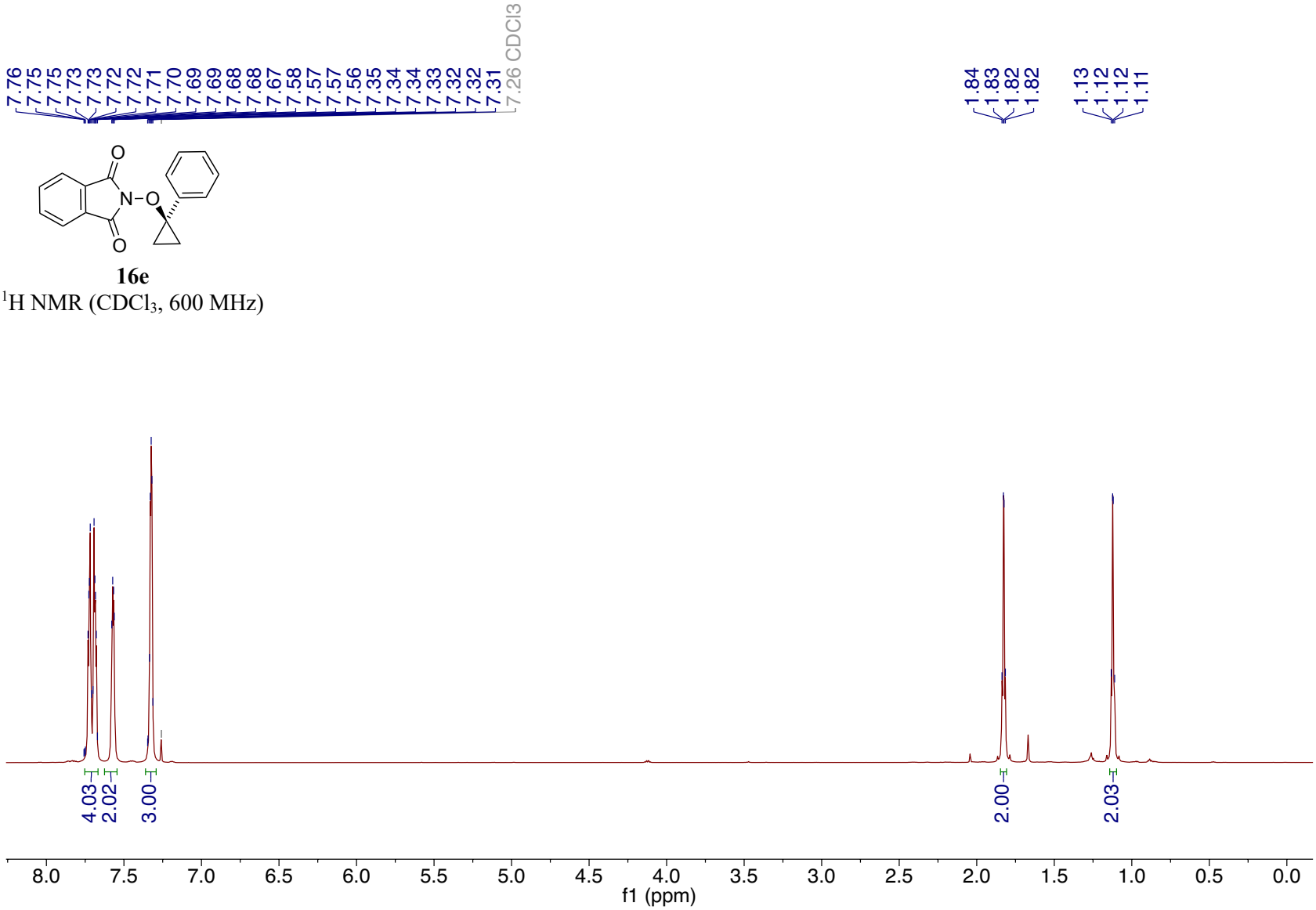


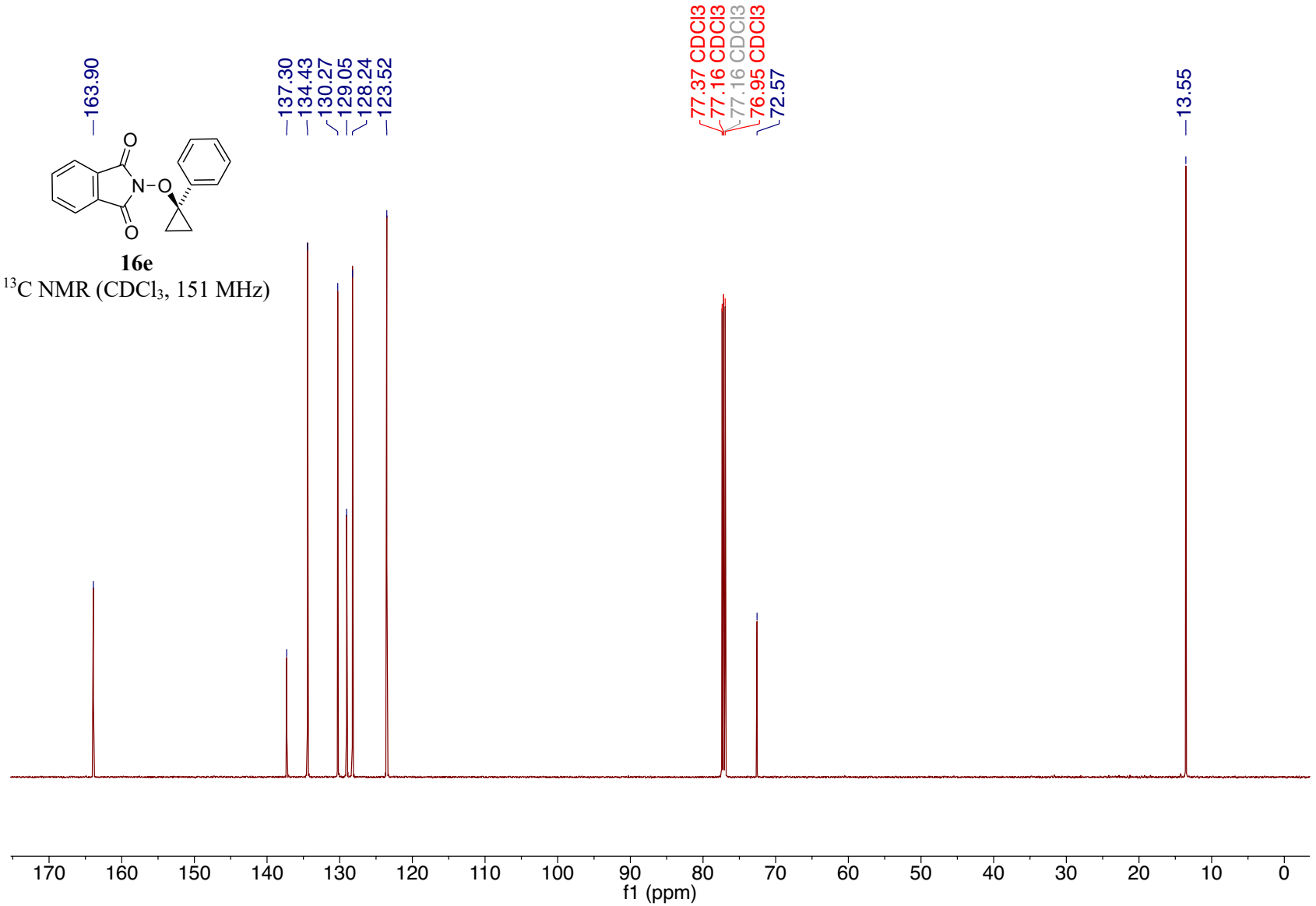
16d

^{13}C NMR ($CDCl_3$, 151 MHz)



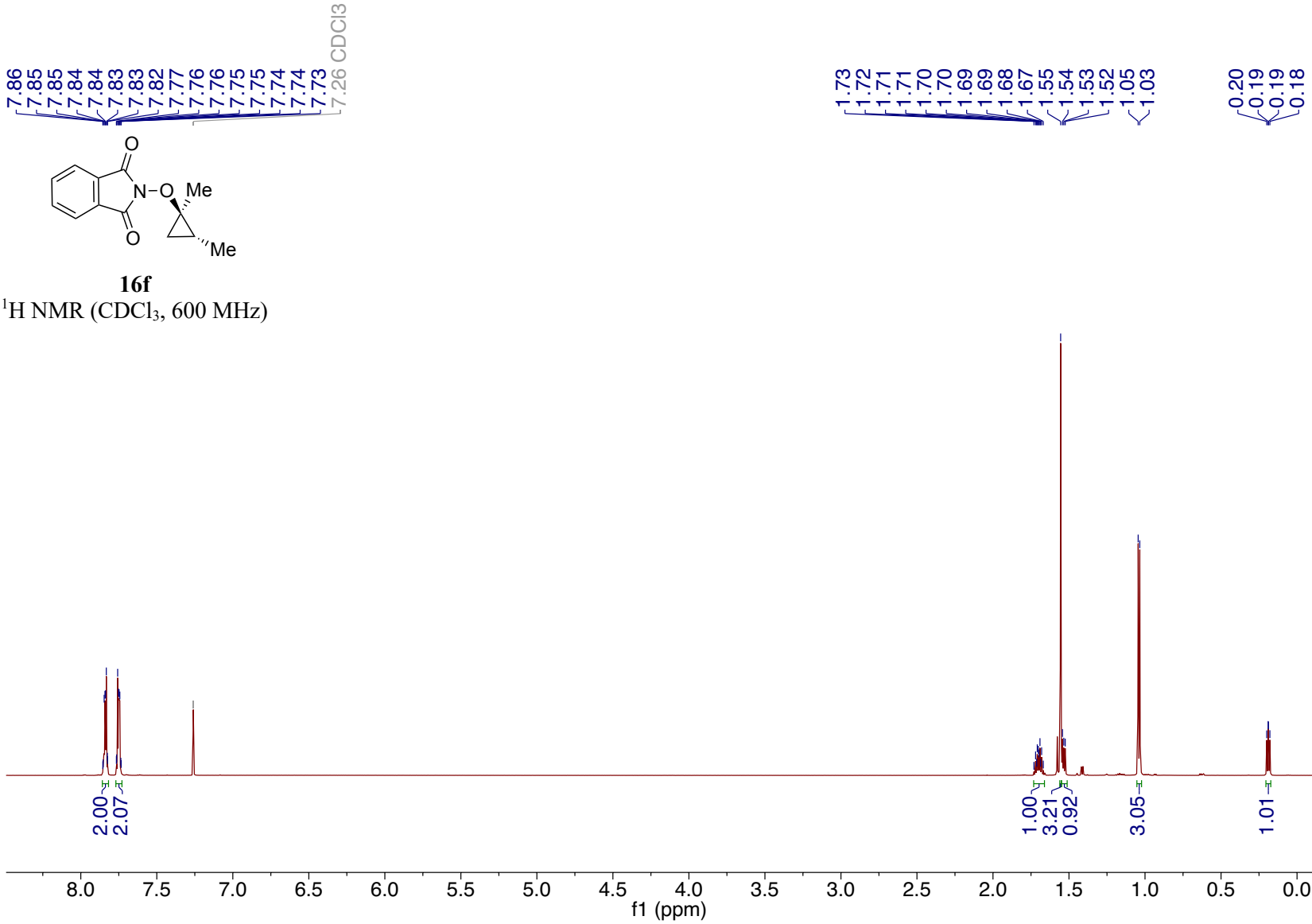
16e

^{1}H NMR ($CDCl_3$, 600 MHz)



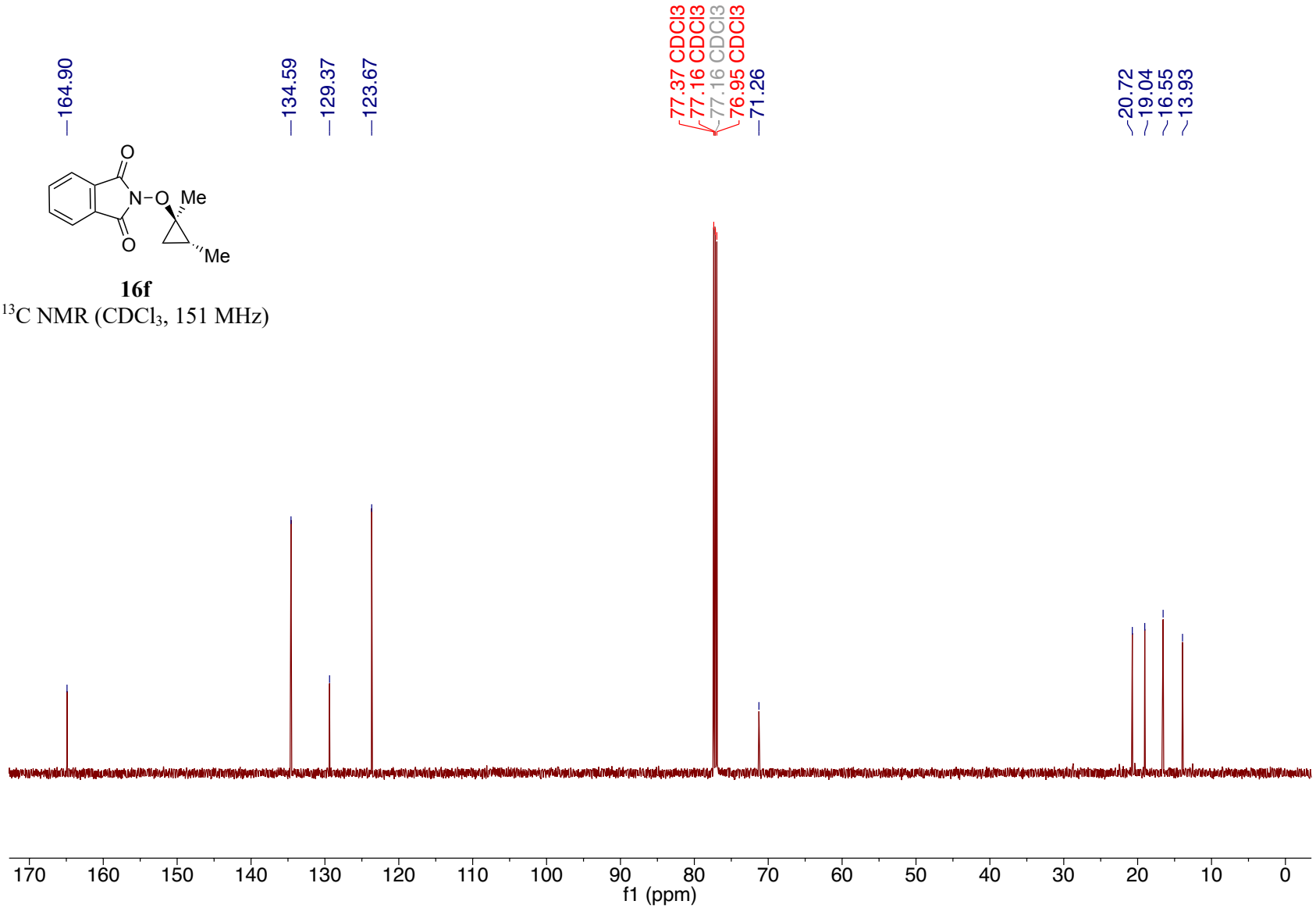
16e

^{13}C NMR ($CDCl_3$, 151 MHz)



16f

^{1}H NMR ($CDCl_3$, 600 MHz)



16f

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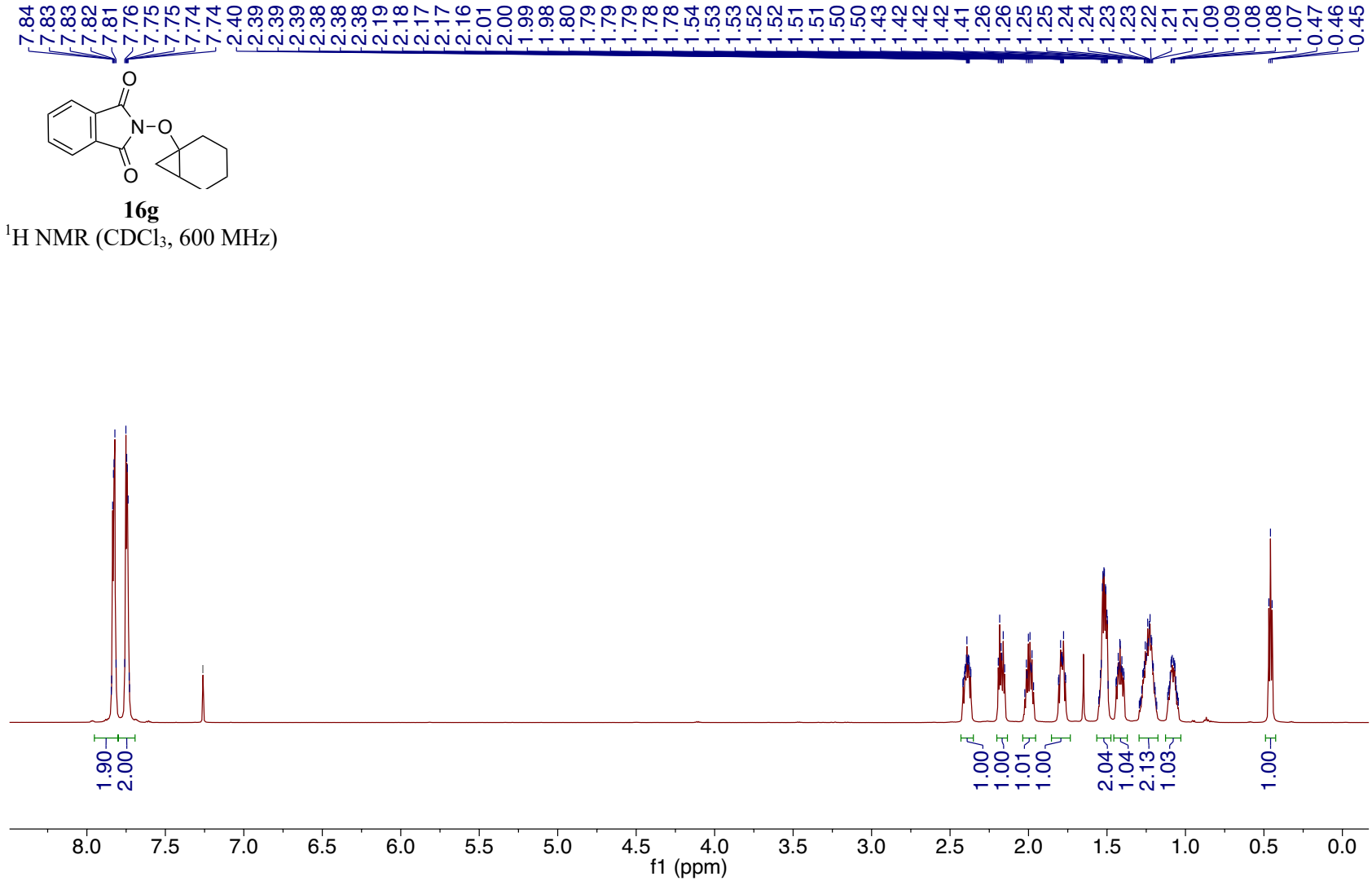

16g

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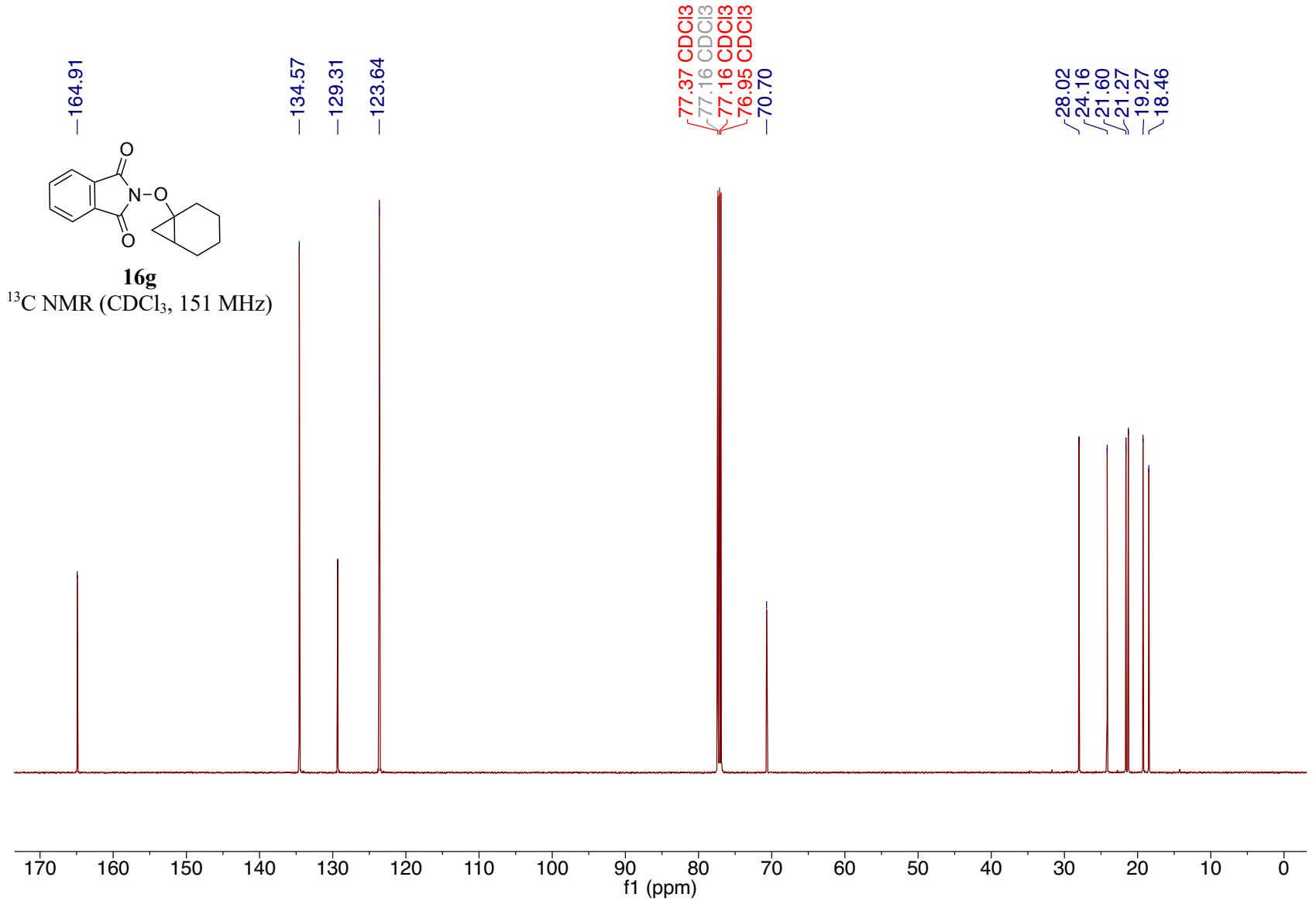

16g

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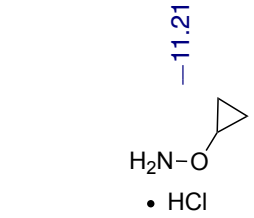
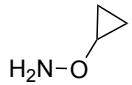


17a

^{1}H NMR (DMSO-*d6*, 600 MHz)



17a

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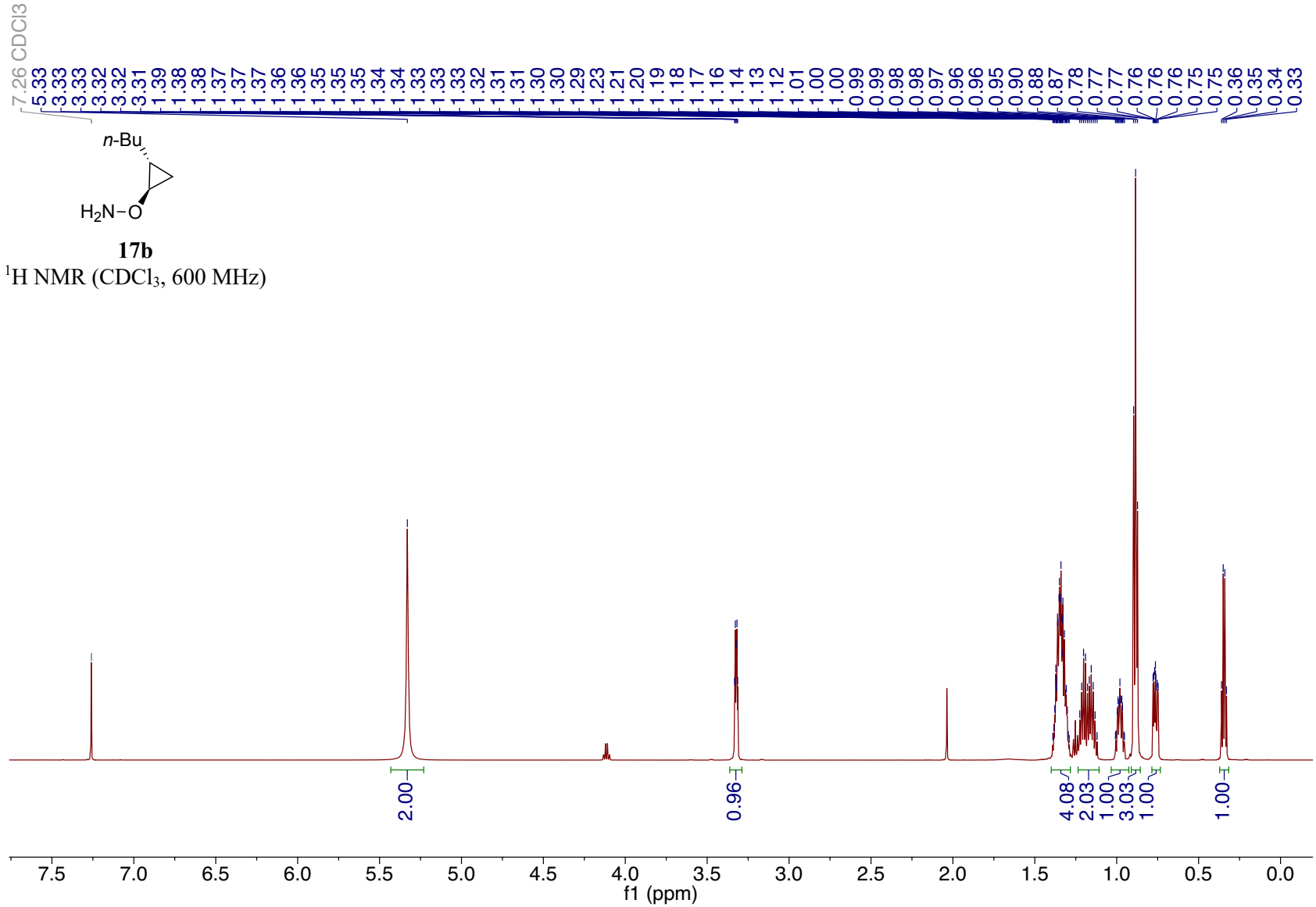

17b

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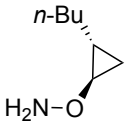

17b

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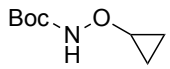

18a

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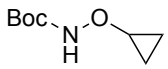

18a

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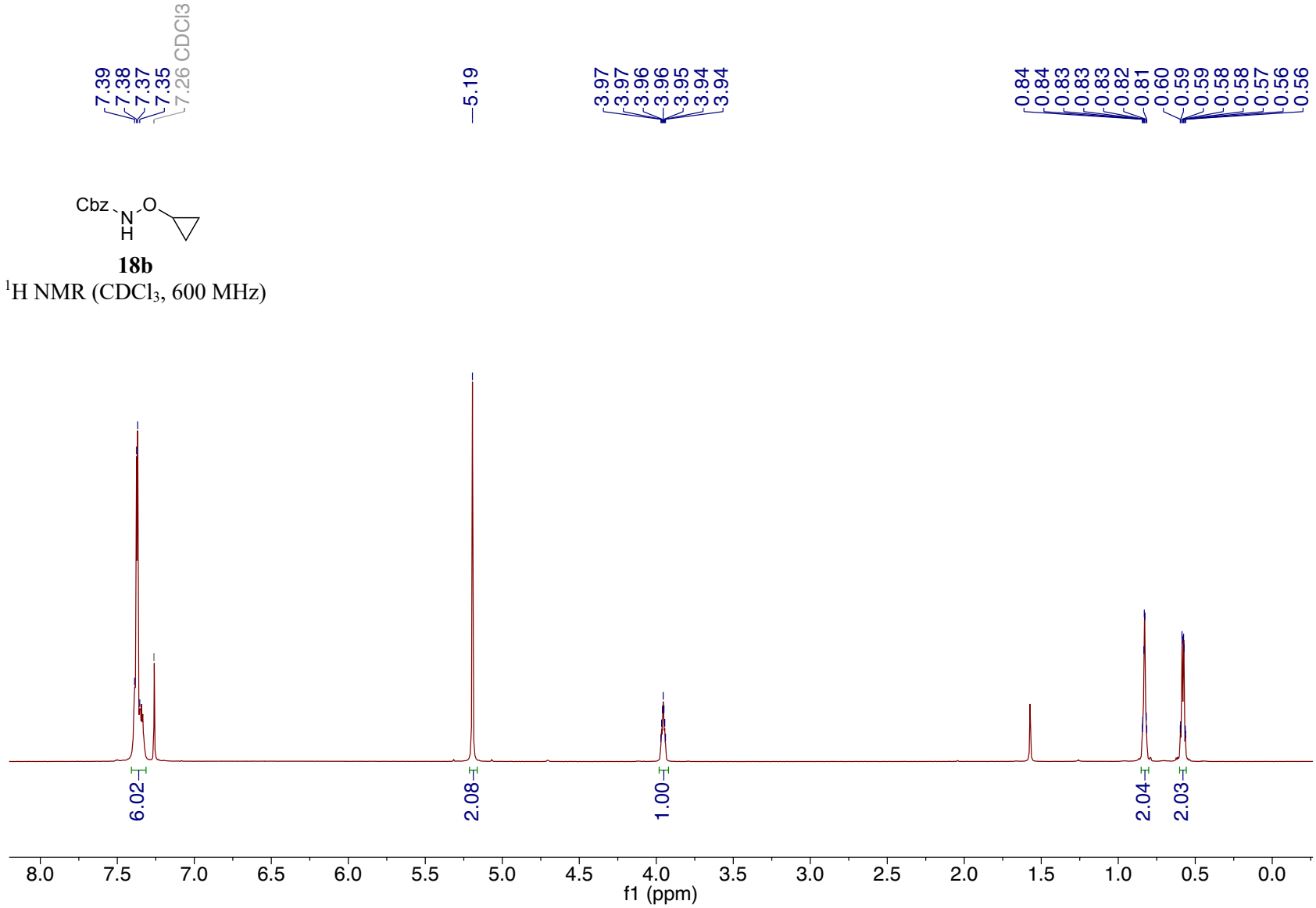

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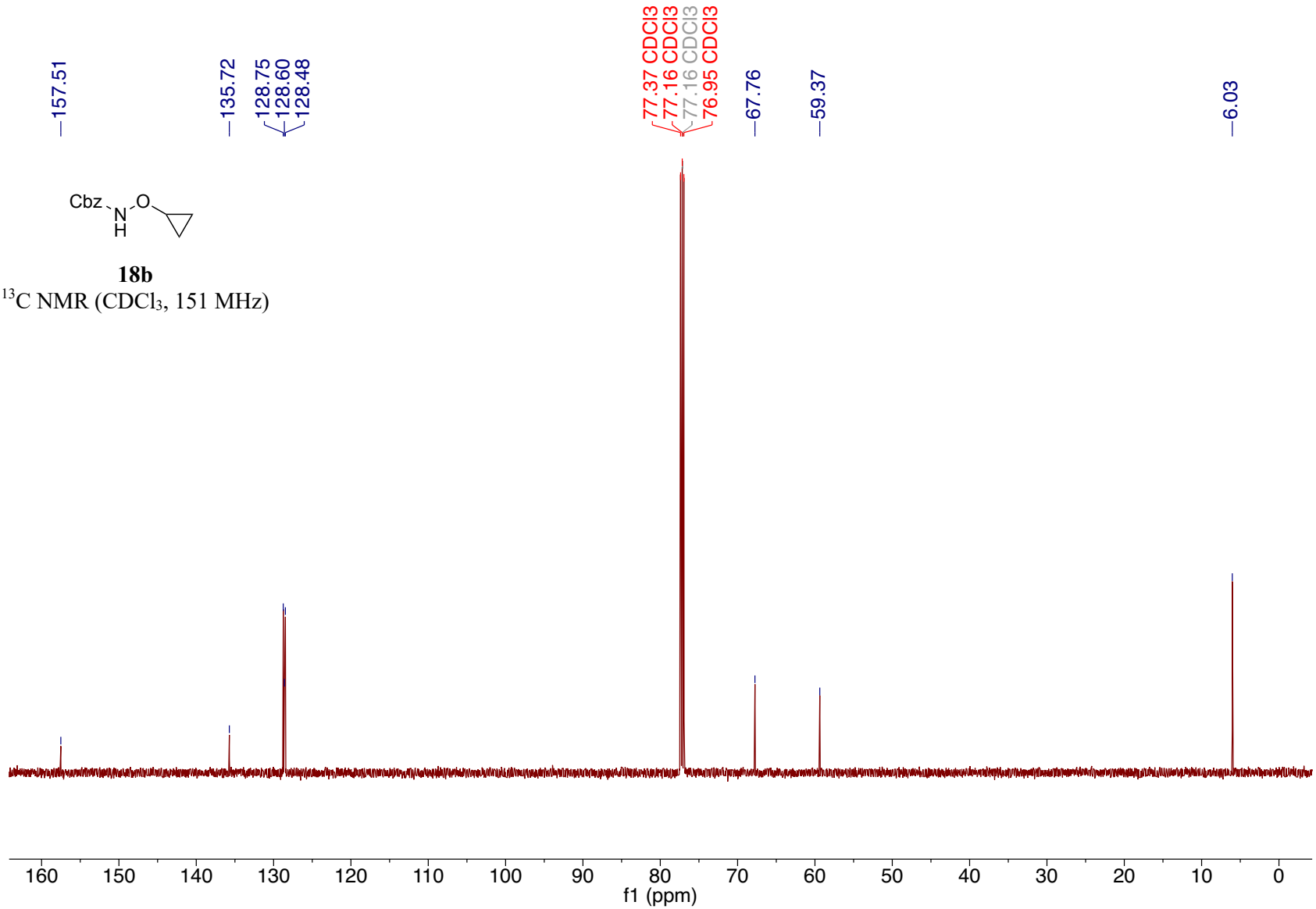

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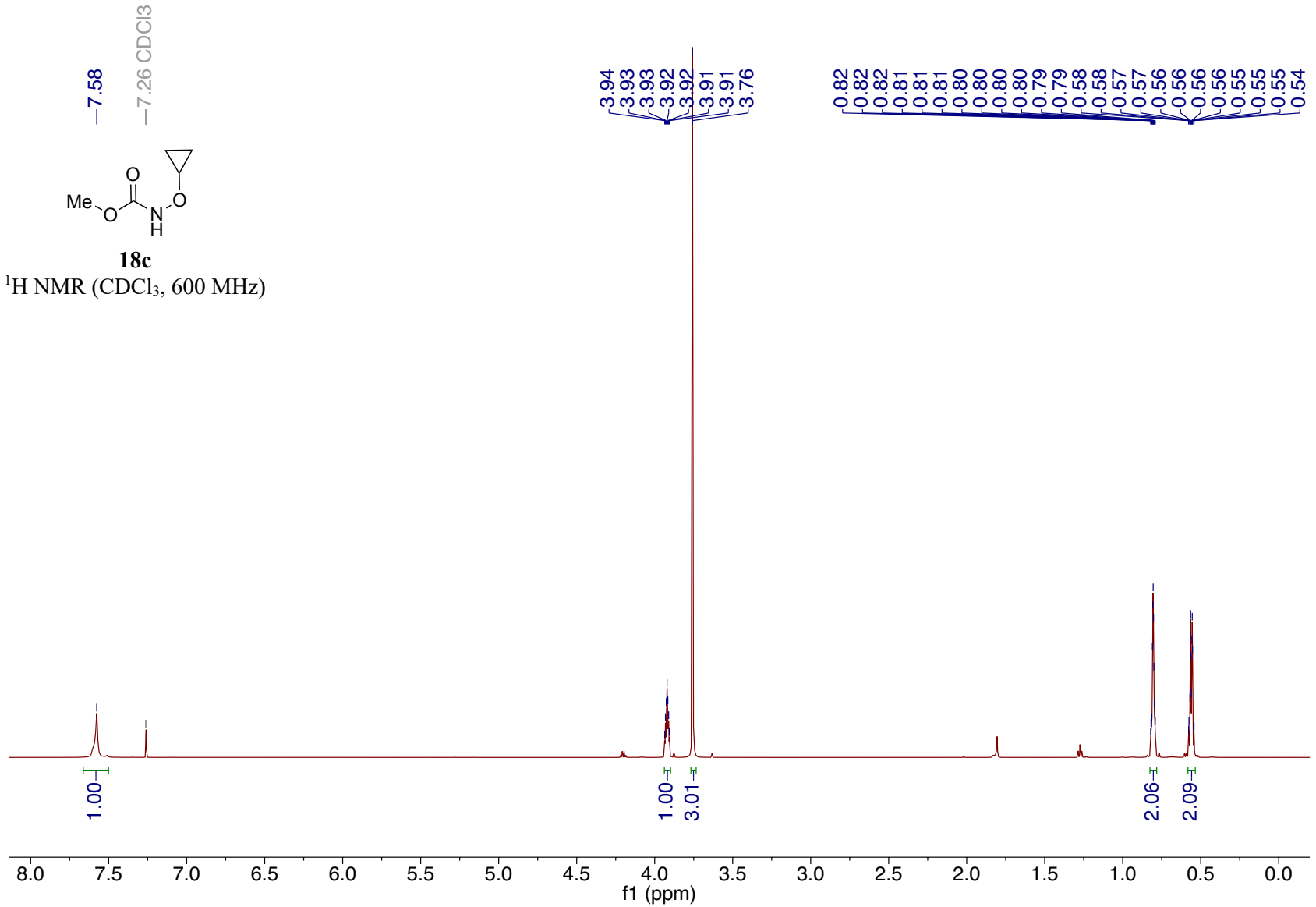

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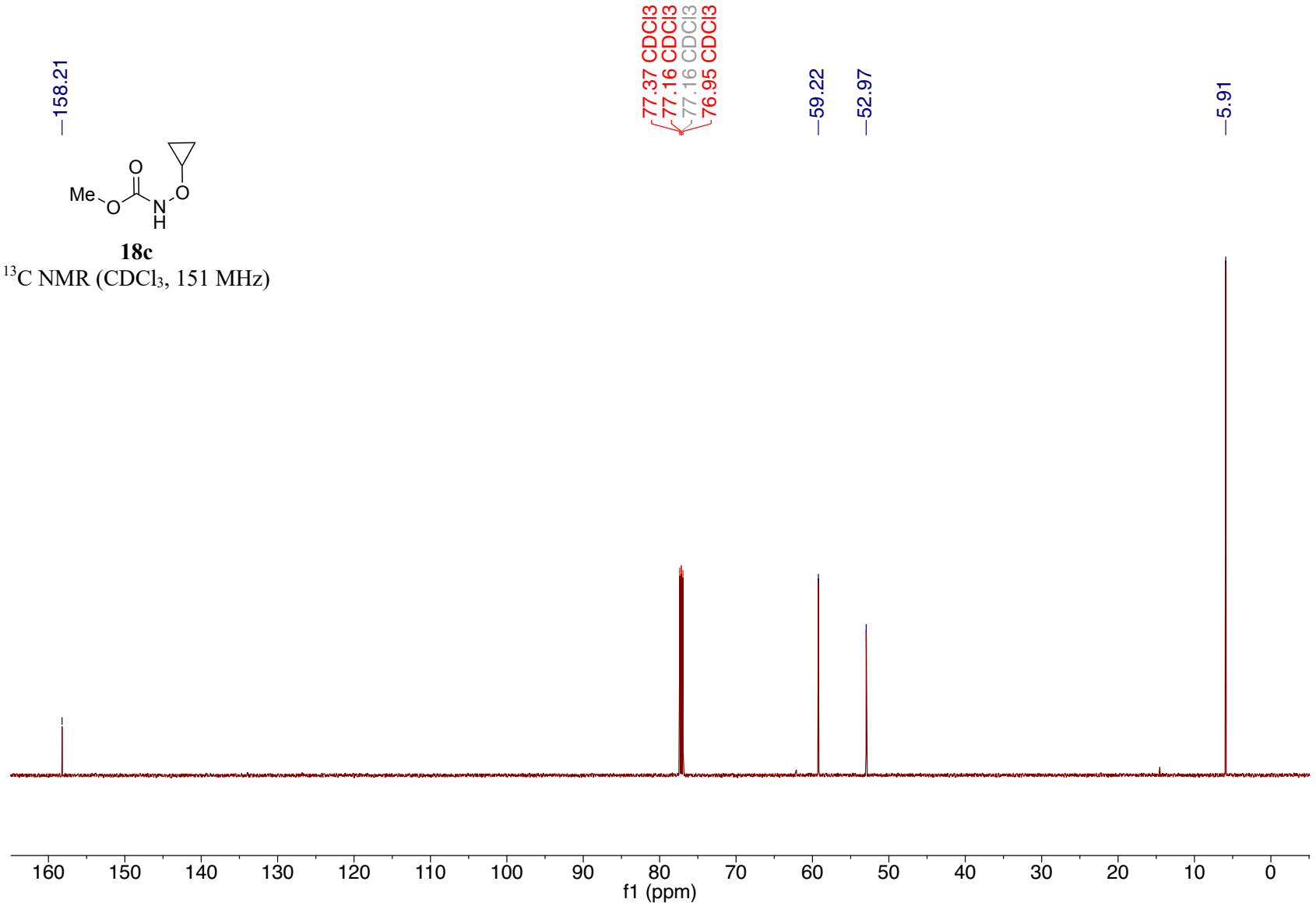

18c

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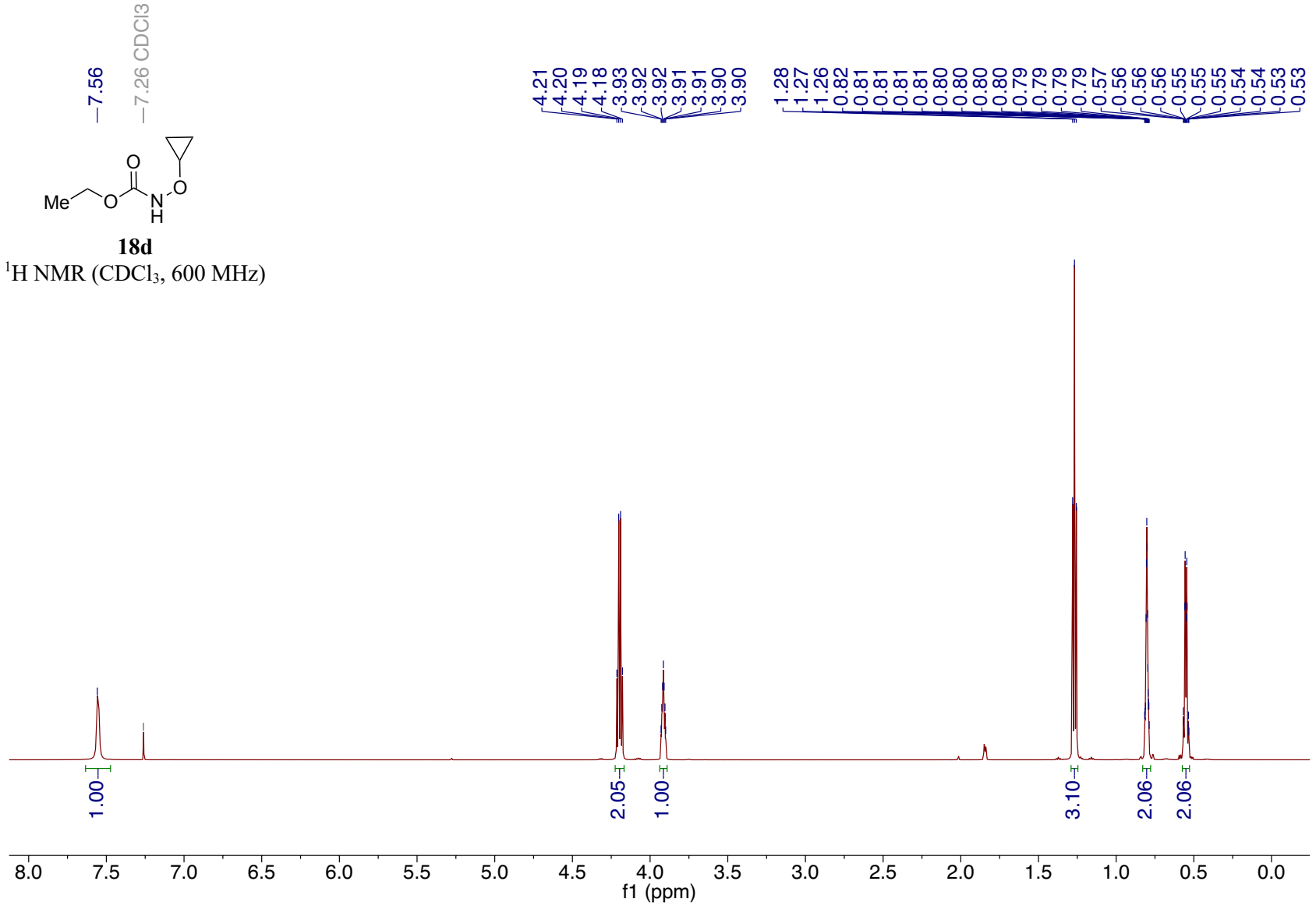
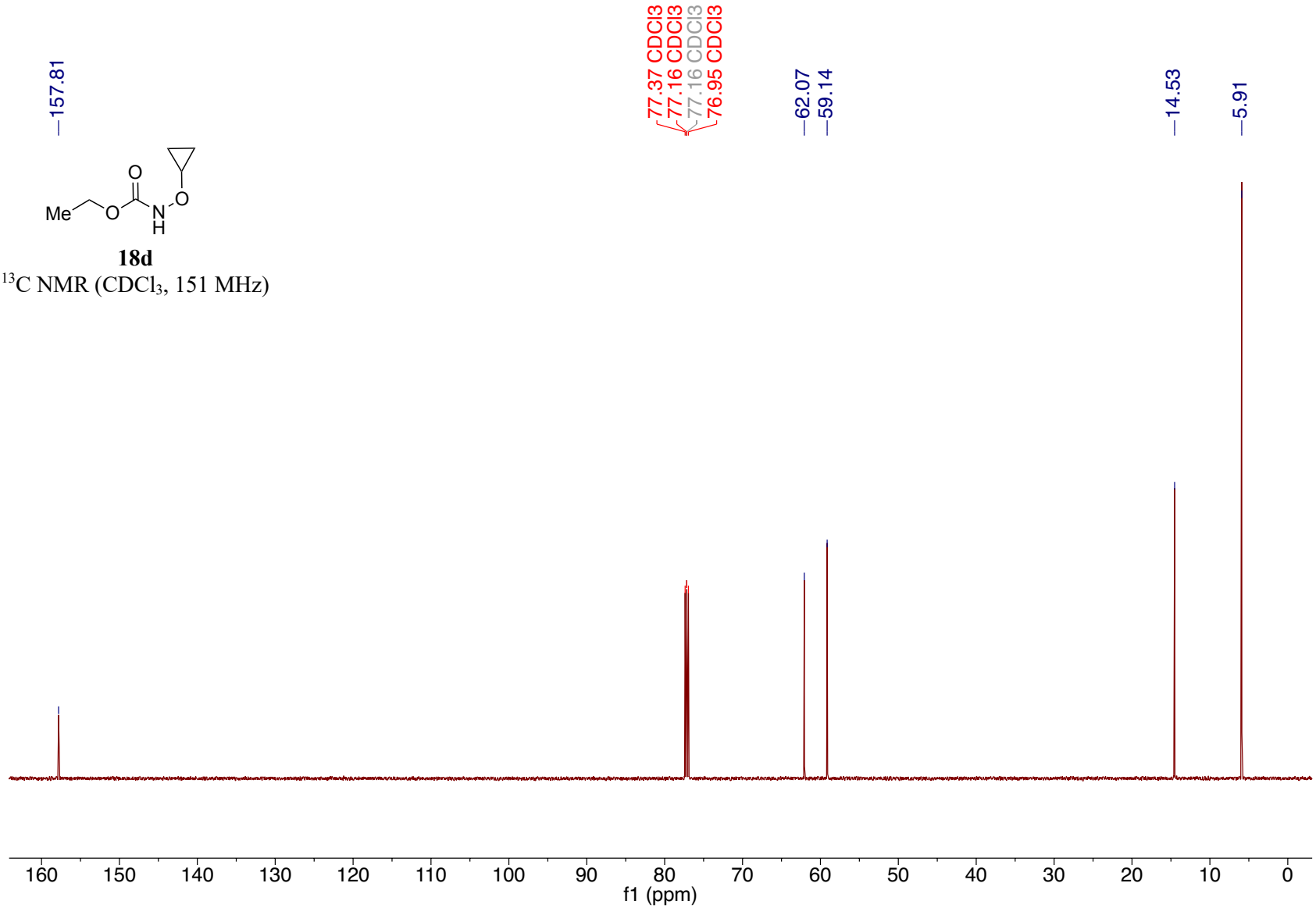


18d

^{1}H NMR ($CDCl_3$, 600 MHz)



18d

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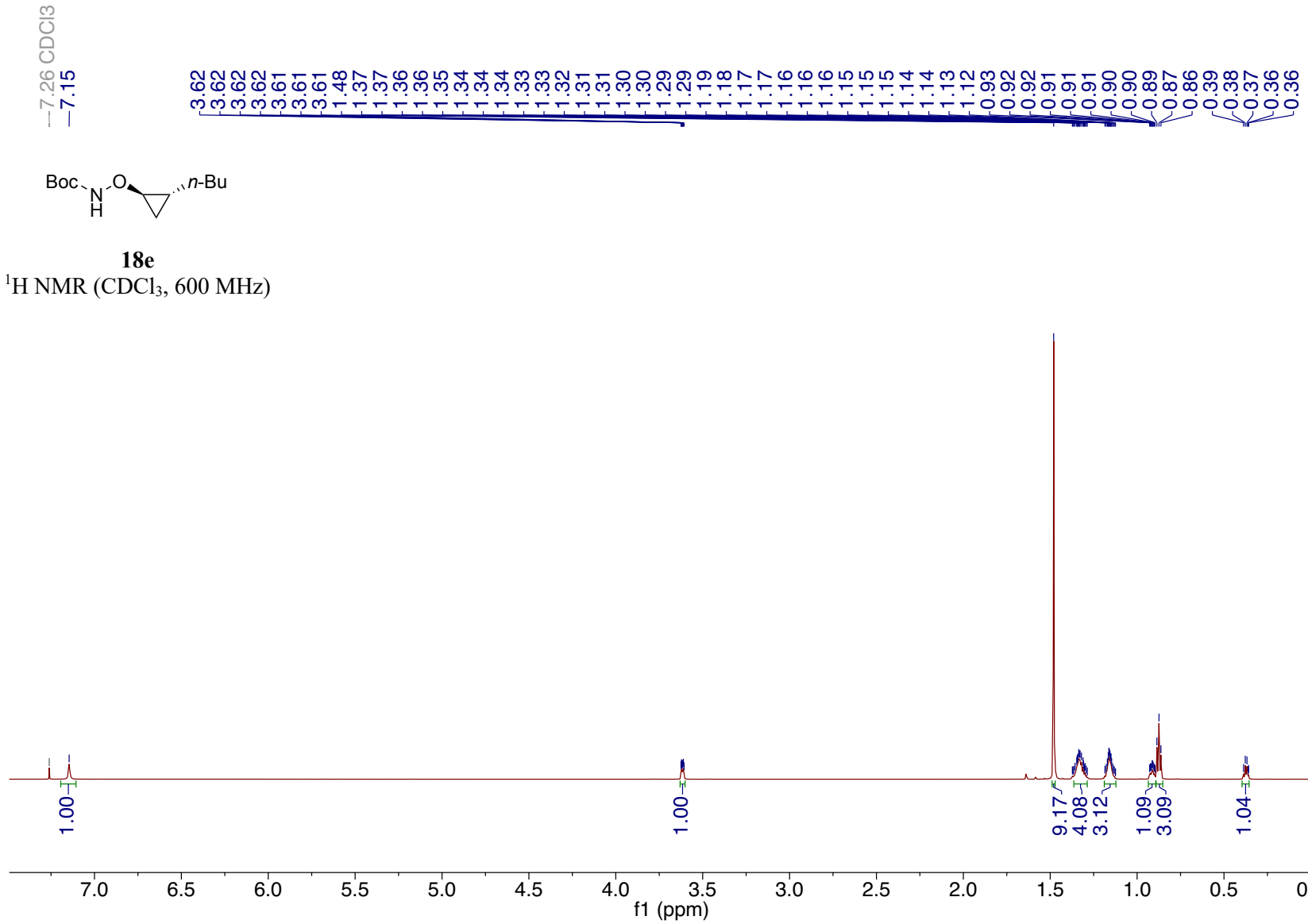

18e

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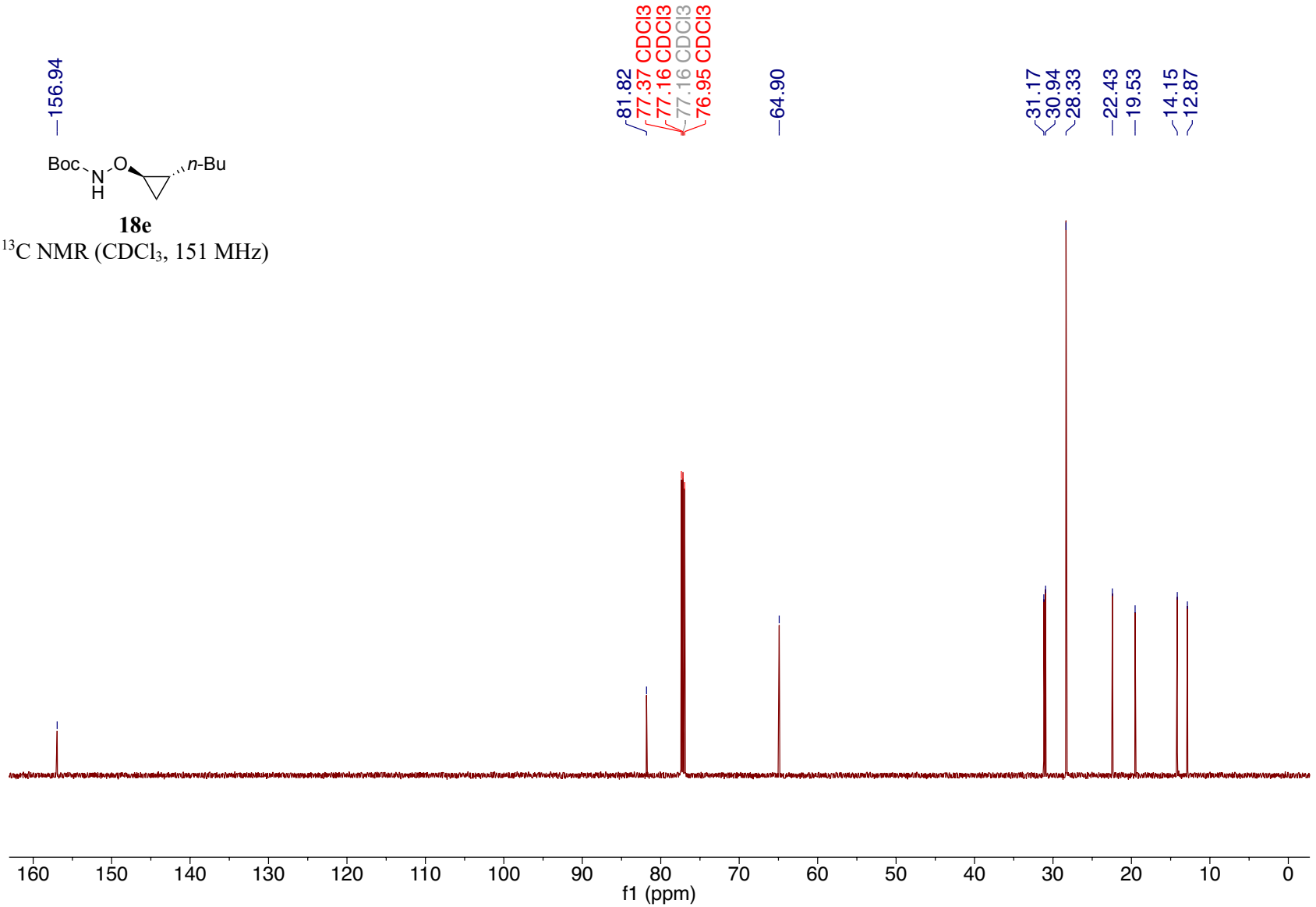

18e

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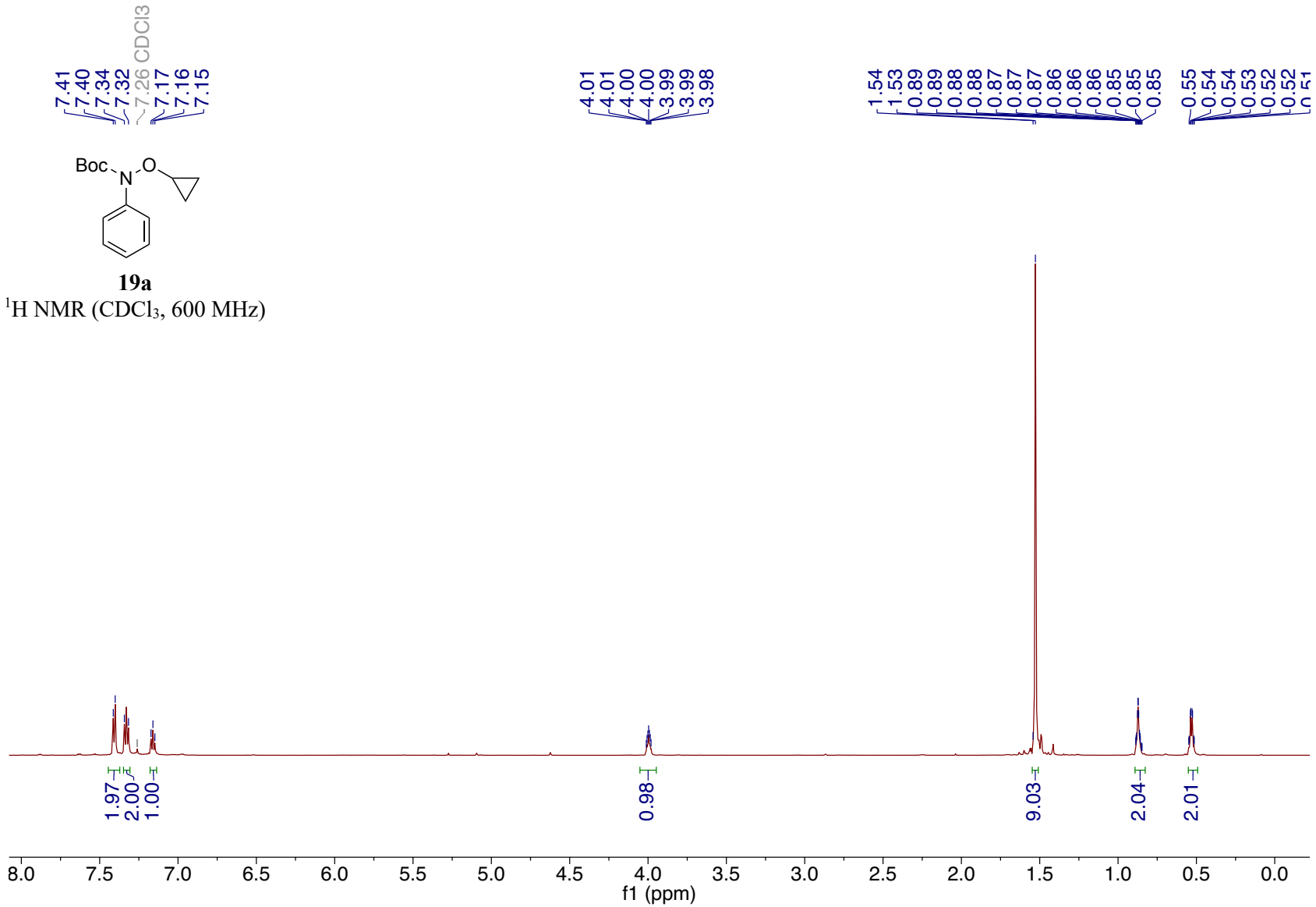

19a

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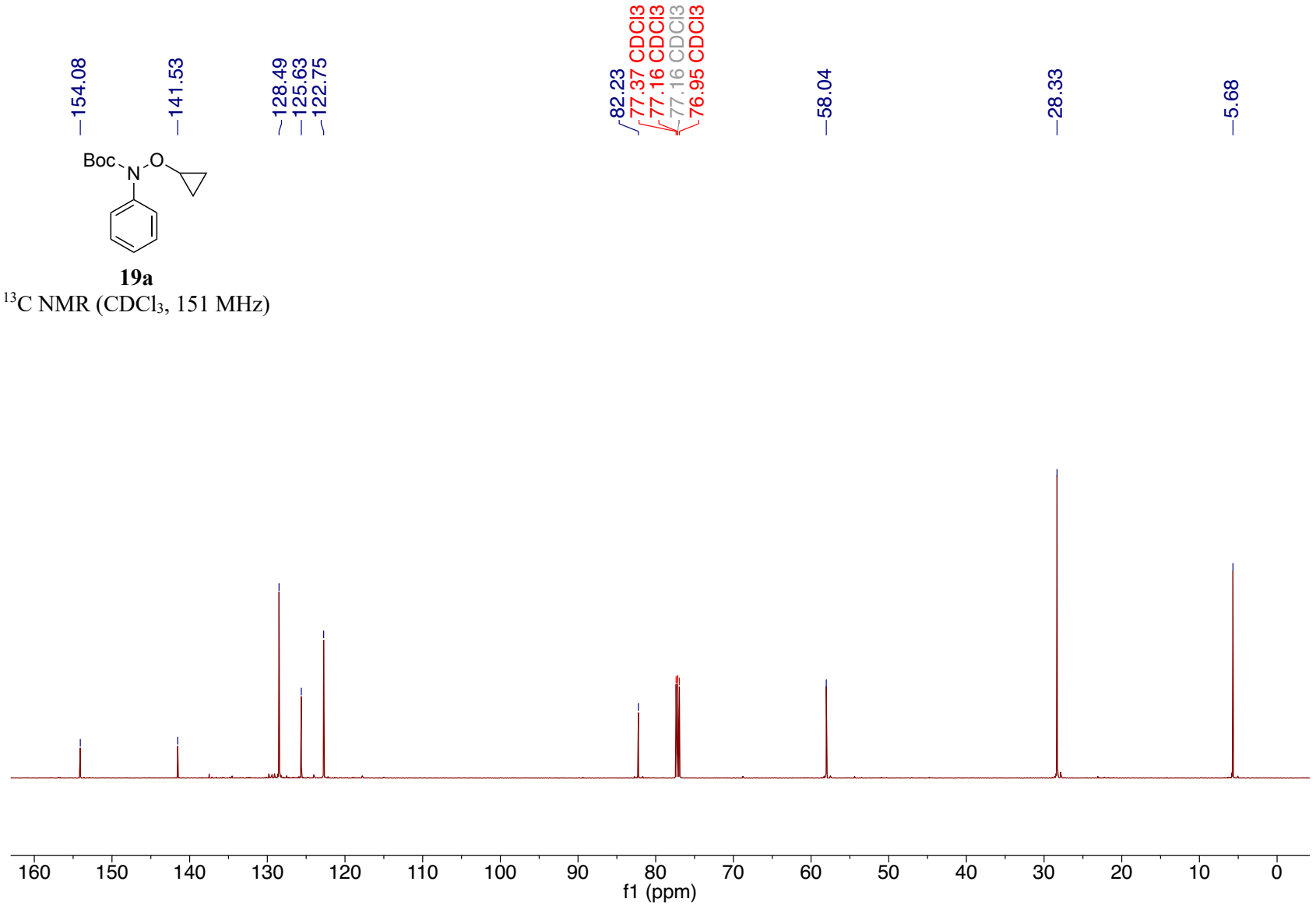

19a

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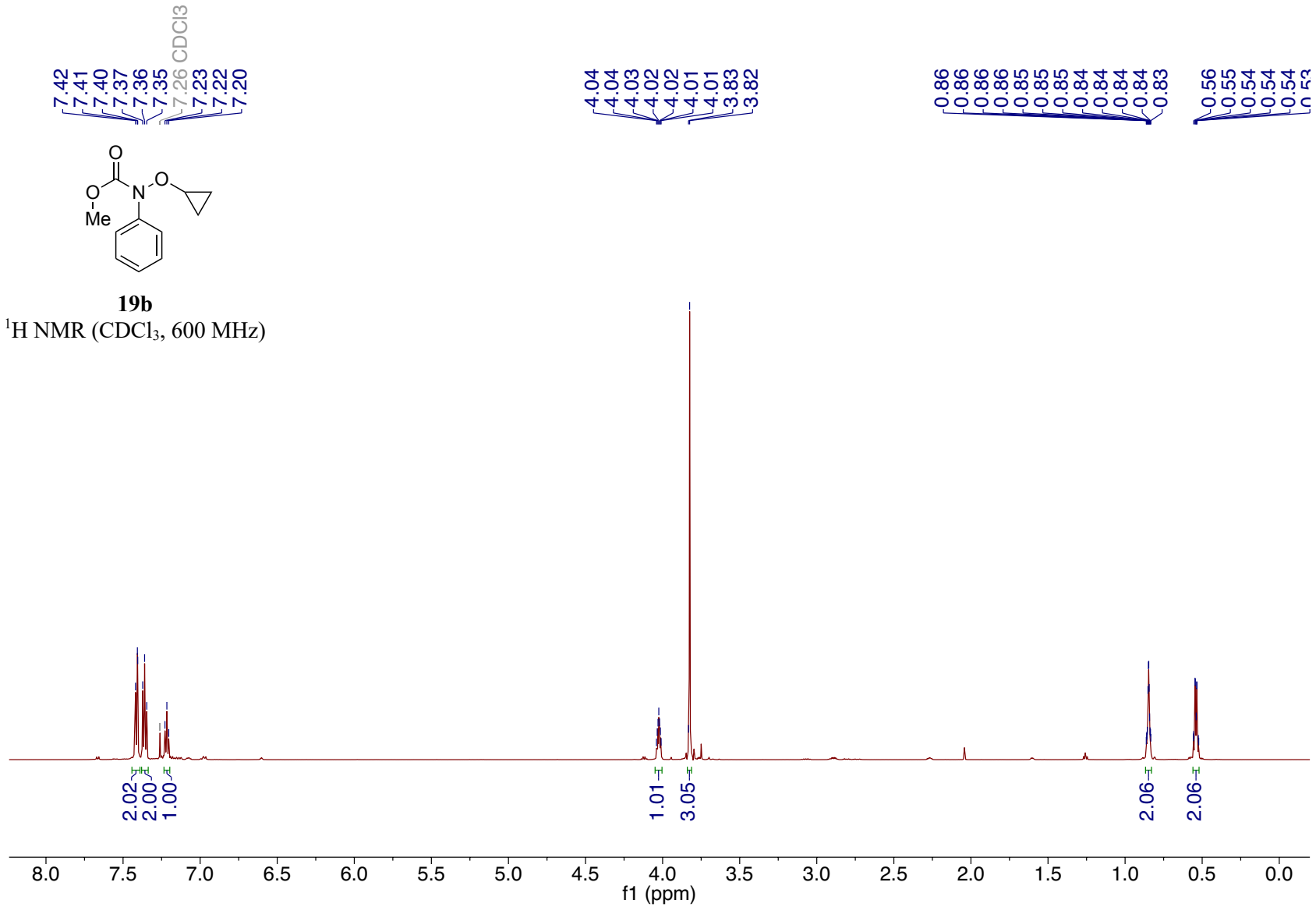

19b

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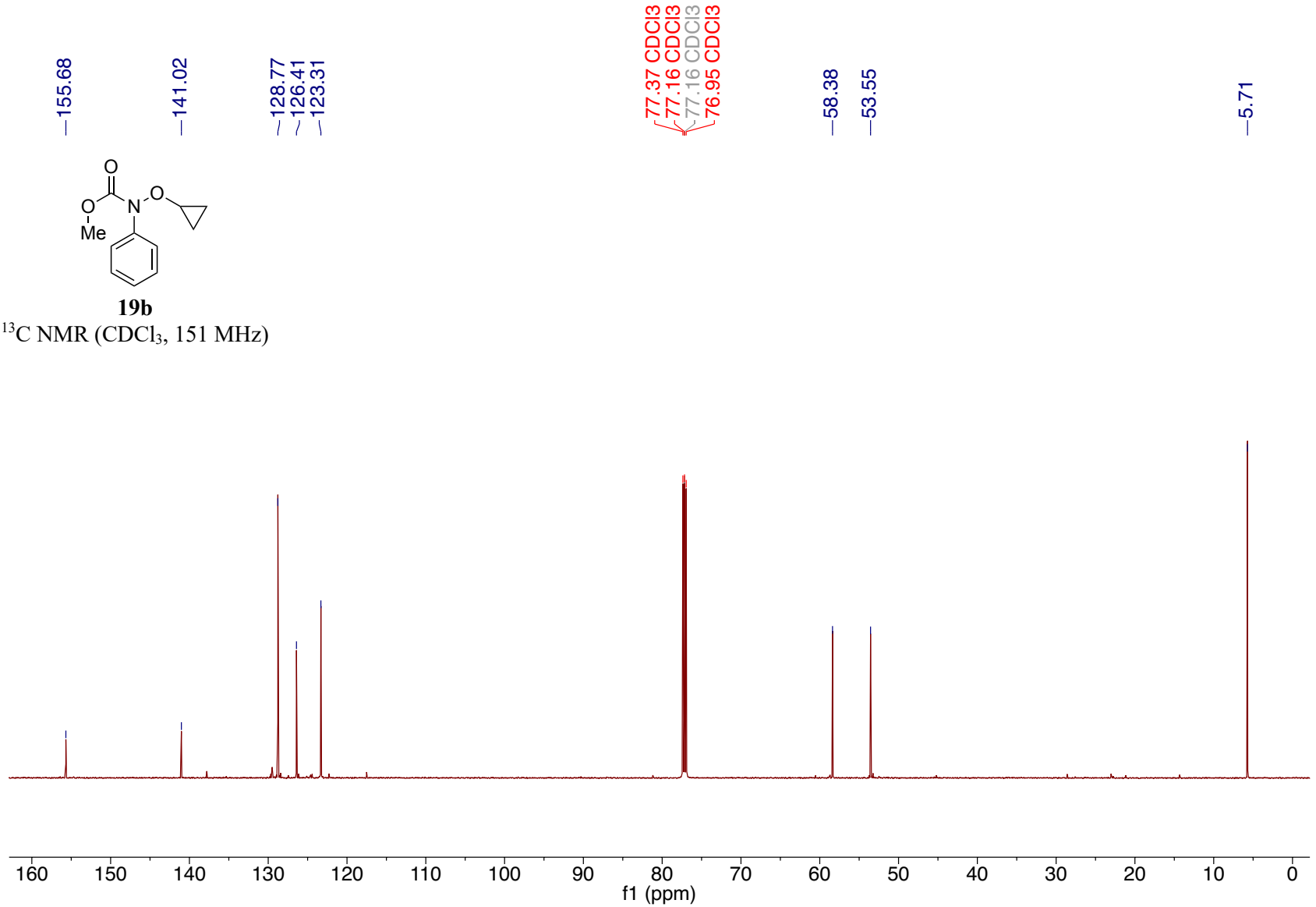

19b

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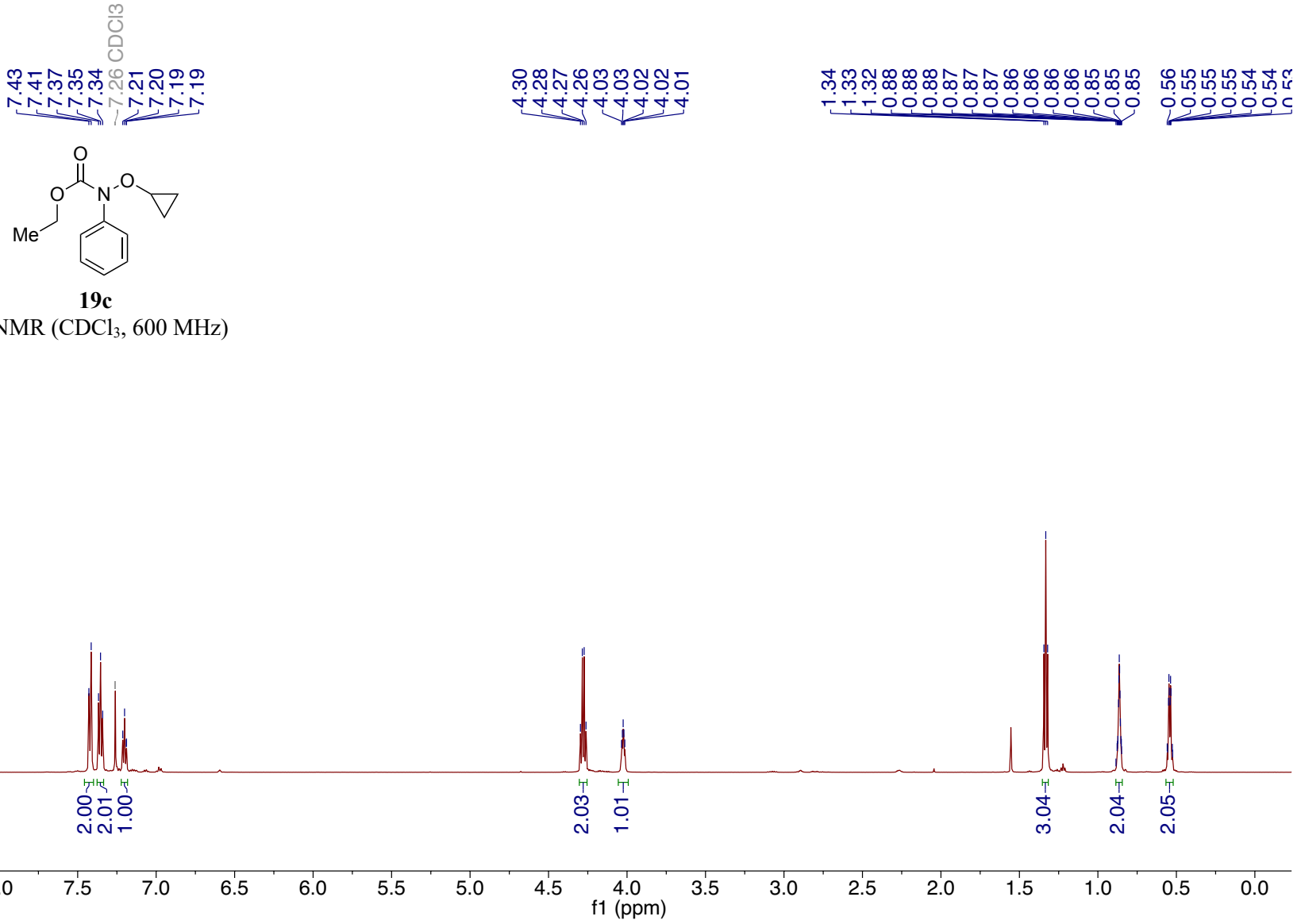

19c

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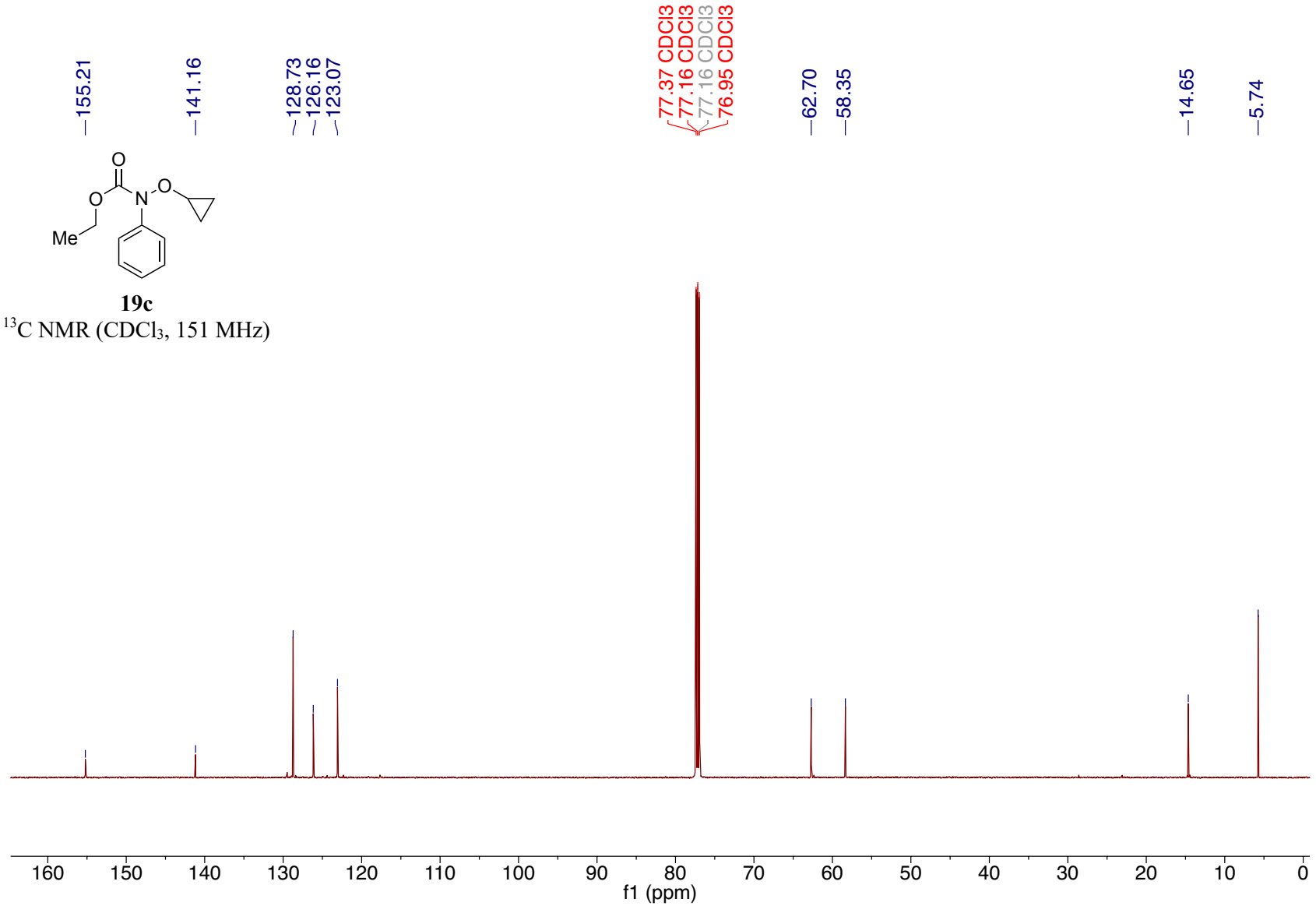

19c

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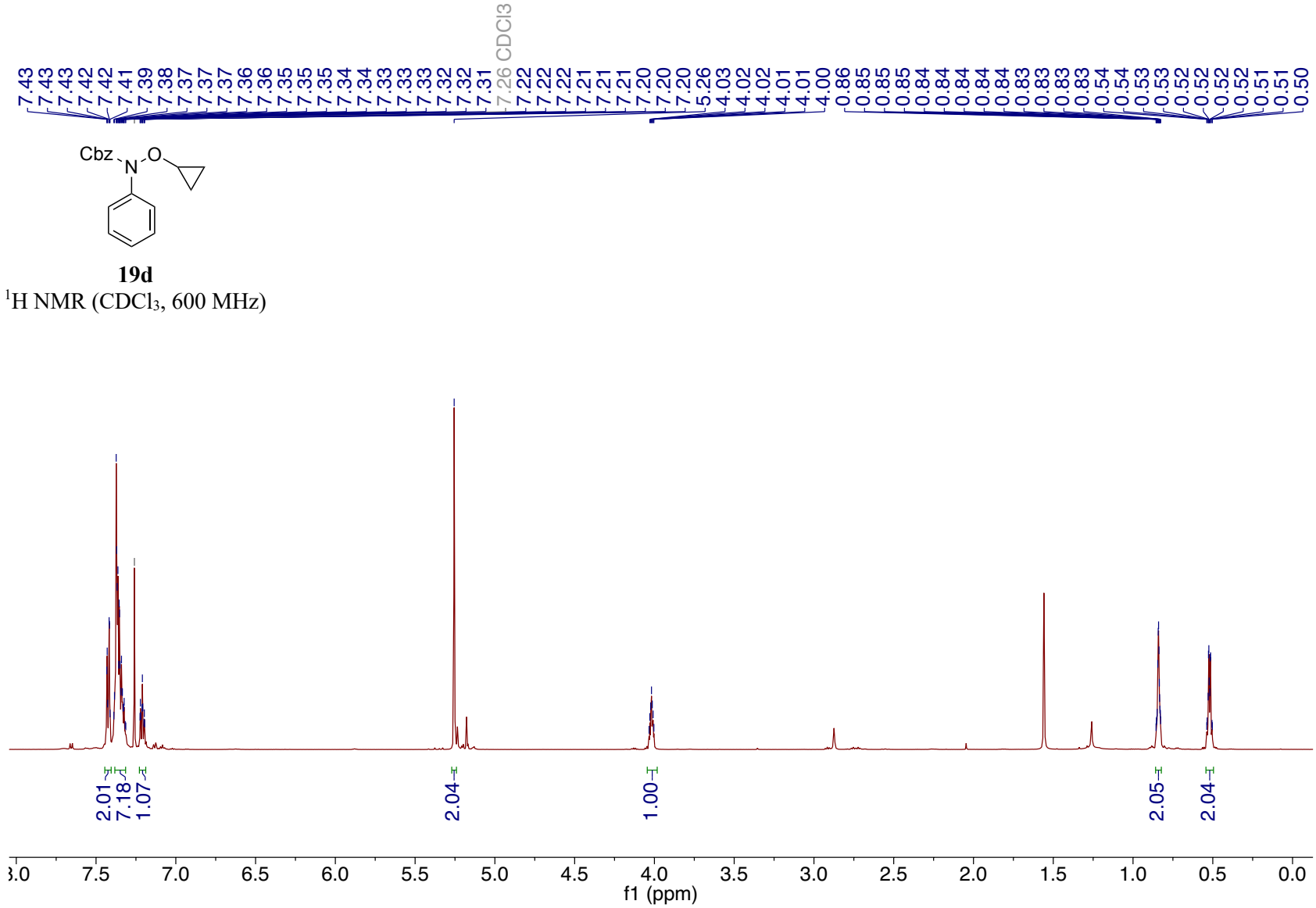

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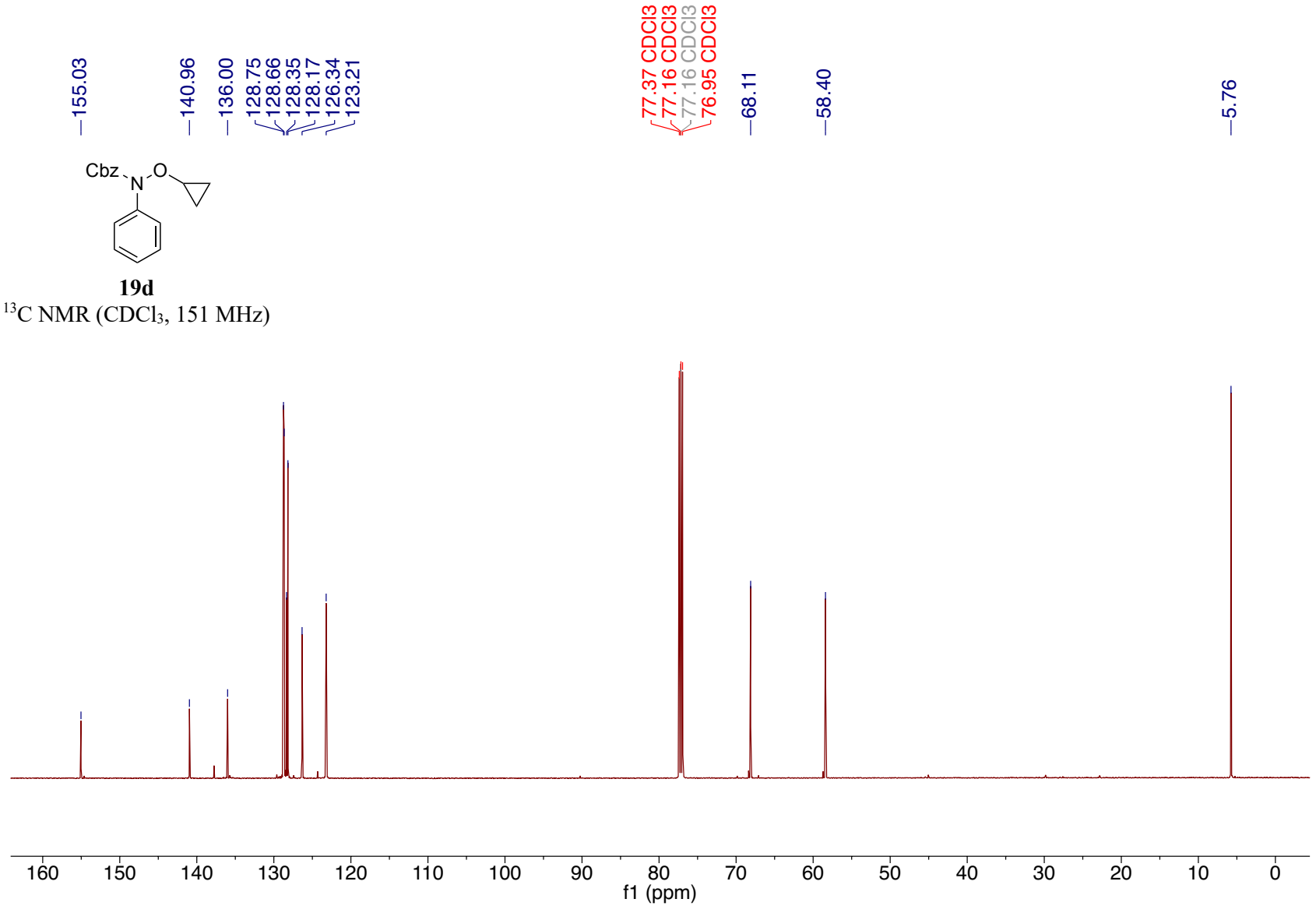

19d

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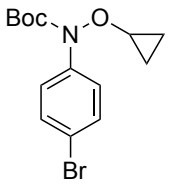

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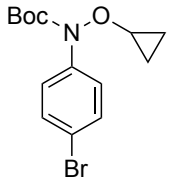

19e

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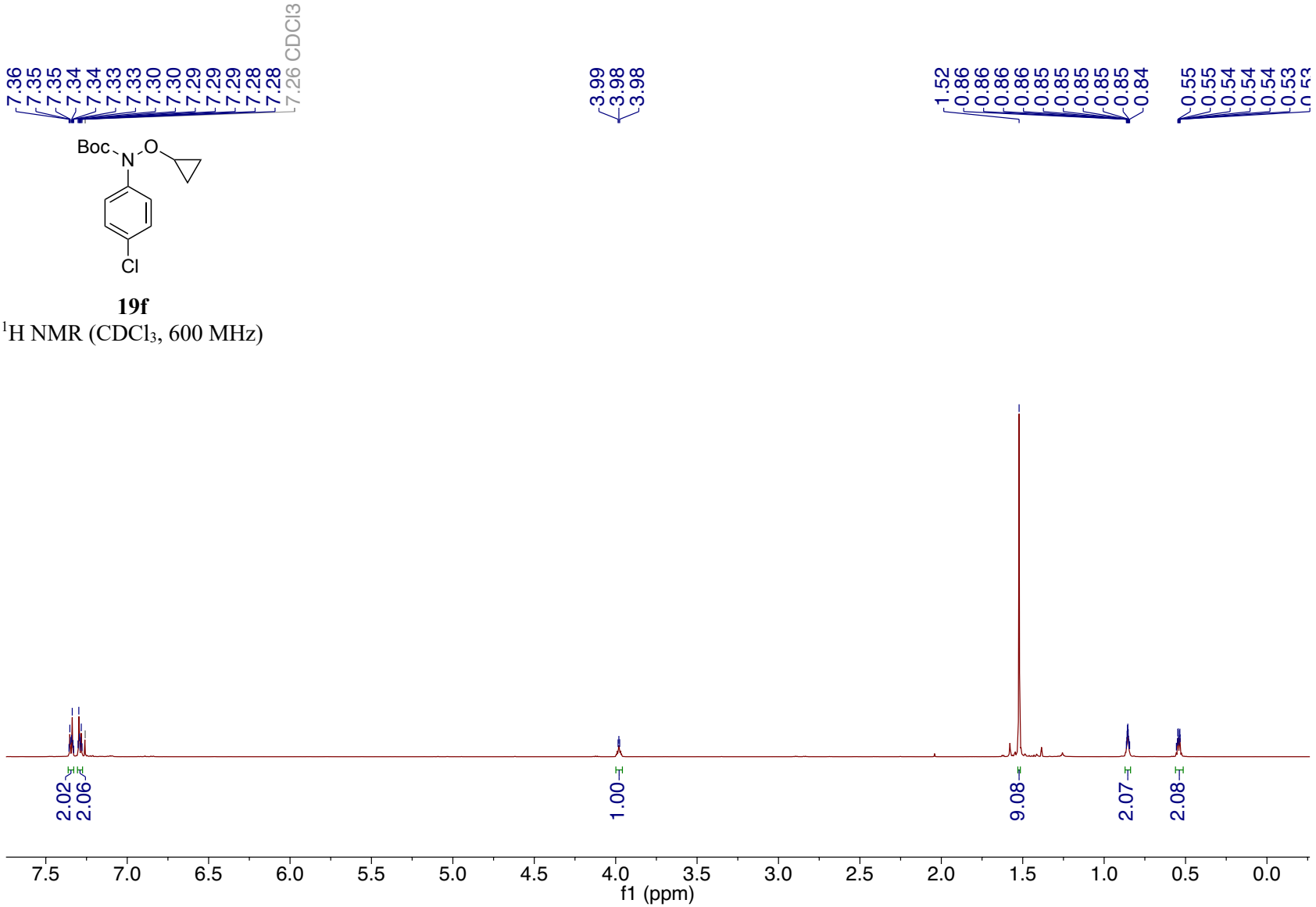

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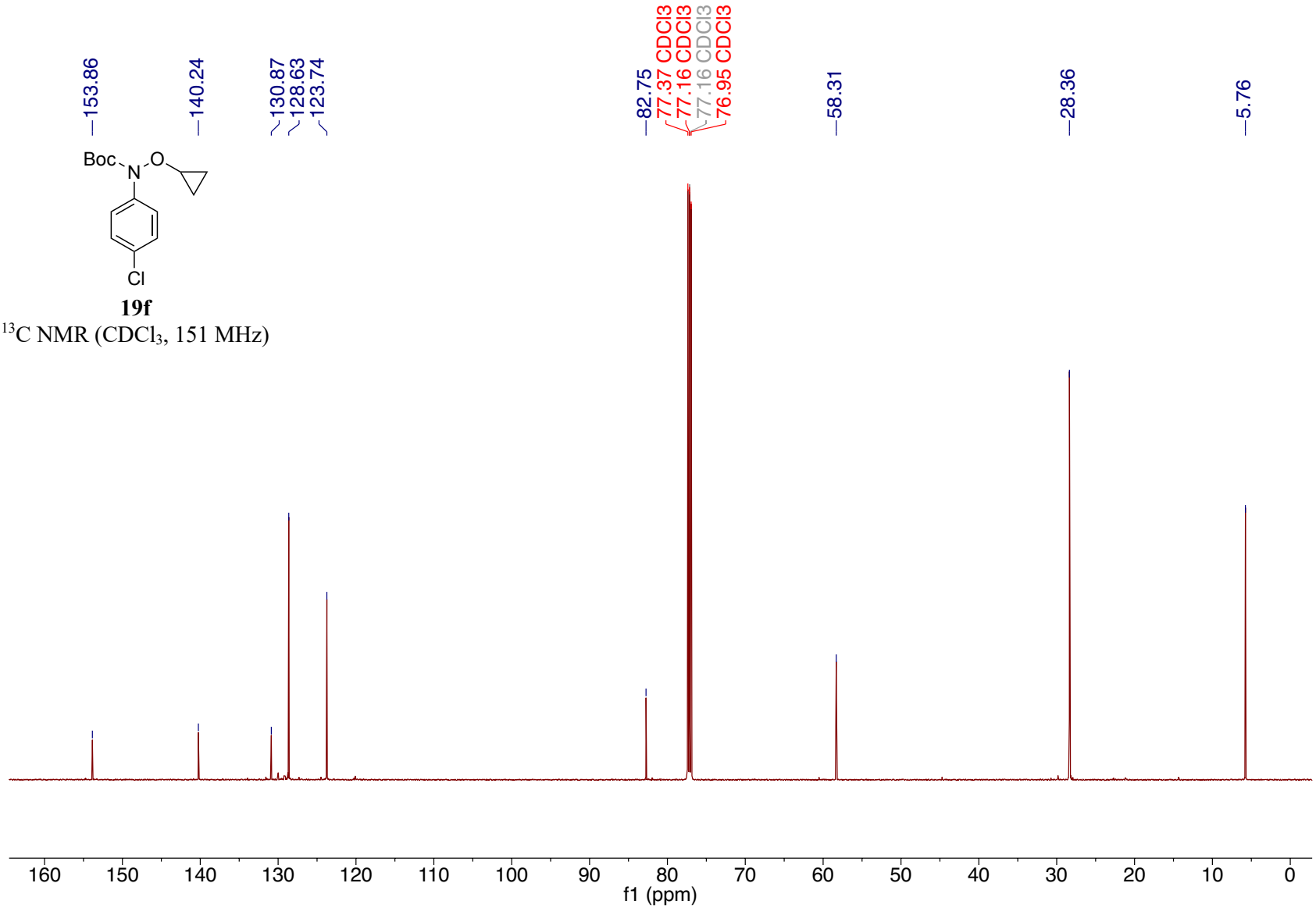
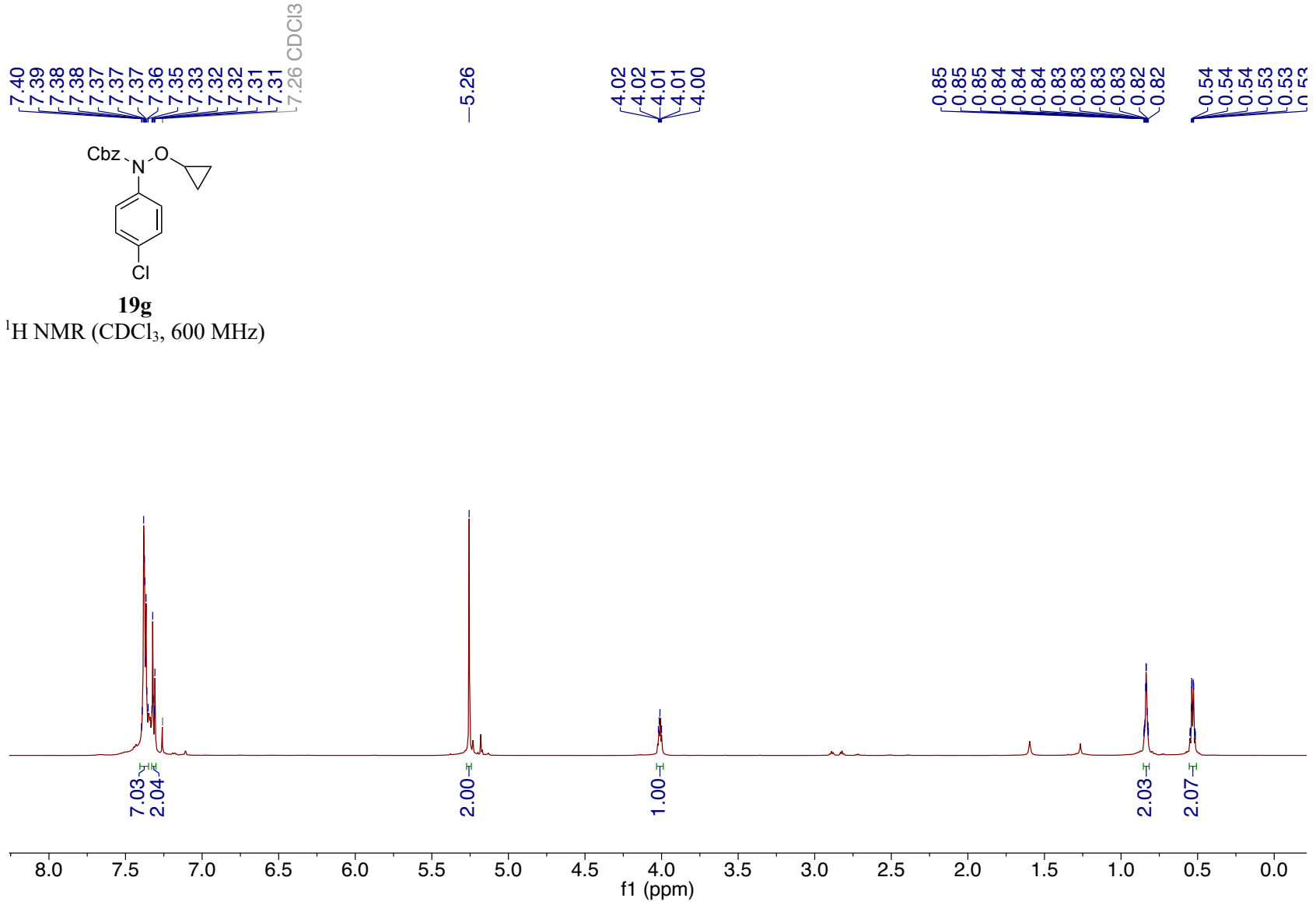


19f

^{13}C NMR ($CDCl_3$, 151 MHz)



19g

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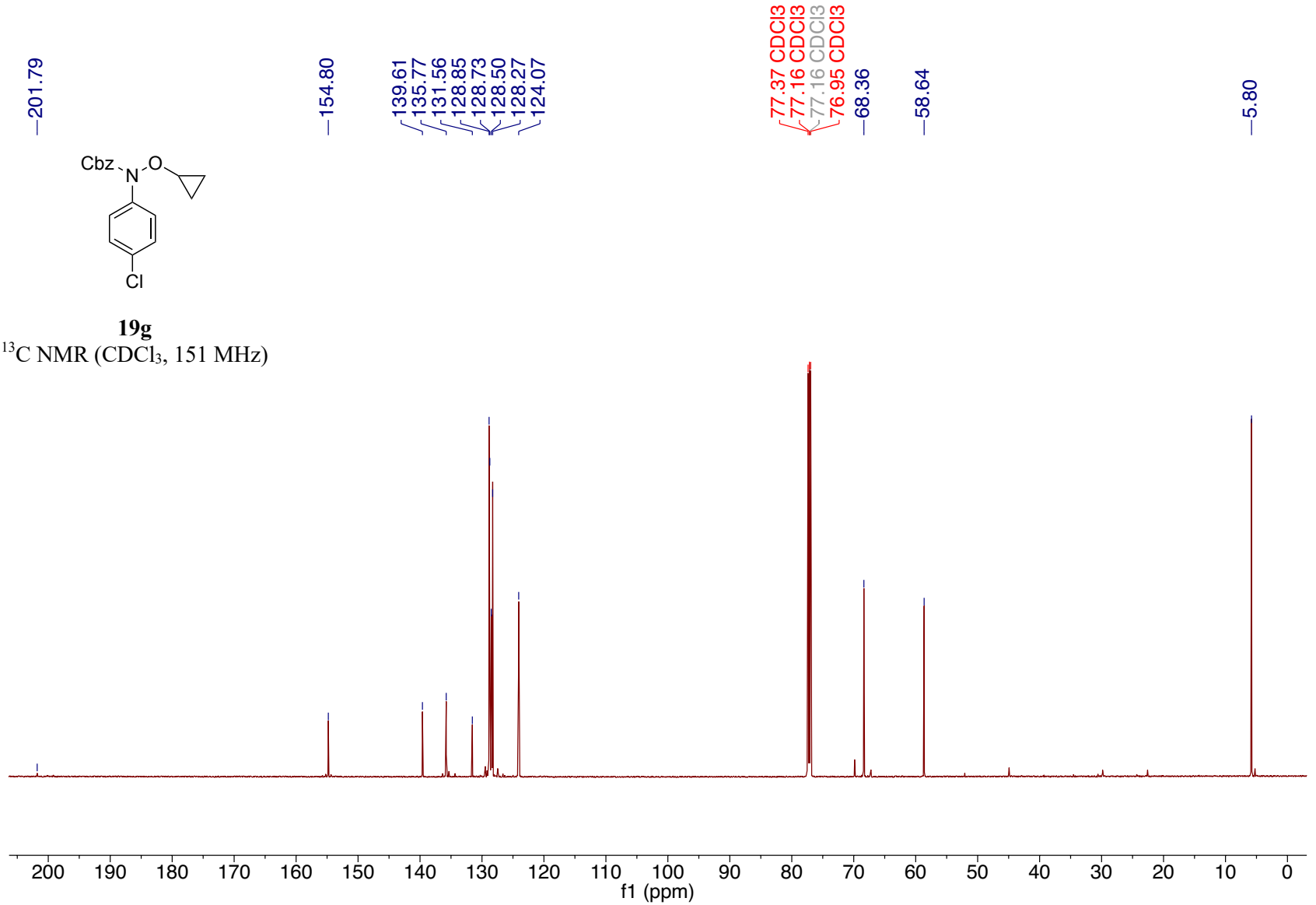

19g

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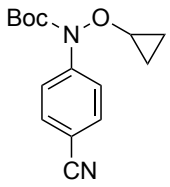

19h

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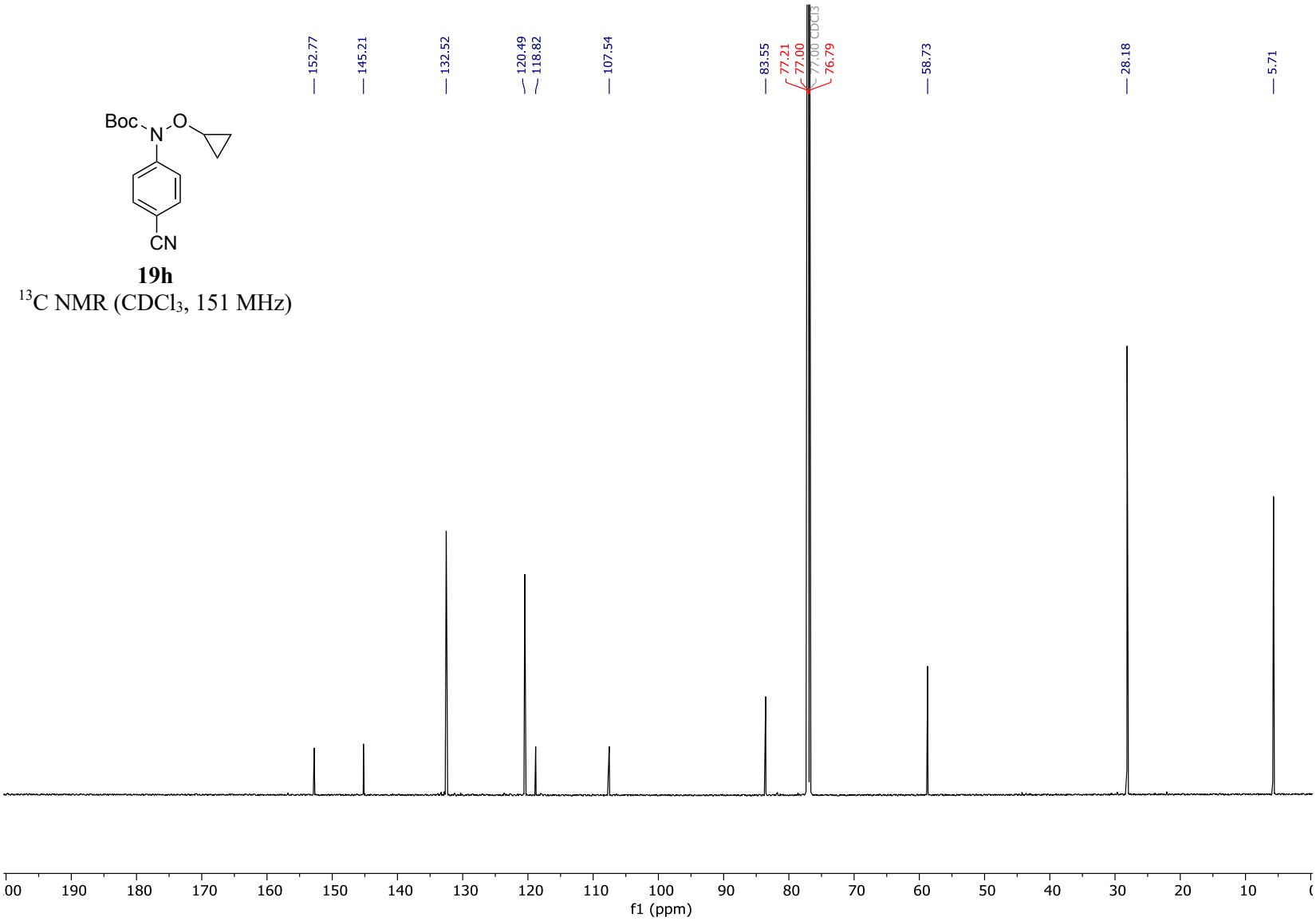

19h

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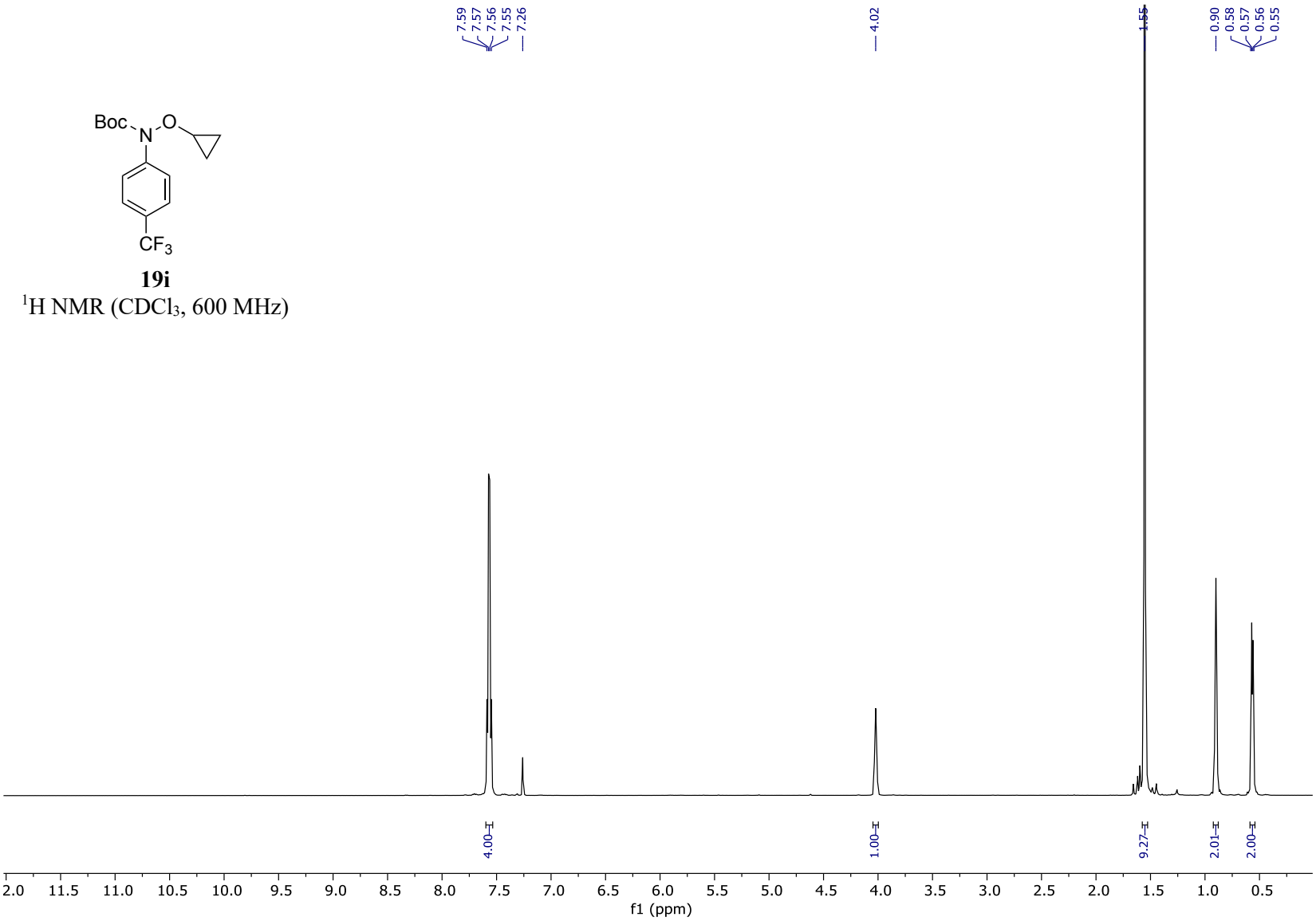

19i

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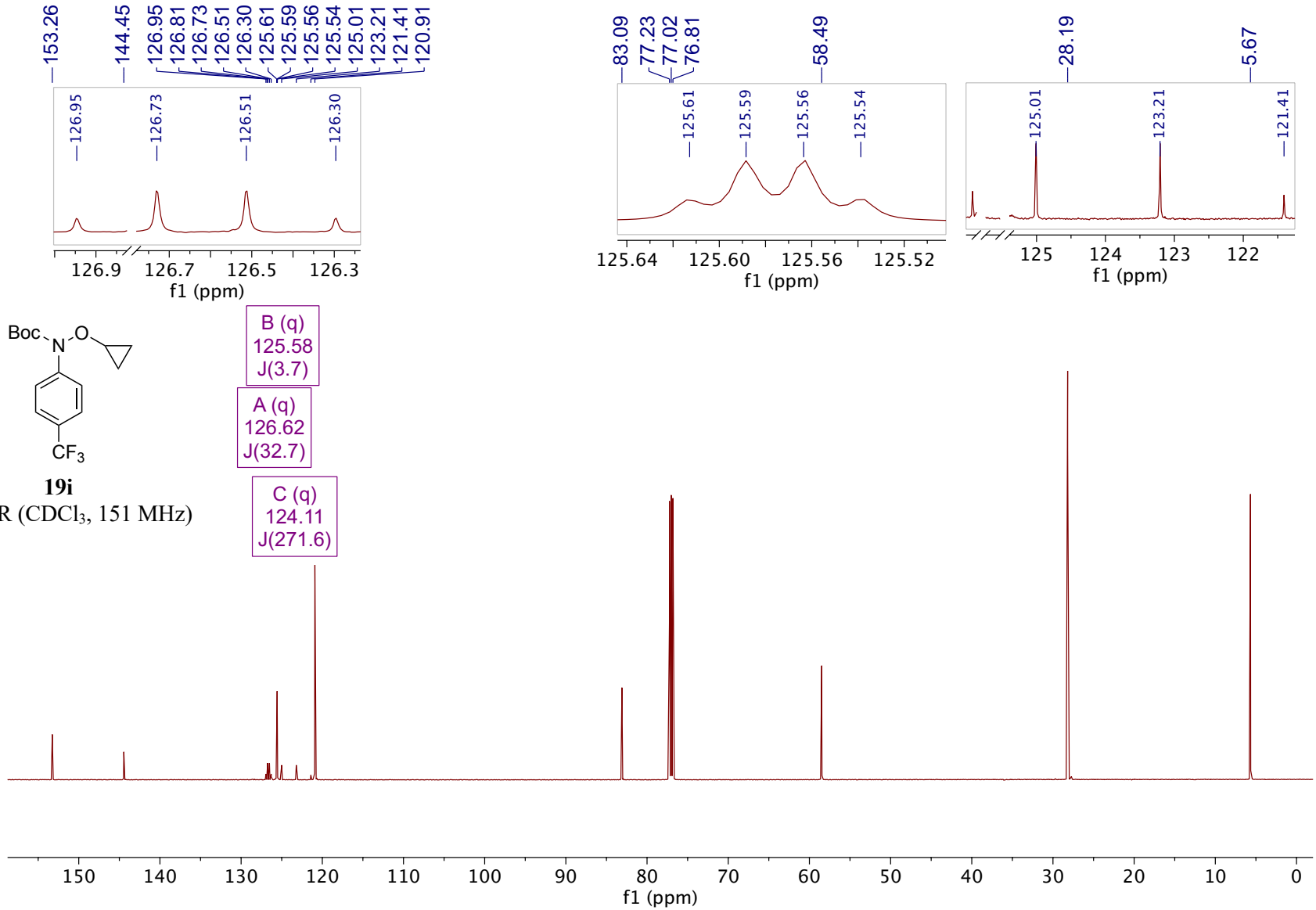
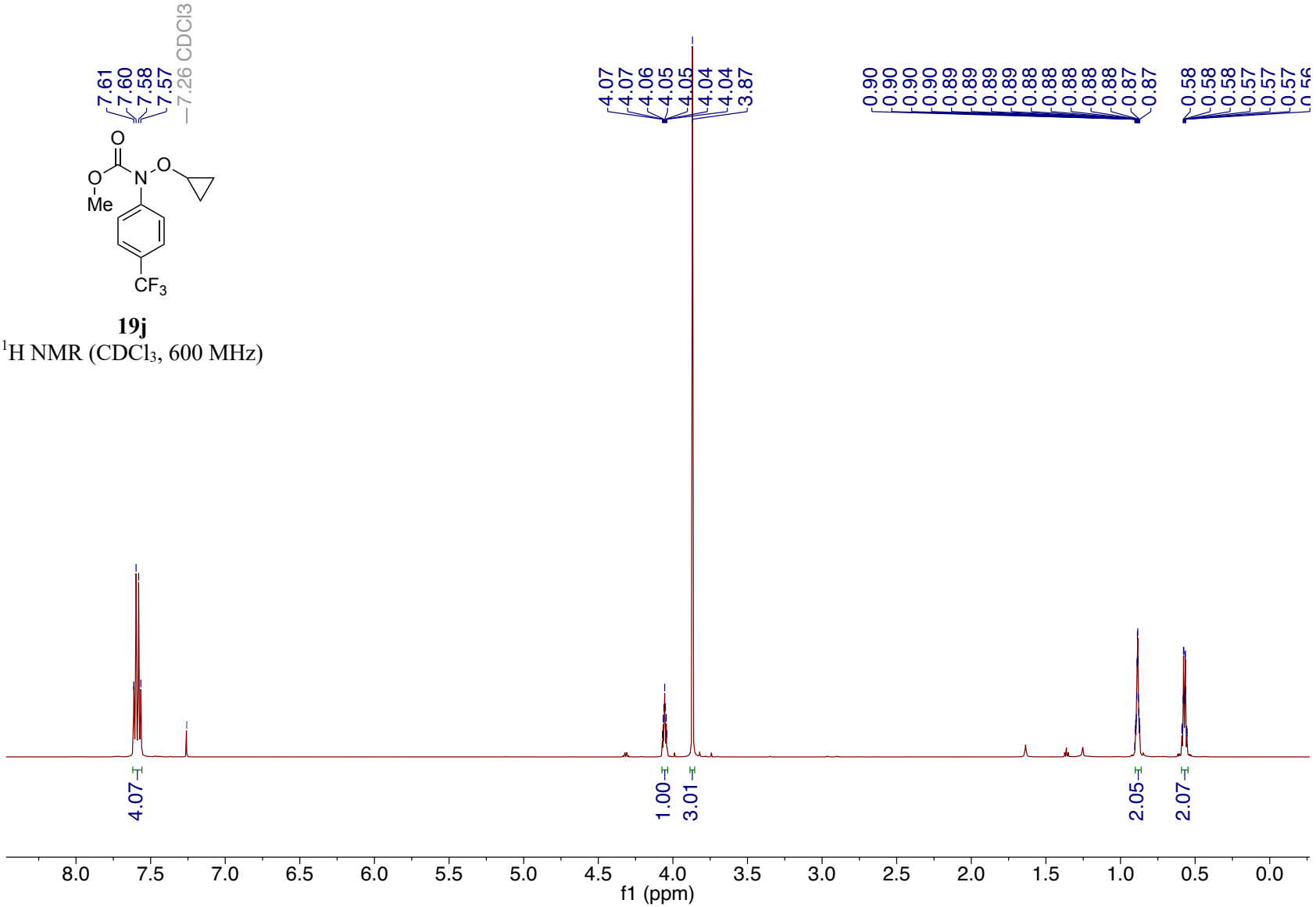


19i

^{13}C NMR ($CDCl_3$, 151 MHz)



19j

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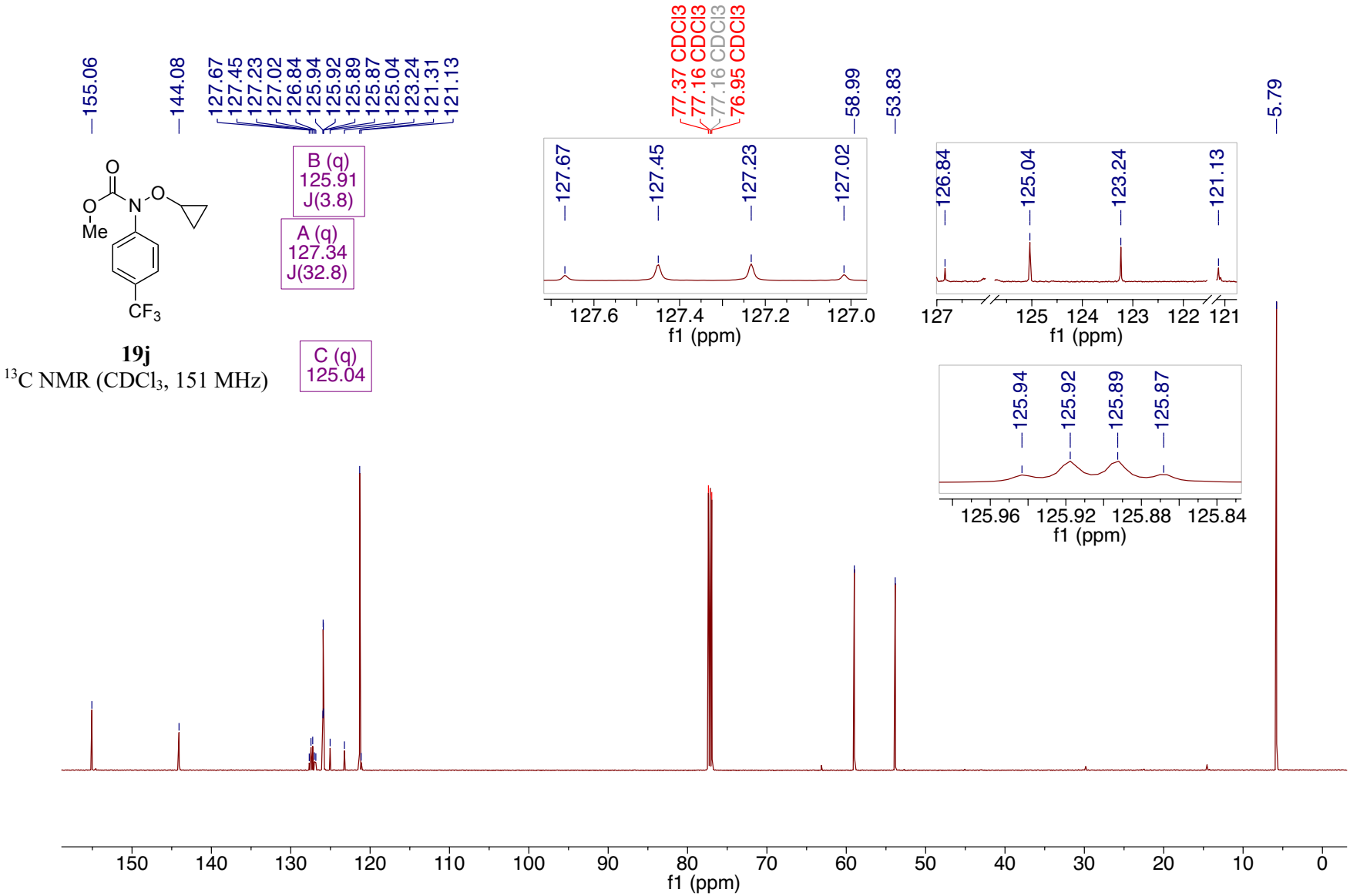
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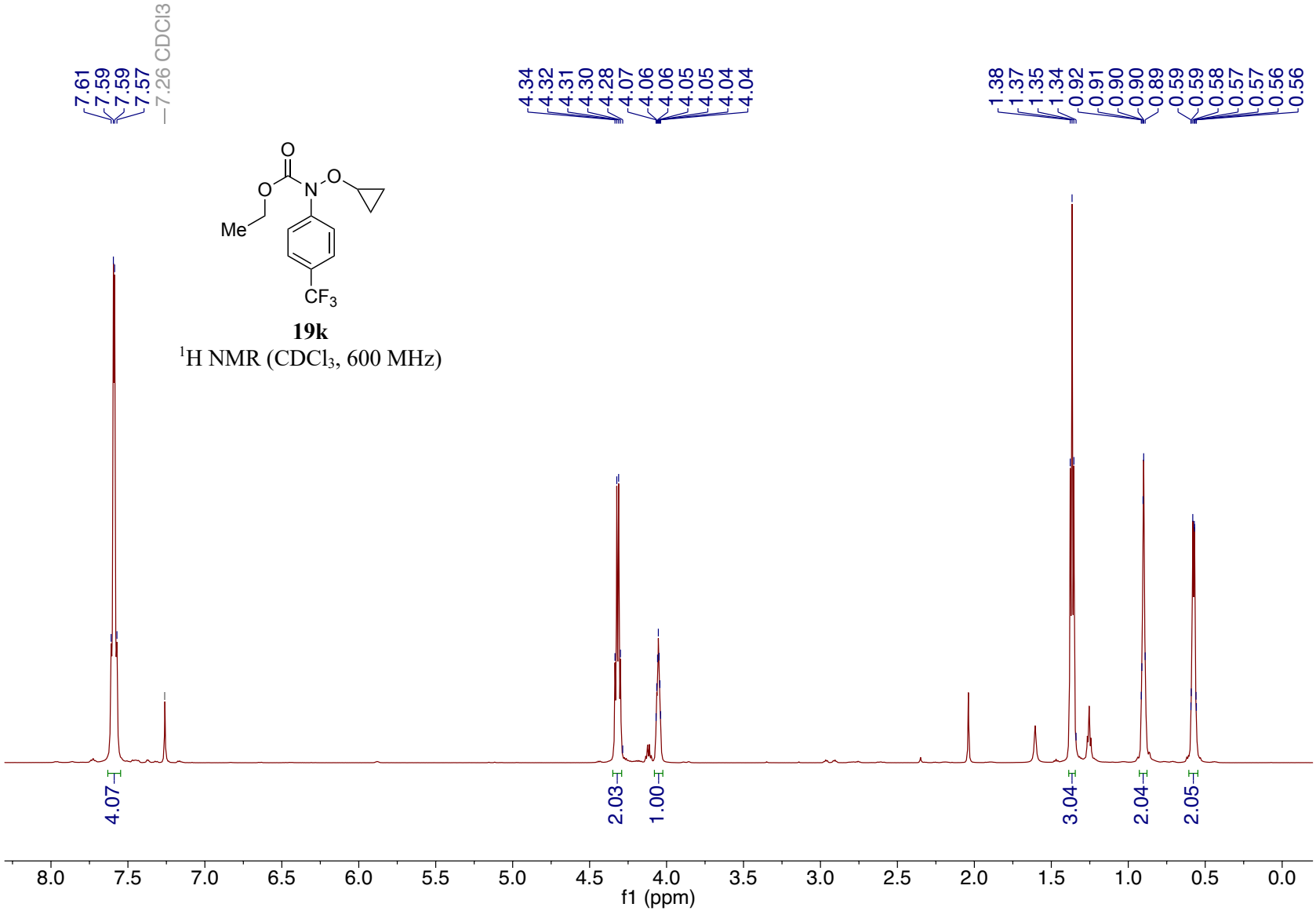
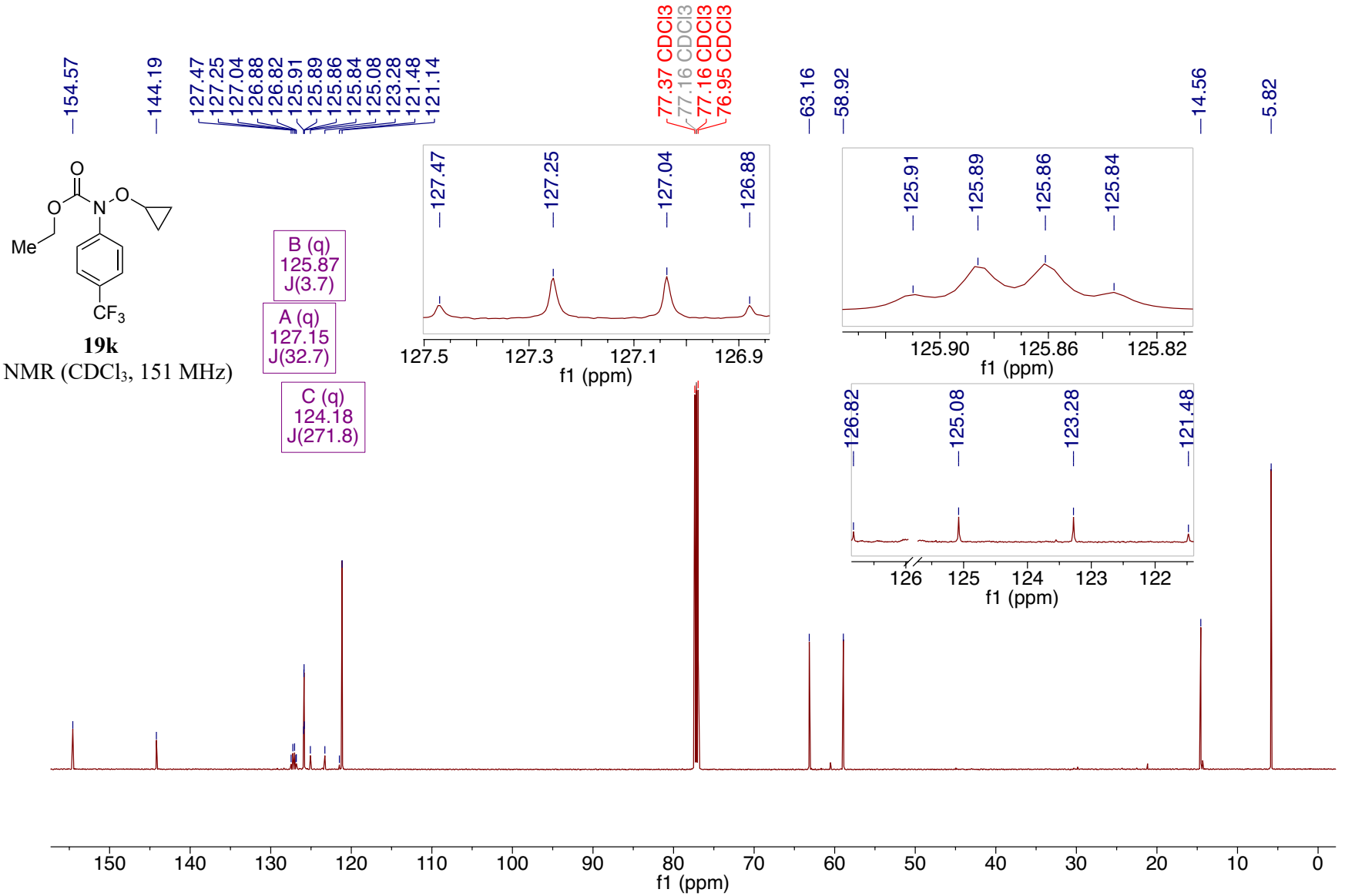
144.08
127.67
127.45
127.23
127.02
126.84
125.94
125.92
125.89
125.87
125.04
123.24
121.31
121.13
77.37 CDCl3
77.16 CDCl3
77.16 CDCl3
76.95 CDCl3
58.99
53.83
5.79
B (q)
125.91
J(3.8)
A (q)
127.34
J(32.8)
C (q)
125.04
O
O
N
O
Me
CF3
19j
13C NMR (CDCl3, 151 MHz)
f1 (ppm)



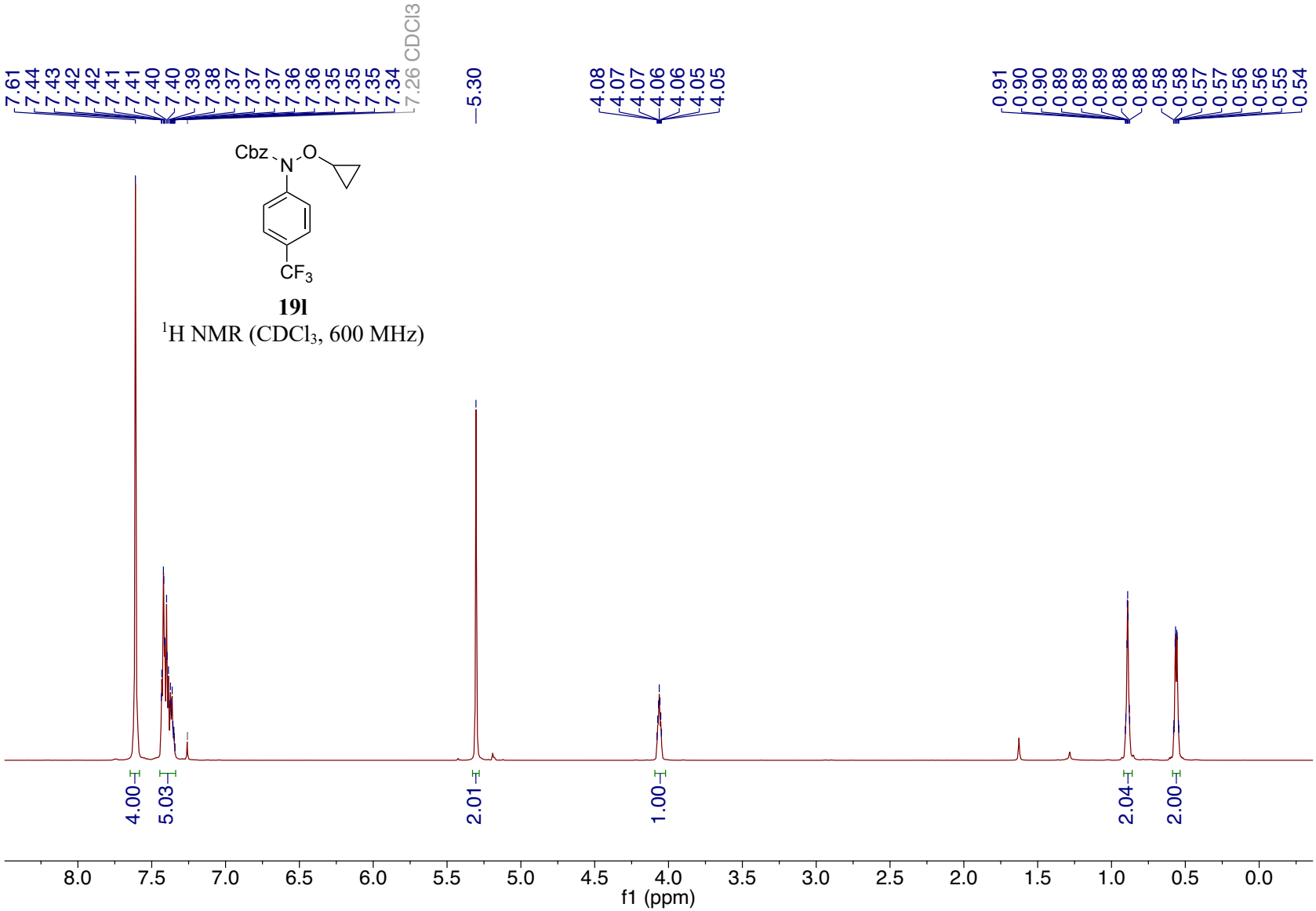
19k

^{1}H NMR ($CDCl_3$, 600 MHz)



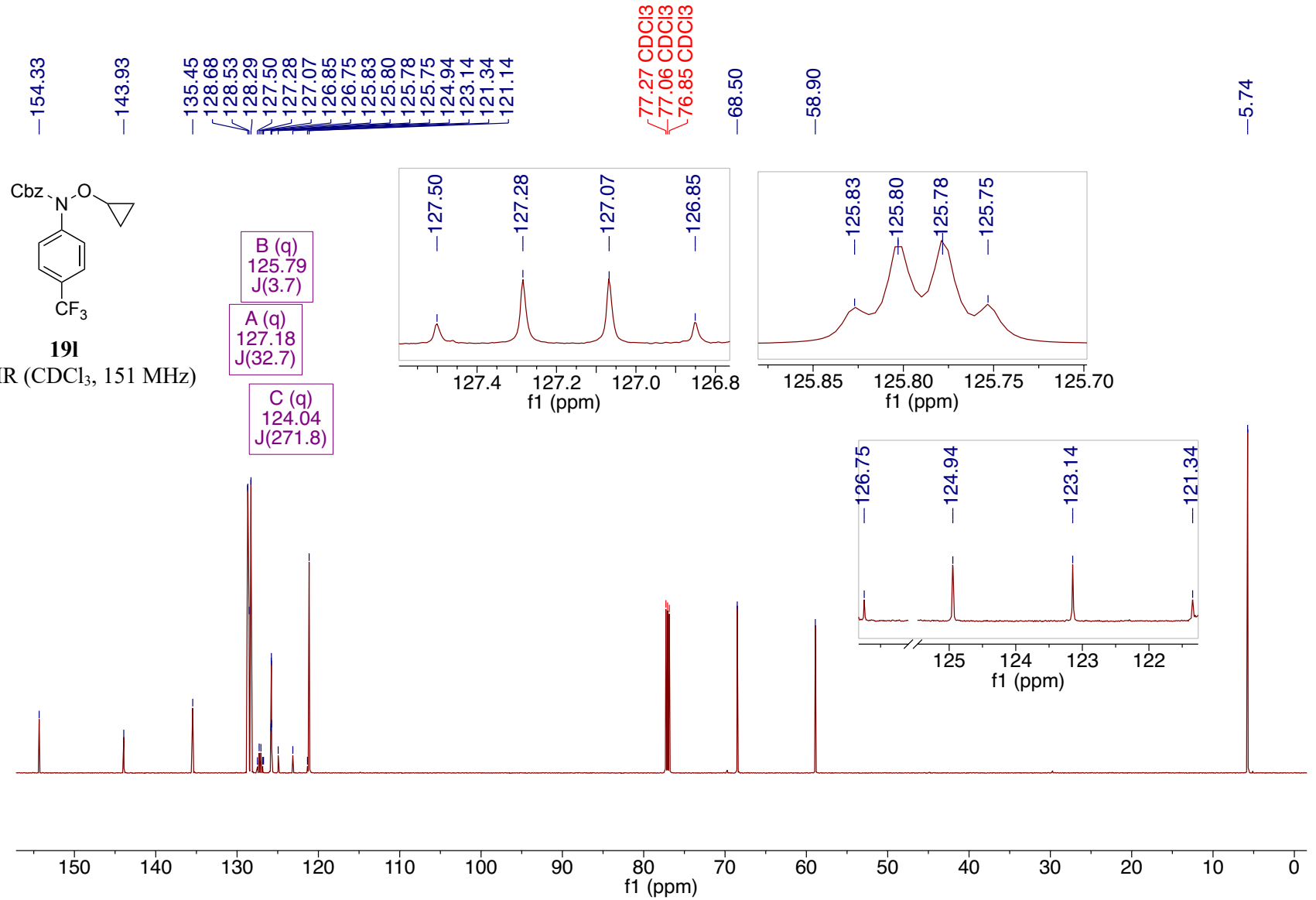
19k

^{13}C NMR ($CDCl_3$, 151 MHz)



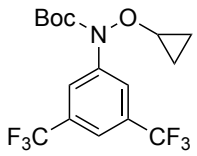
19l

^{1}H NMR ($CDCl_3$, 600 MHz)



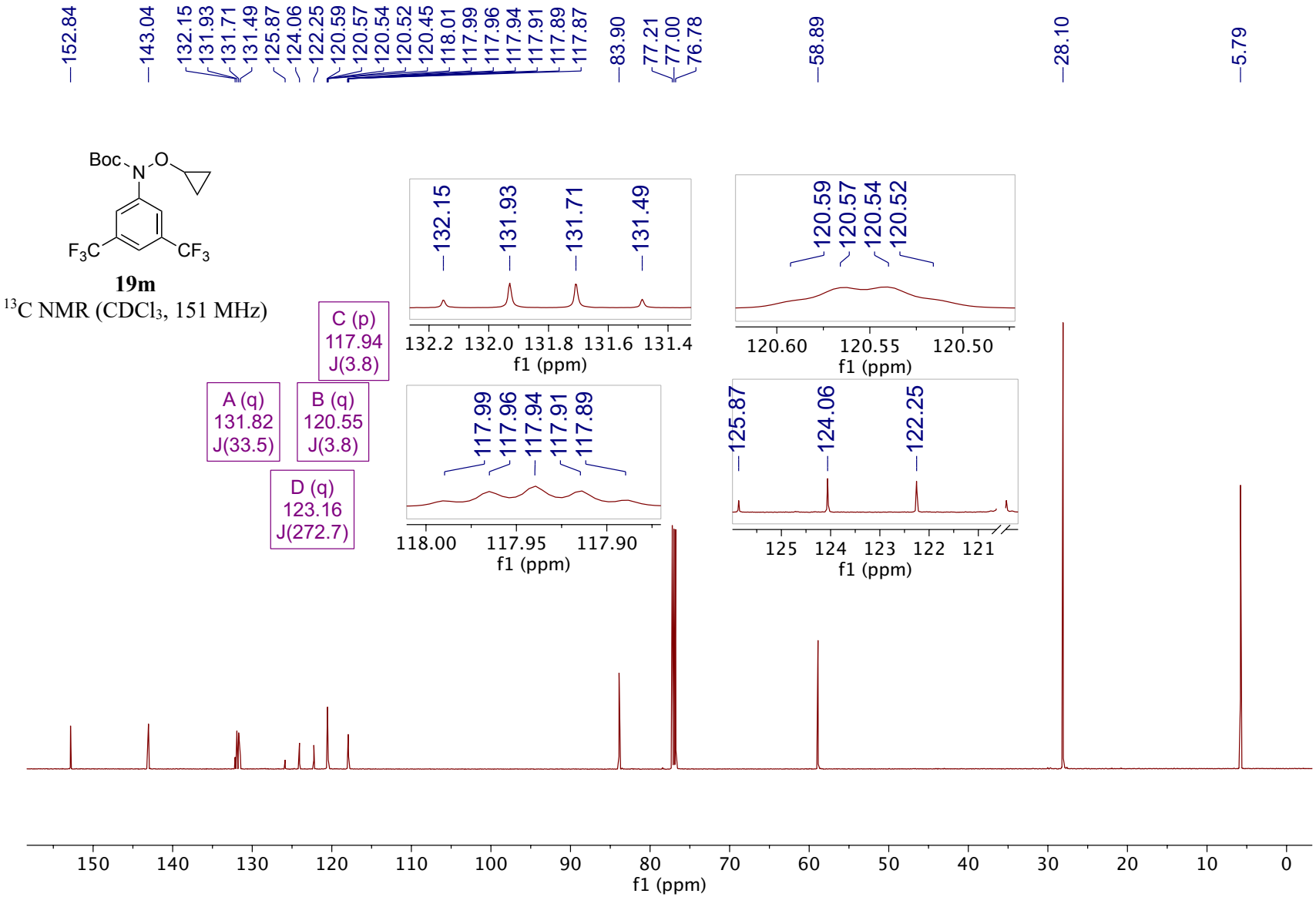
19l

^{13}C NMR ($CDCl_3$, 151 MHz)



19m

^{1}H NMR ($CDCl_3$, 600 MHz)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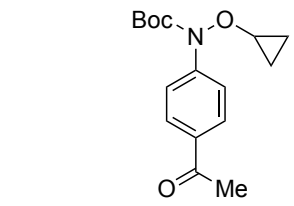
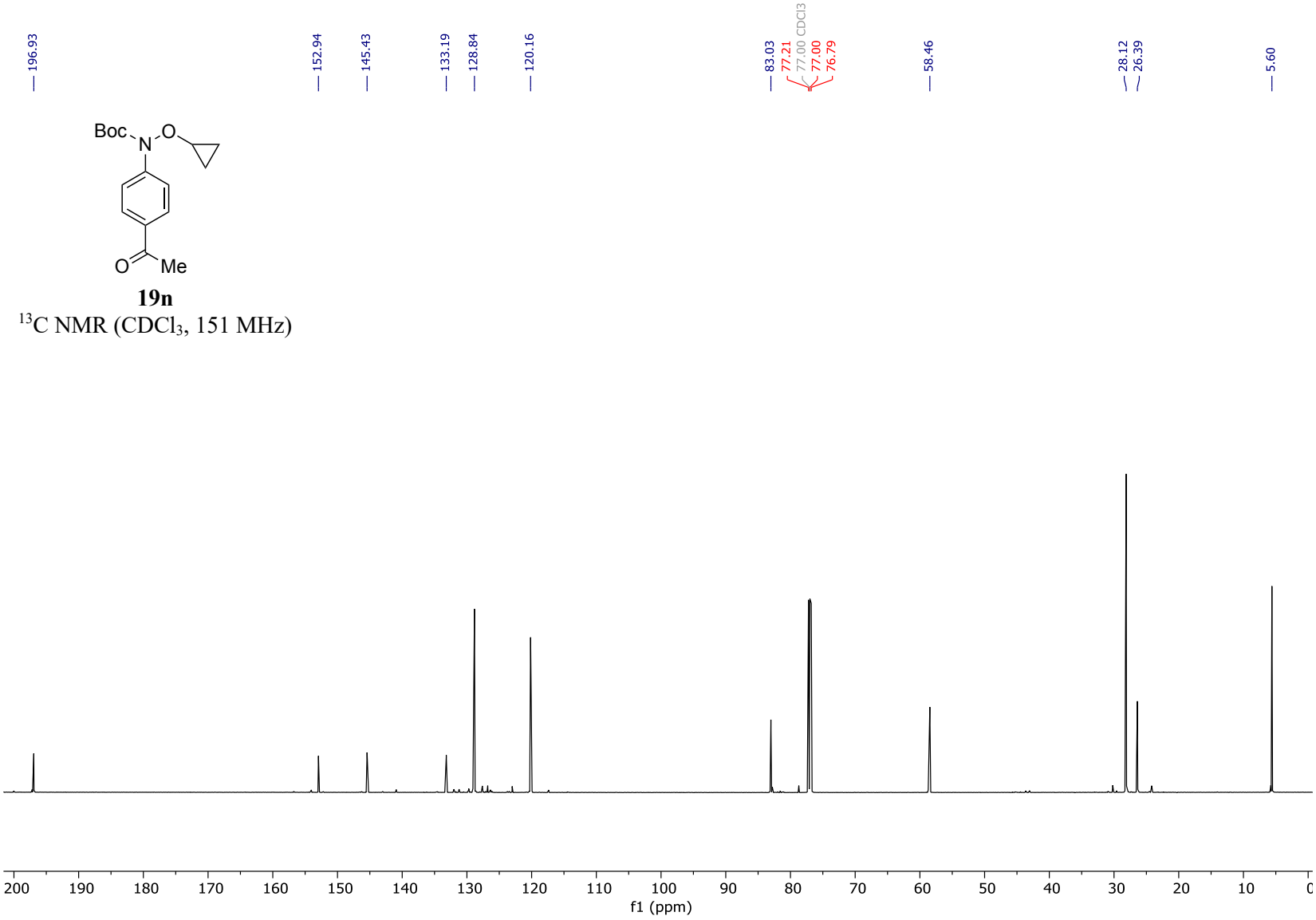
120.45
118.01
117.99
117.96
117.94
117.91
117.89
117.87
83.90
77.21
77.00
76.78
58.89
28.10
5.79
Boc
N
O
F3C
CF3
19m
13C NMR (CDCl3, 151 MHz)
C (p)
117.94
J(3.8)
A (q)
131.82
J(33.5)
B (q)
120.55
J(3.8)
D (q)
123.16
J(272.7)
f1 (ppm)



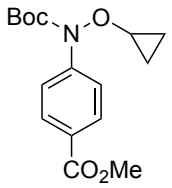
19n

^{1}H NMR ($CDCl_3$, 600 MHz)



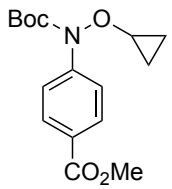
19n

^{13}C NMR ($CDCl_3$, 151 MHz)



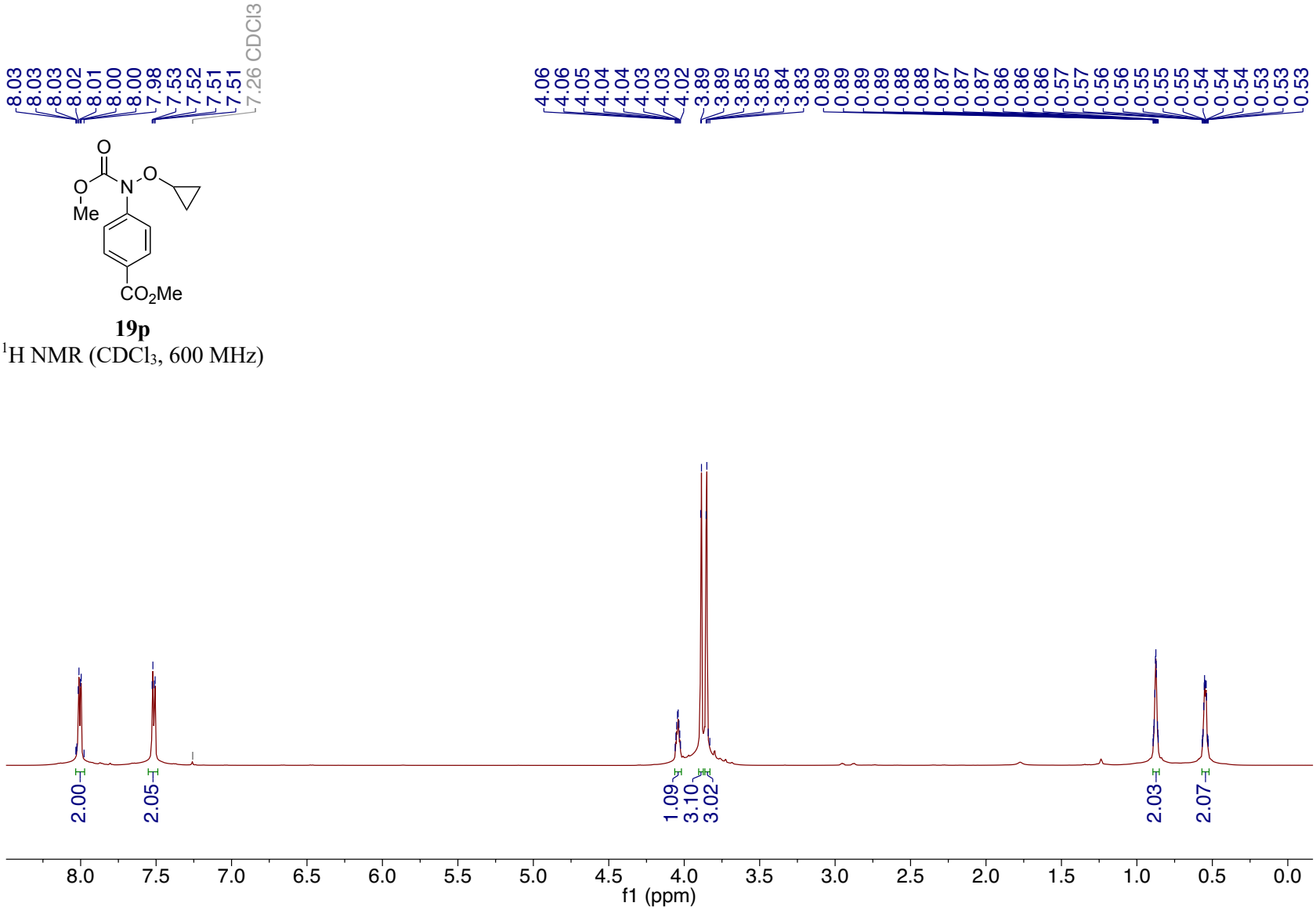
19o

^{1}H NMR ($CDCl_3$, 600 MHz)



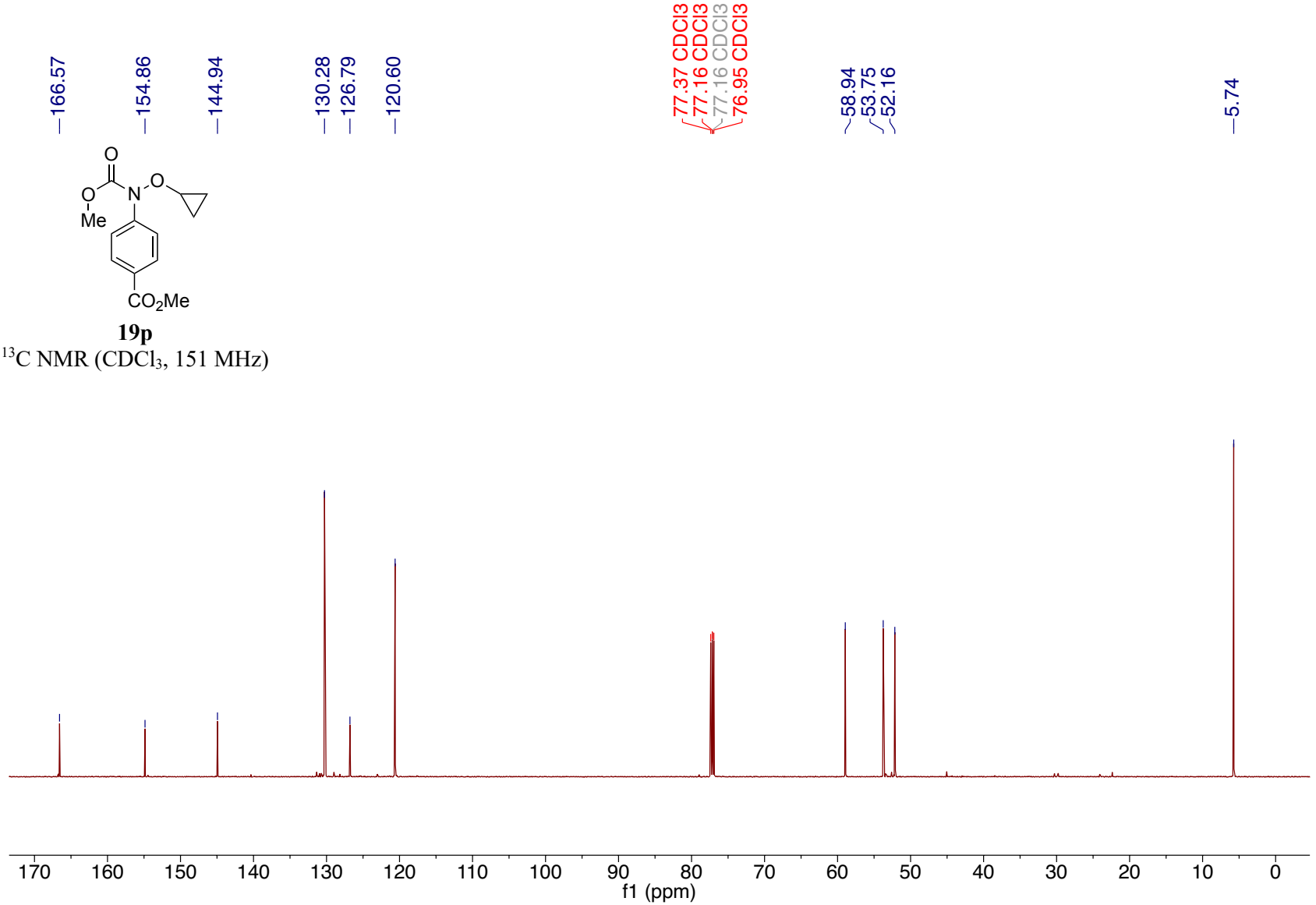
19o

^{13}C NMR ($CDCl_3$, 151 MHz)



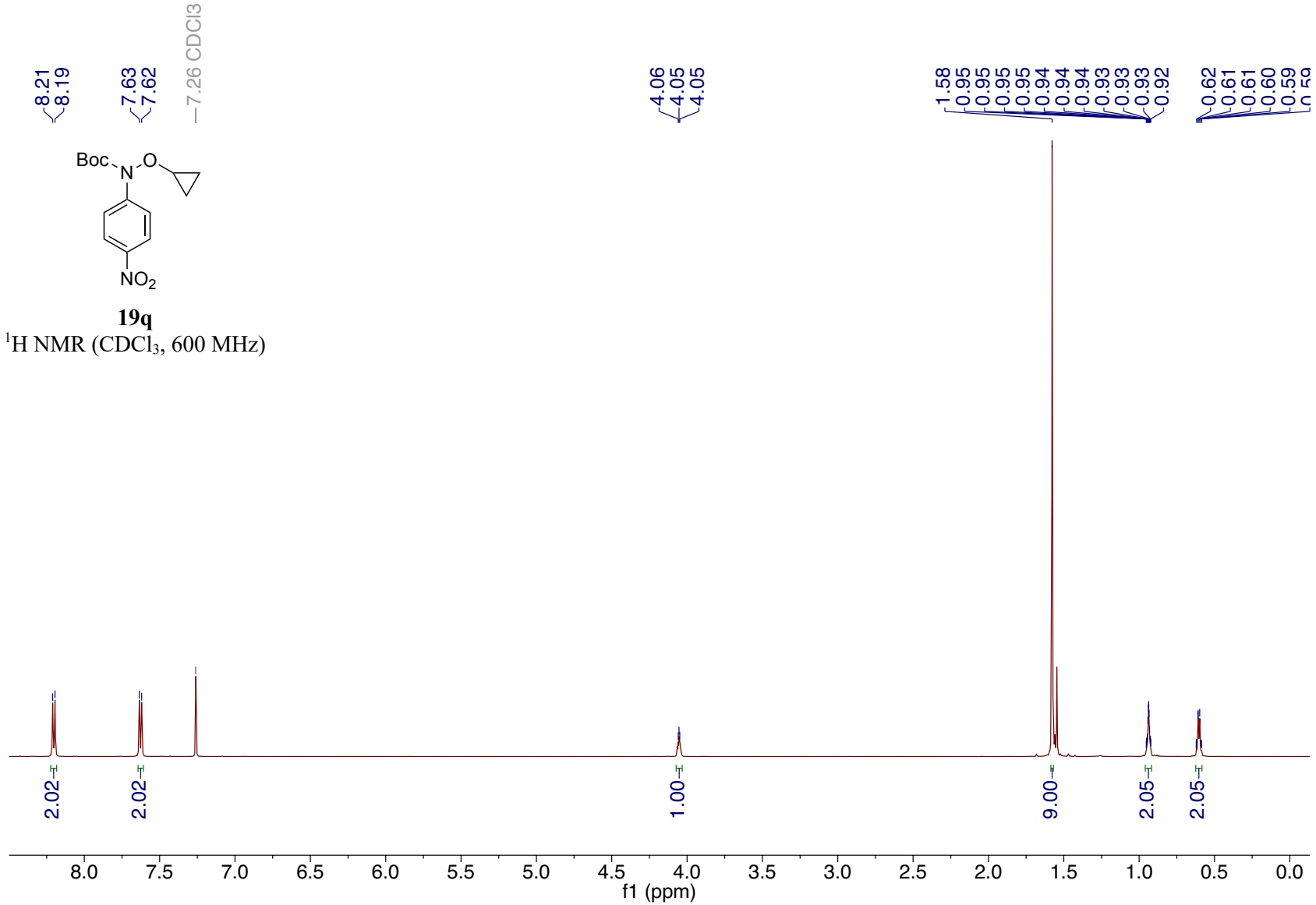
19p

^{1}H NMR ($CDCl_3$, 600 MHz)



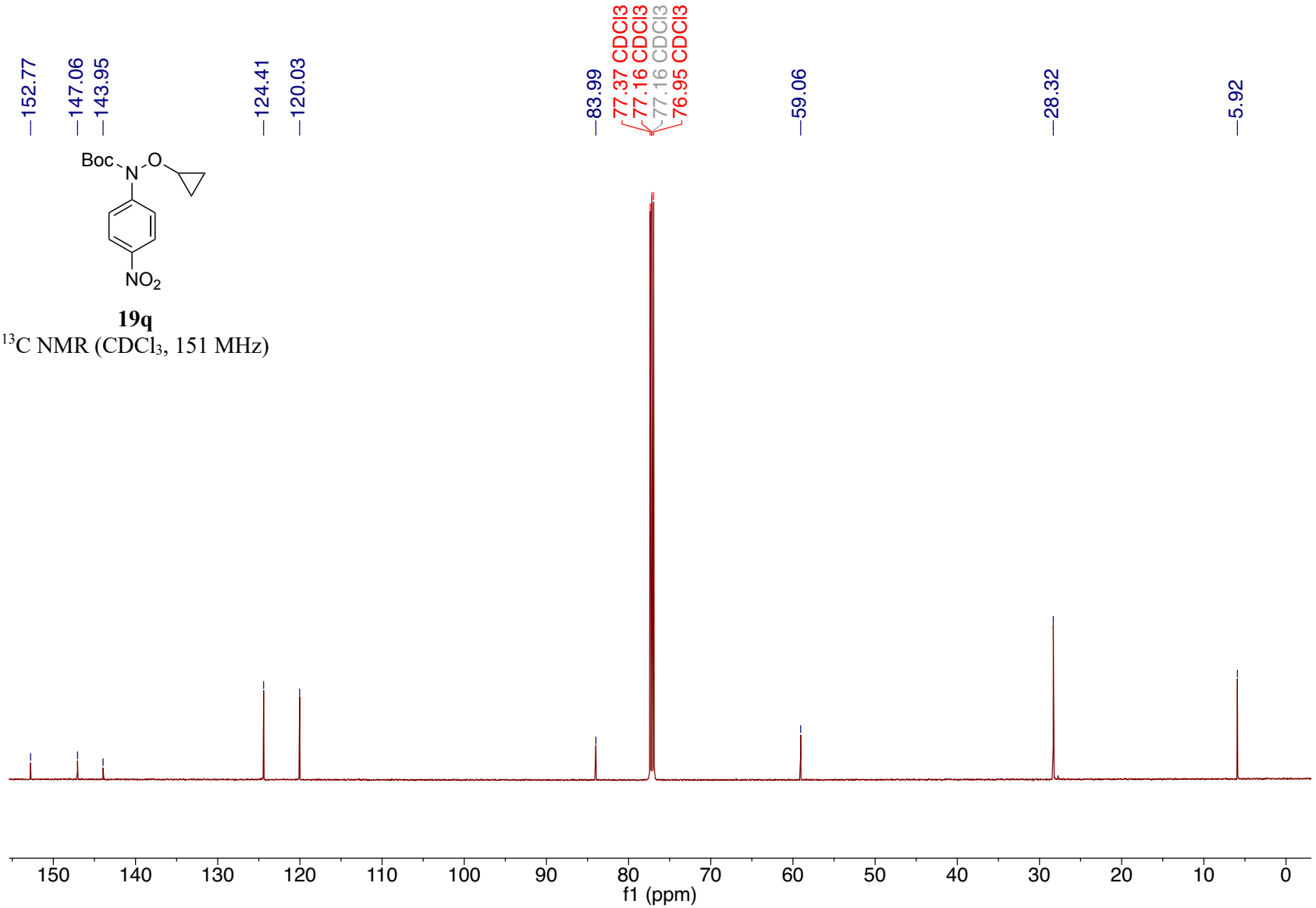
19p

^{13}C NMR ($CDCl_3$, 151 MHz)



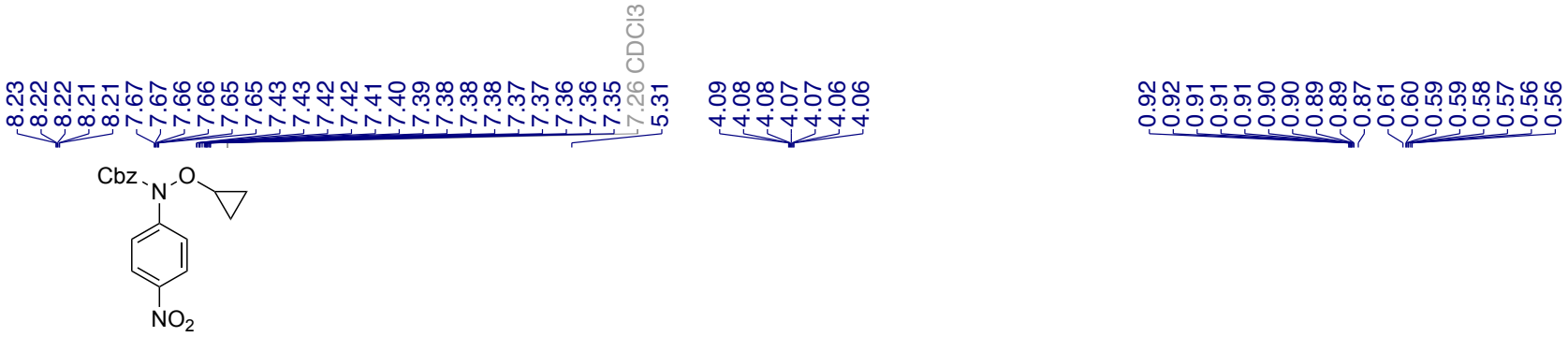
19q

^{1}H NMR ($CDCl_3$, 600 MHz)



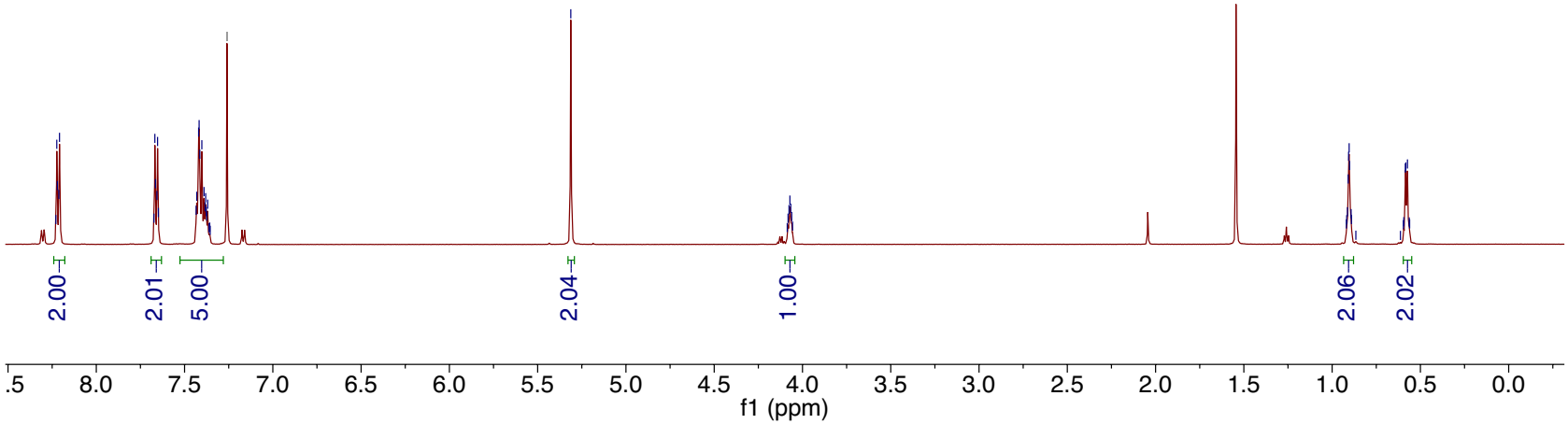
19q

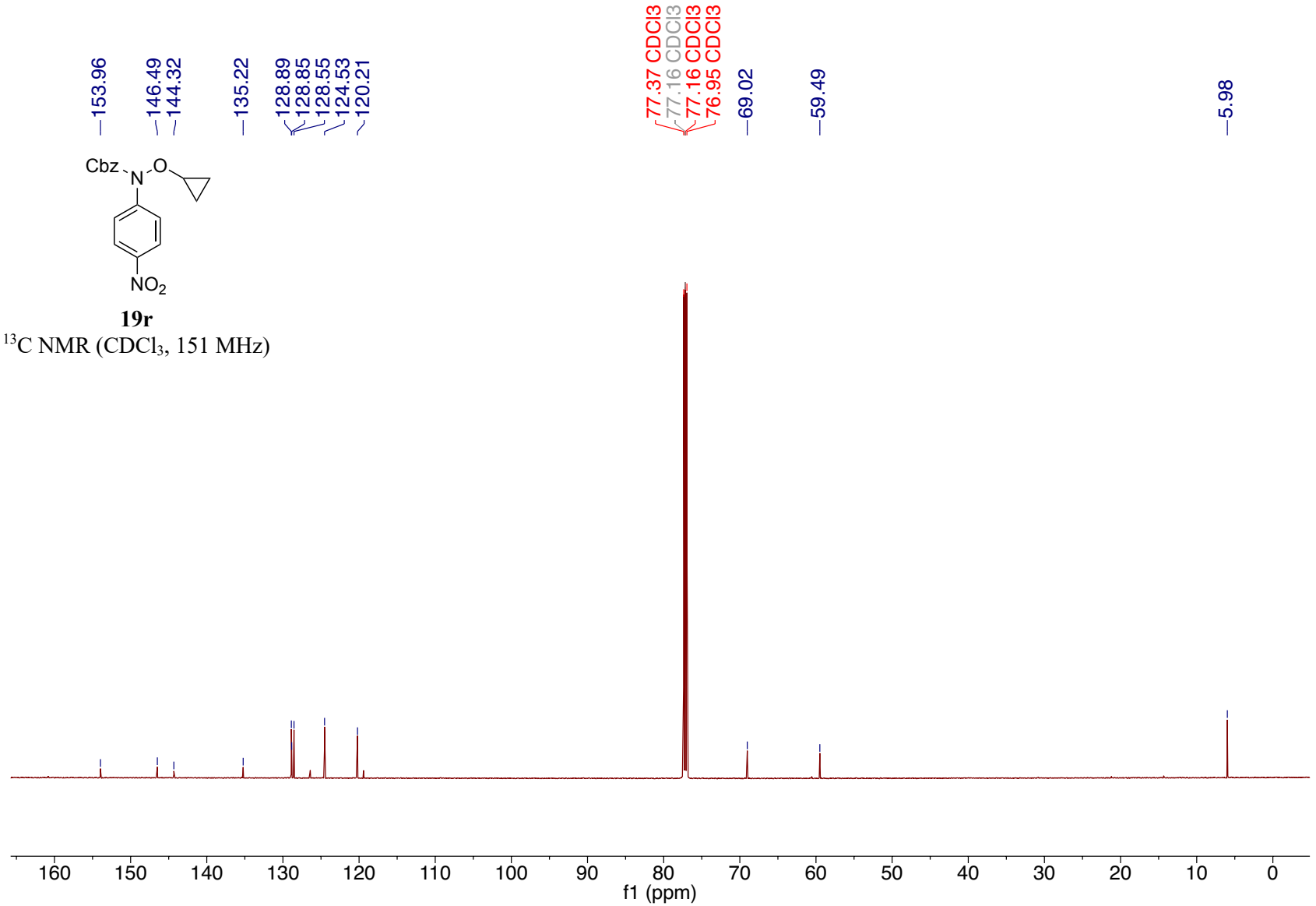
^{13}C NMR ($CDCl_3$, 151 MHz)



19r

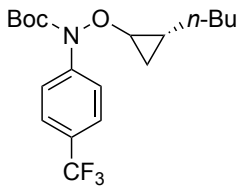
^{1}H NMR ($CDCl_3$, 600 MHz)





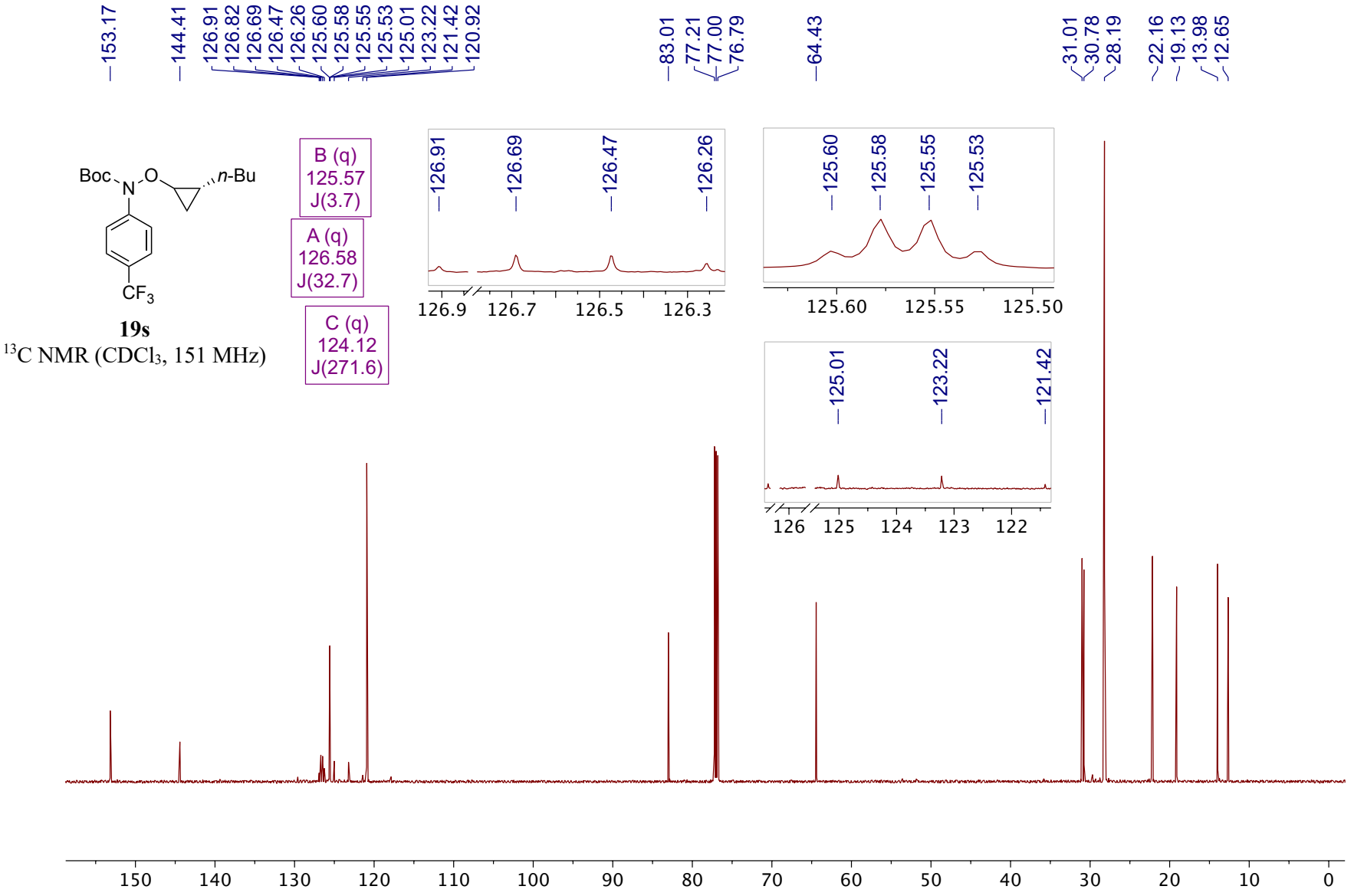
19r

^{13}C NMR ($CDCl_3$, 151 MHz)



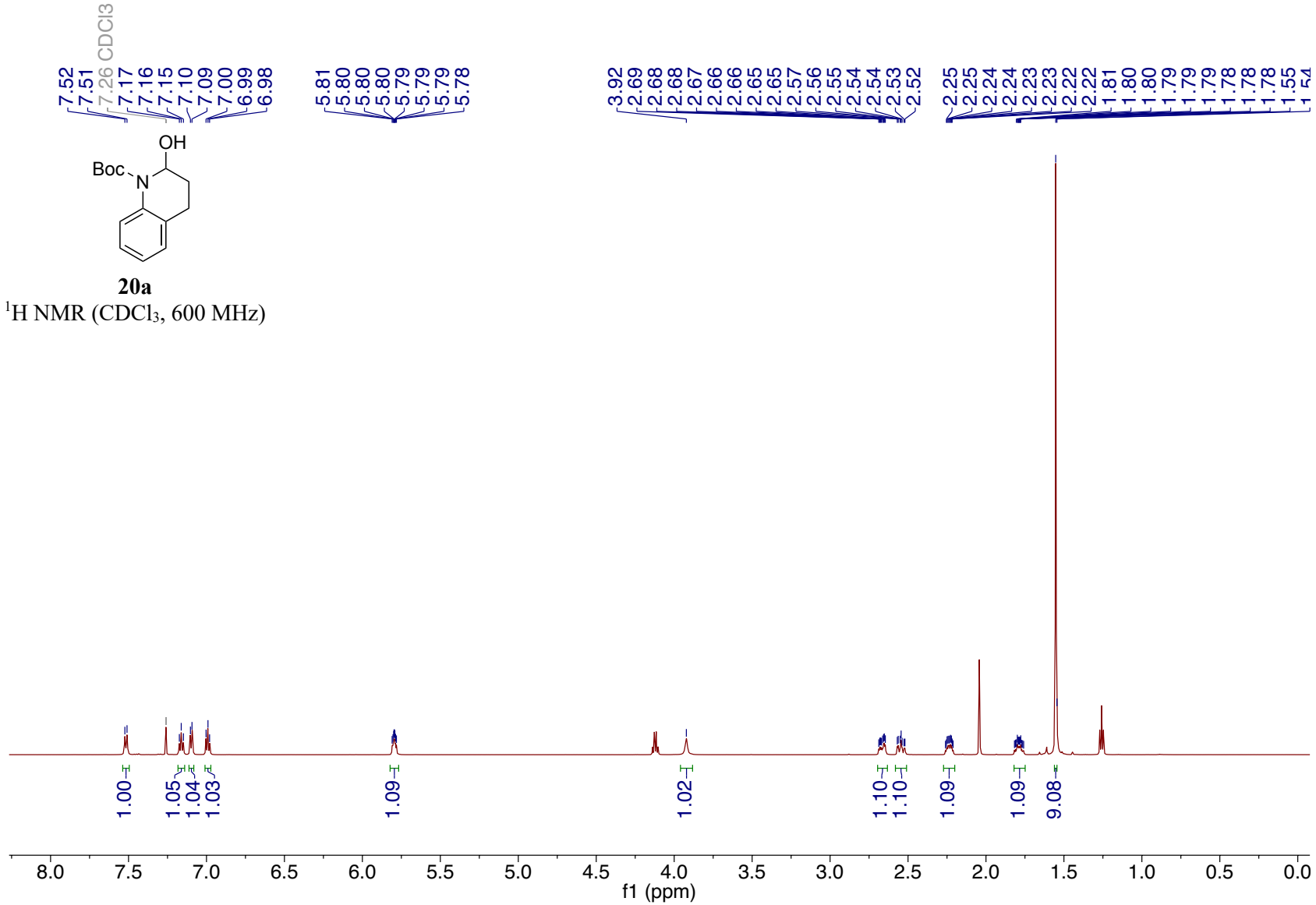
19s

^{1}H NMR ($CDCl_3$, 600 MHz)



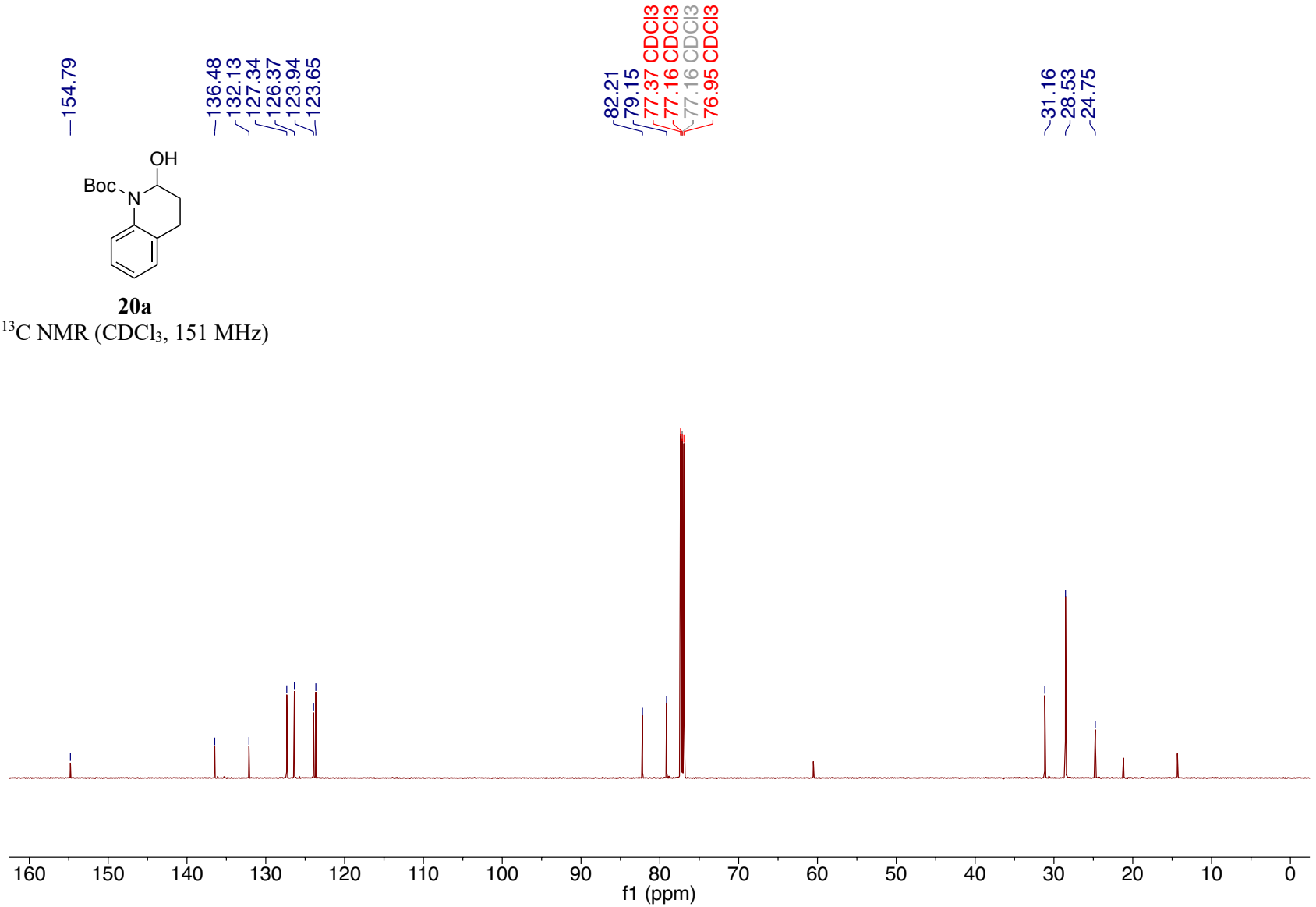
19s

^{13}C NMR ($CDCl_3$, 151 MHz)



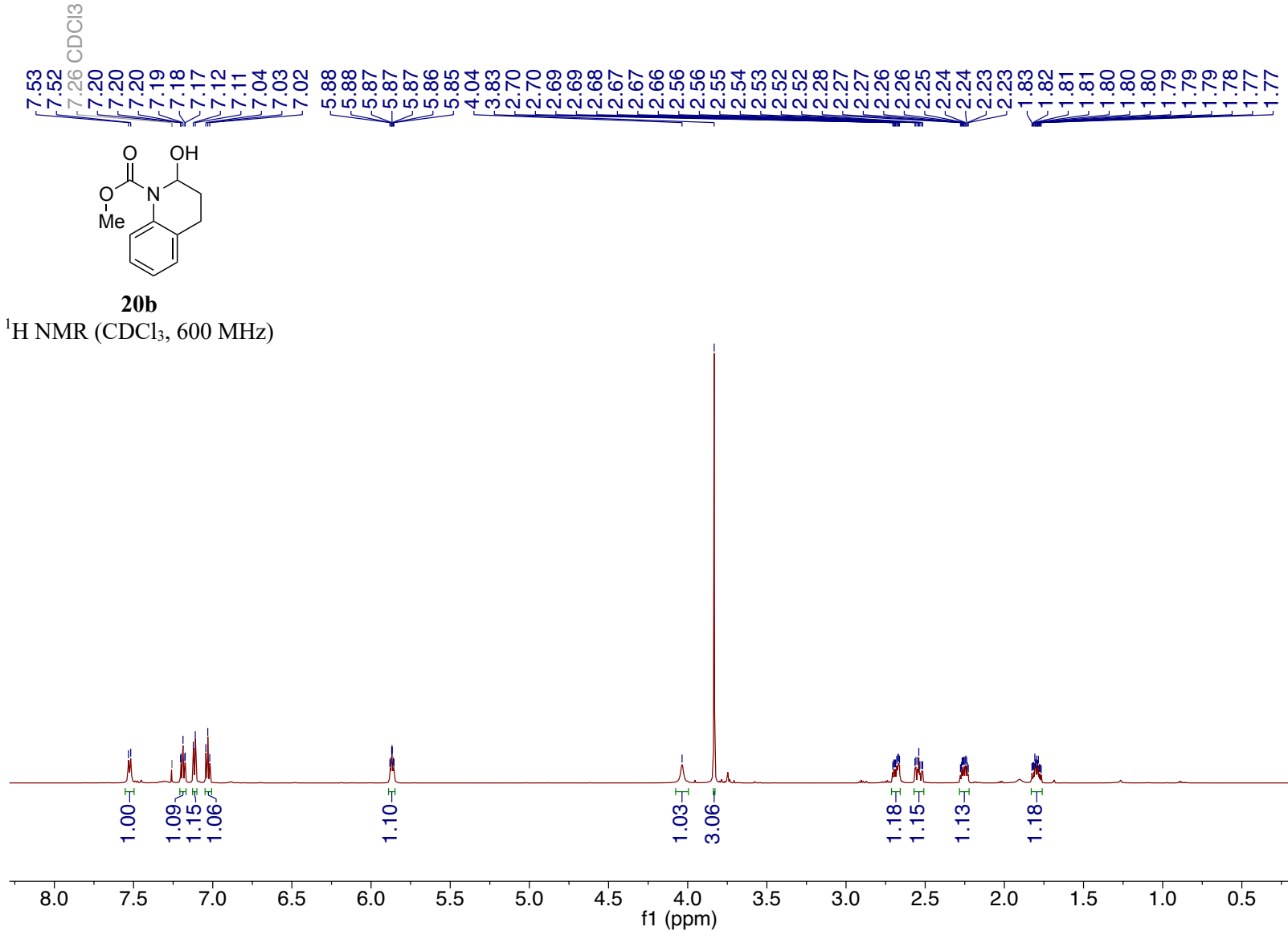
20a

^{1}H NMR ($CDCl_3$, 600 MHz)



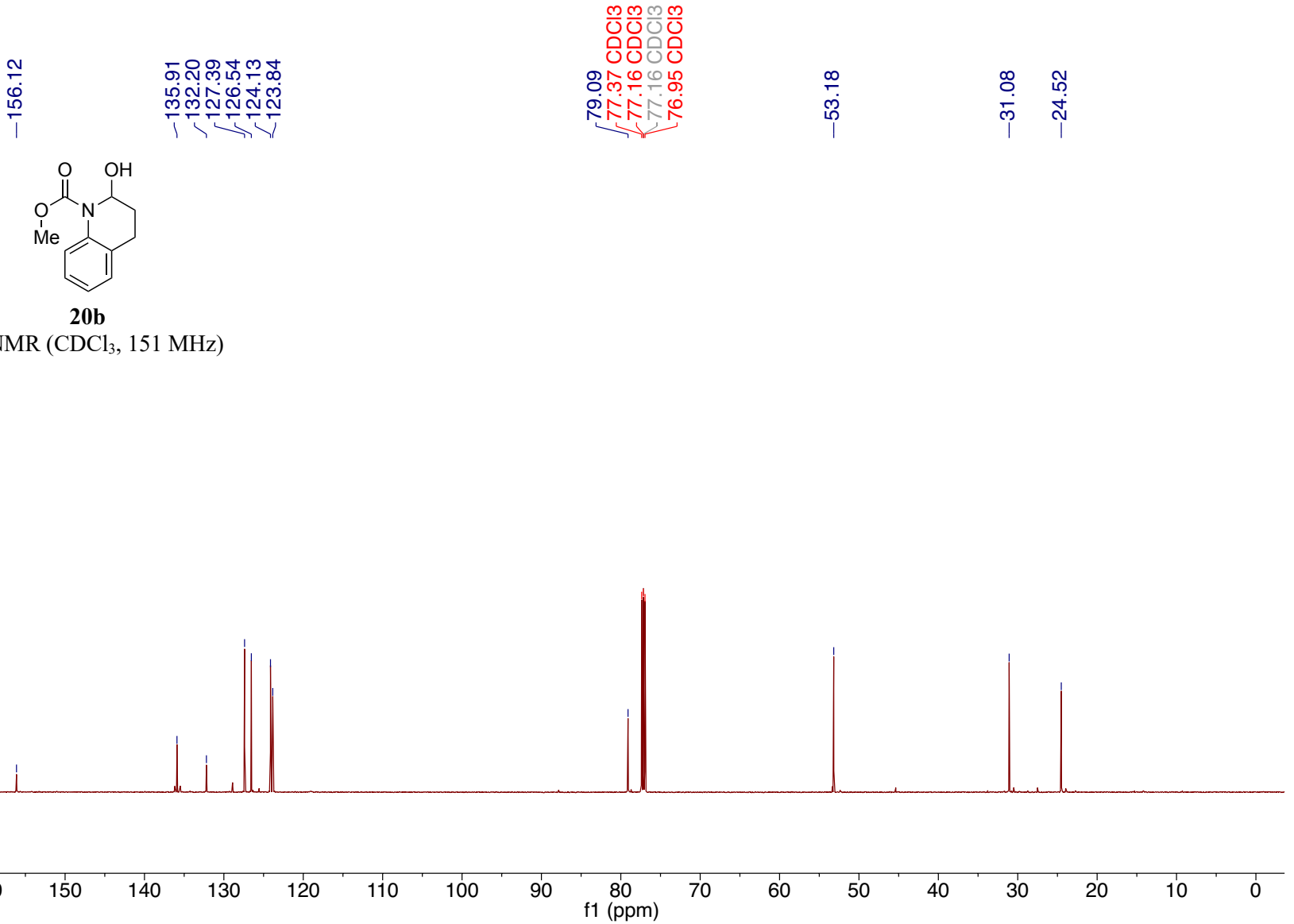
20a

^{13}C NMR ($CDCl_3$, 151 MHz)



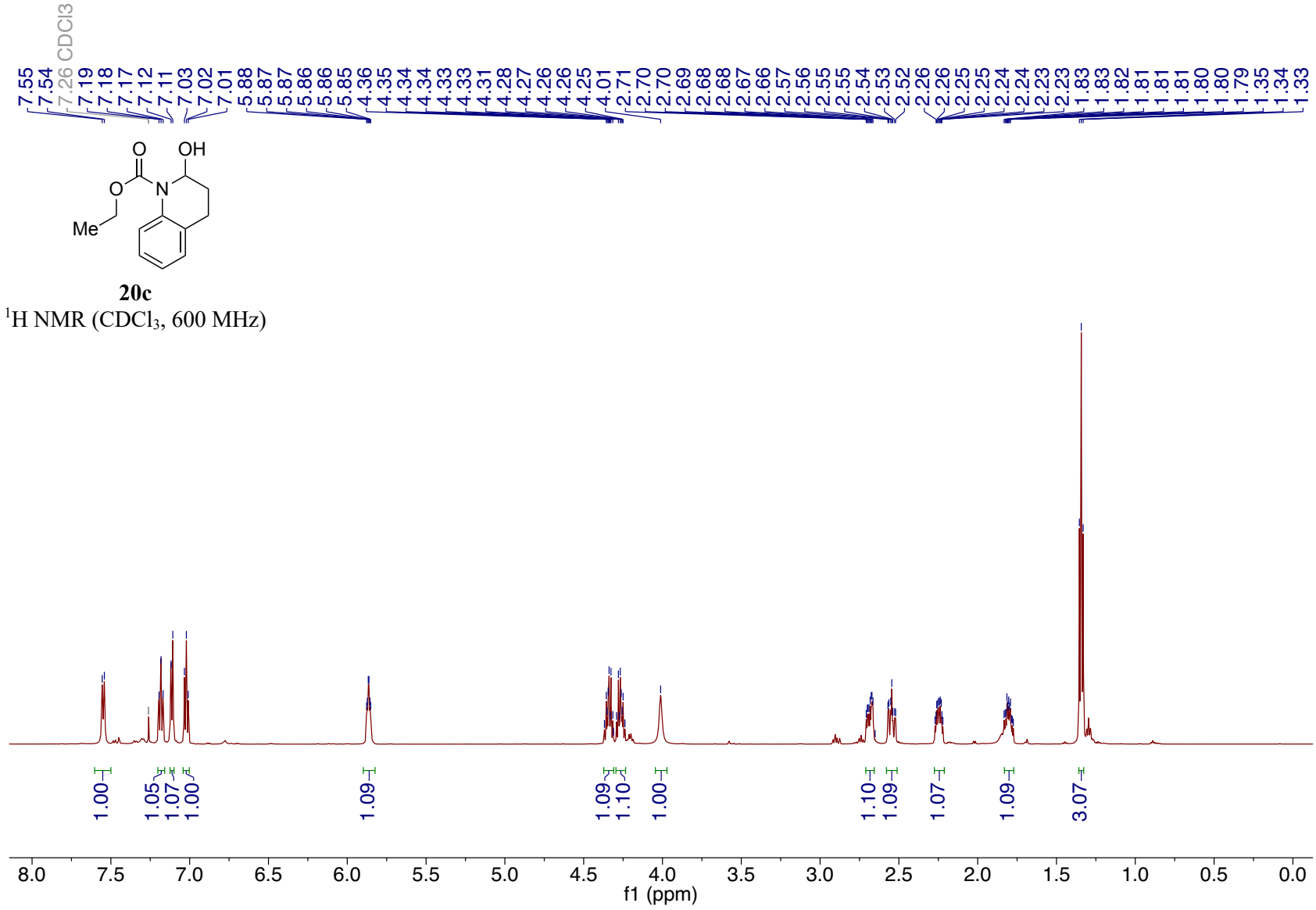
20b

^{1}H NMR ($CDCl_3$, 600 MHz)



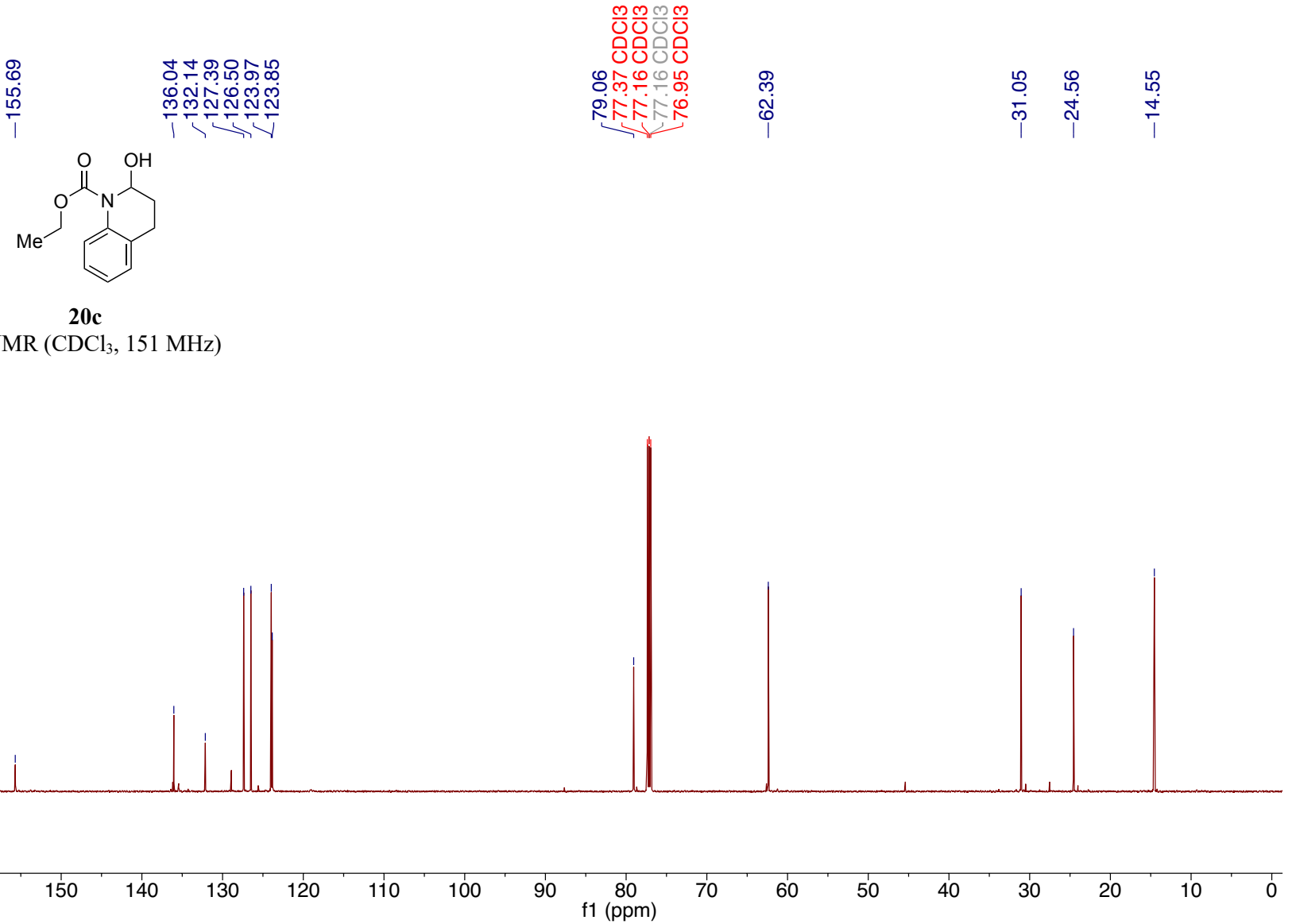
20b

^{13}C NMR ($CDCl_3$, 151 MHz)



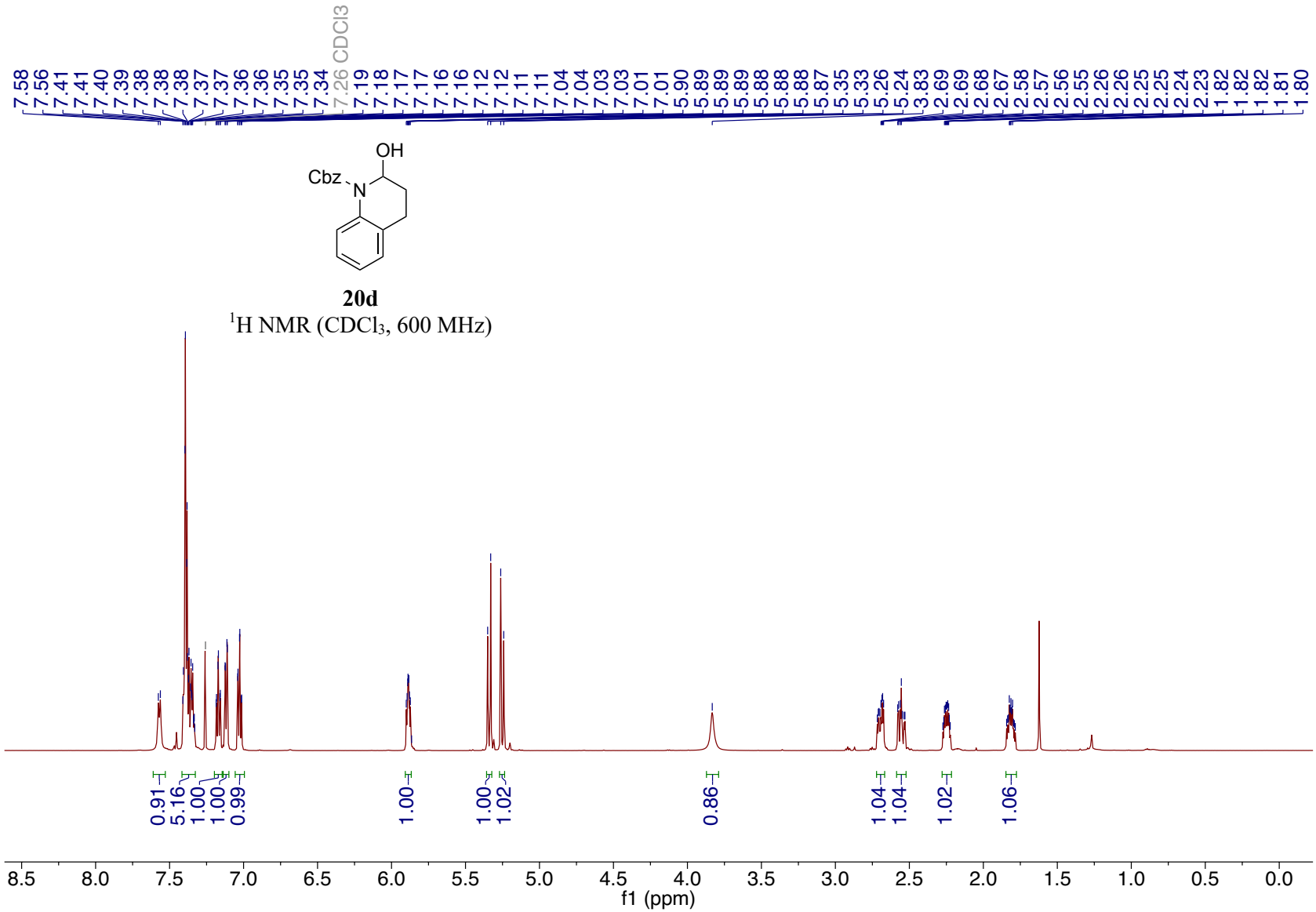
20c

^{1}H NMR ($CDCl_3$, 600 MHz)



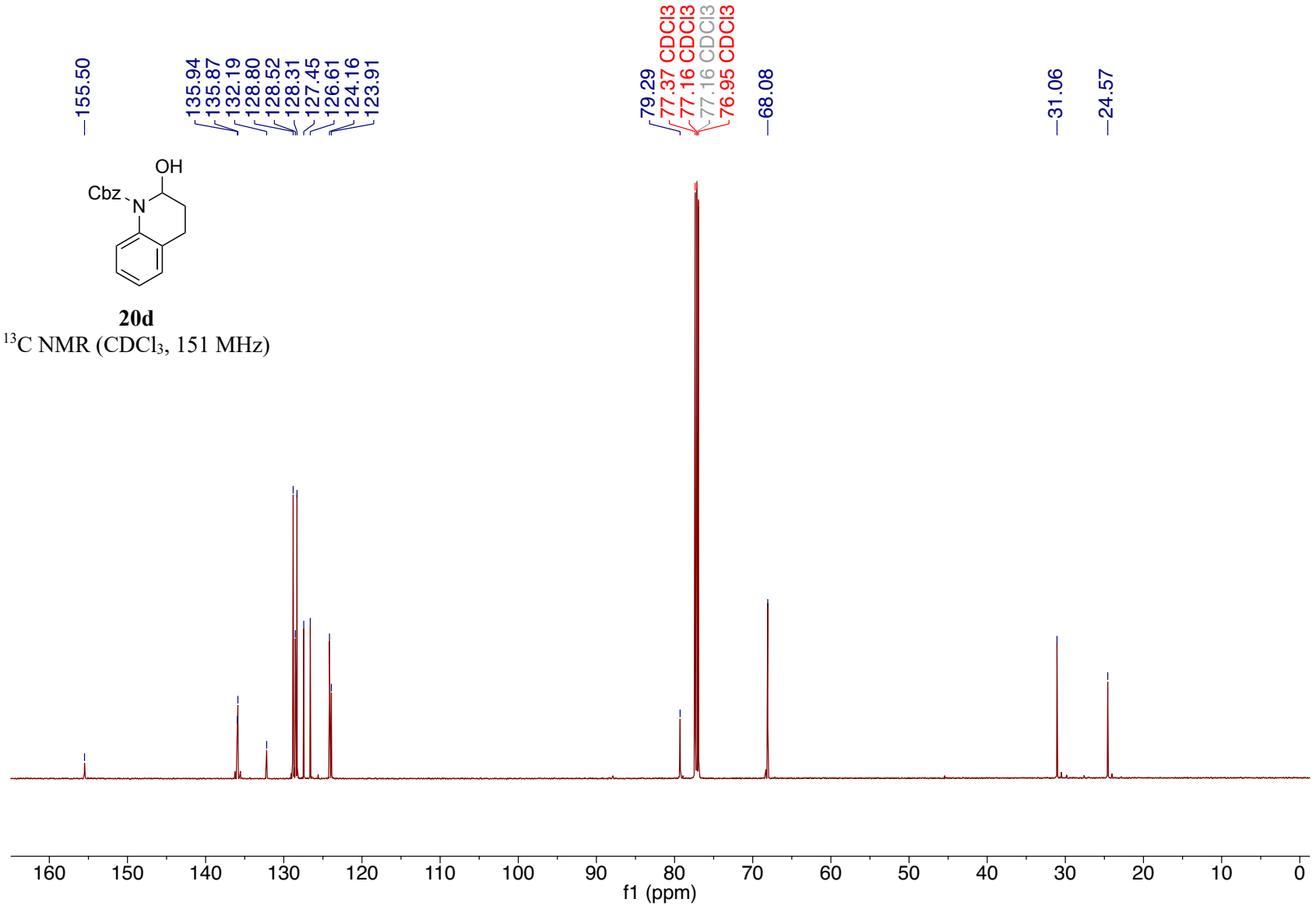
20c

^{13}C NMR ($CDCl_3$, 151 MHz)



20d

^{1}H NMR ($CDCl_3$, 600 MHz)



20d

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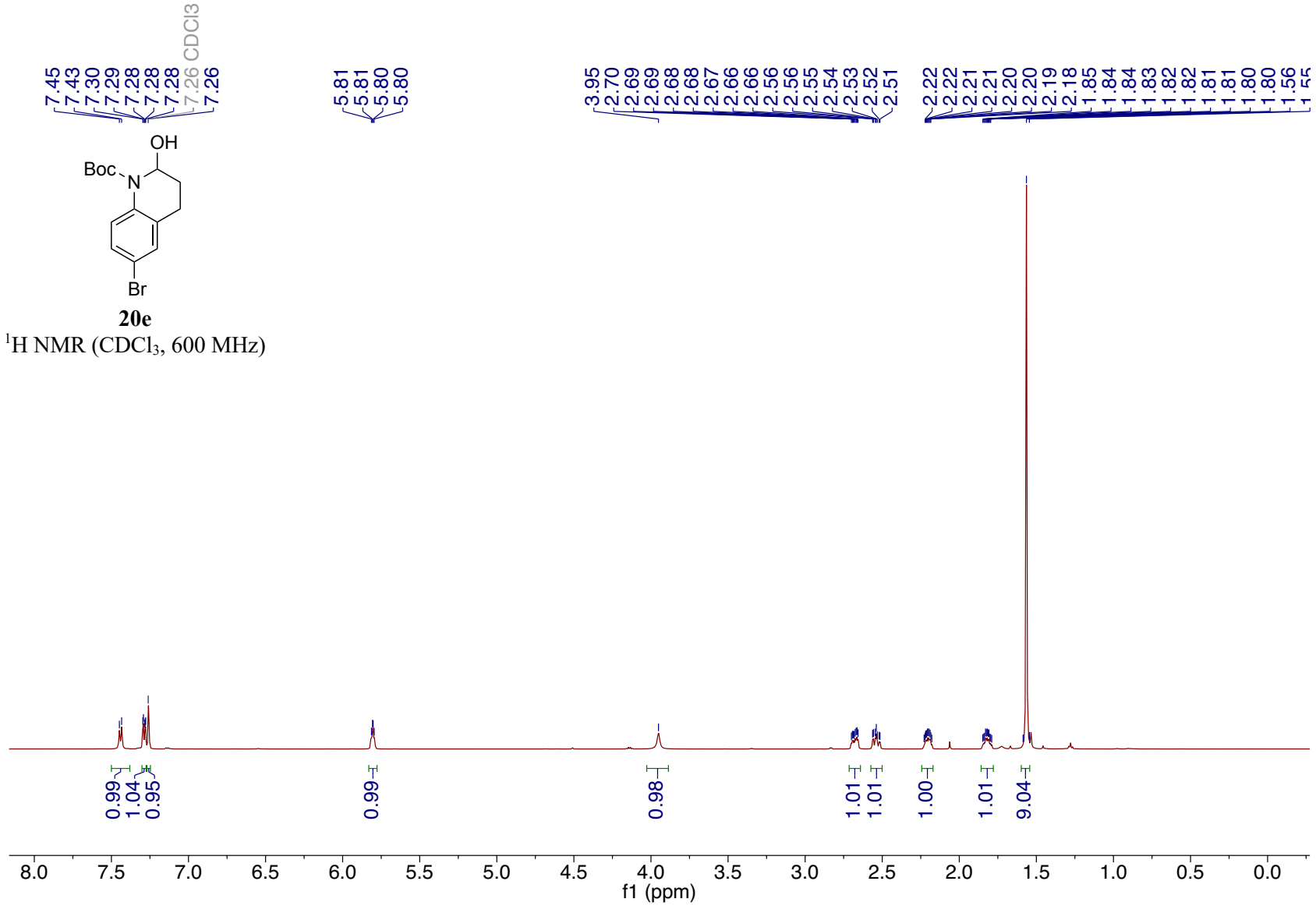
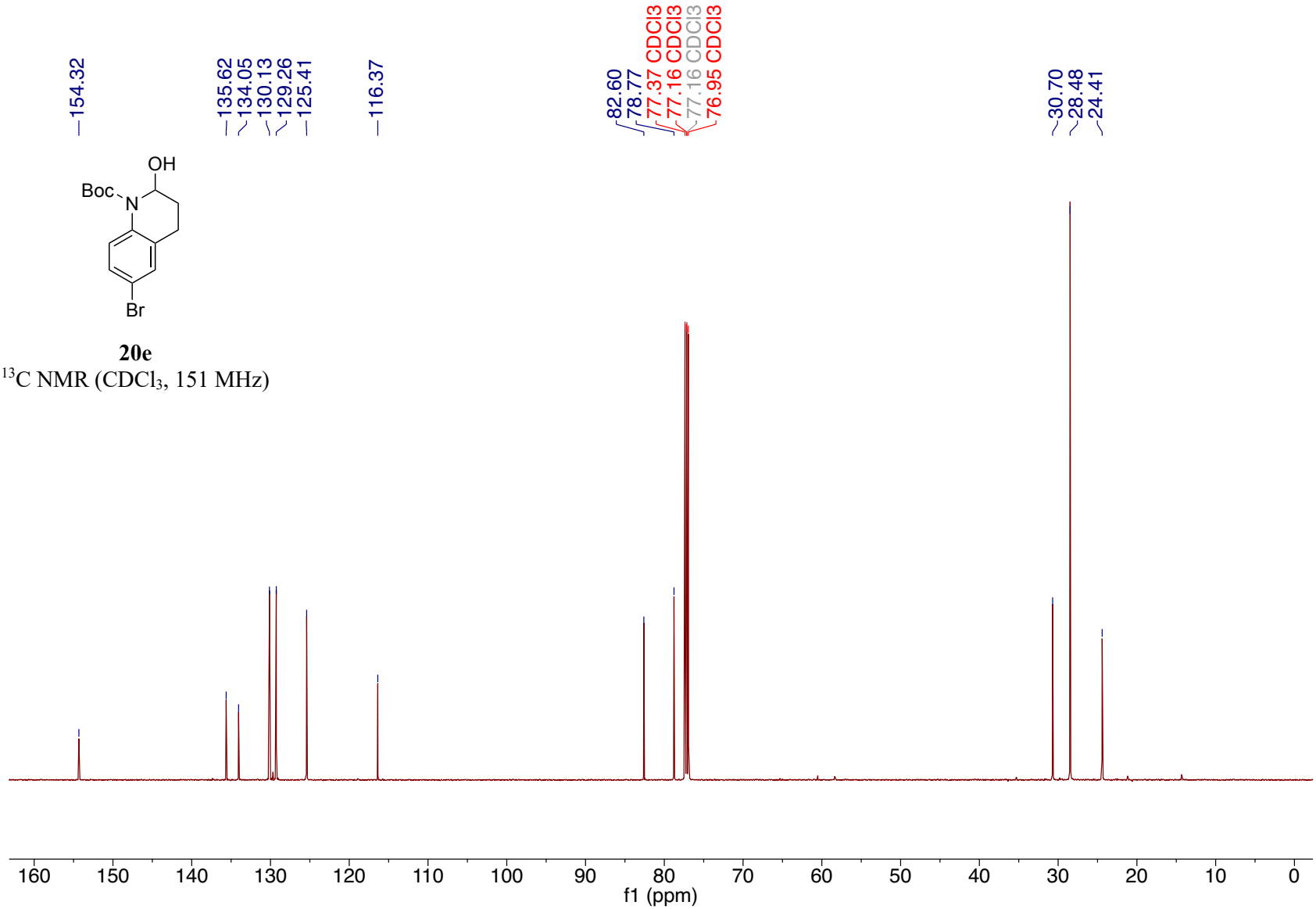


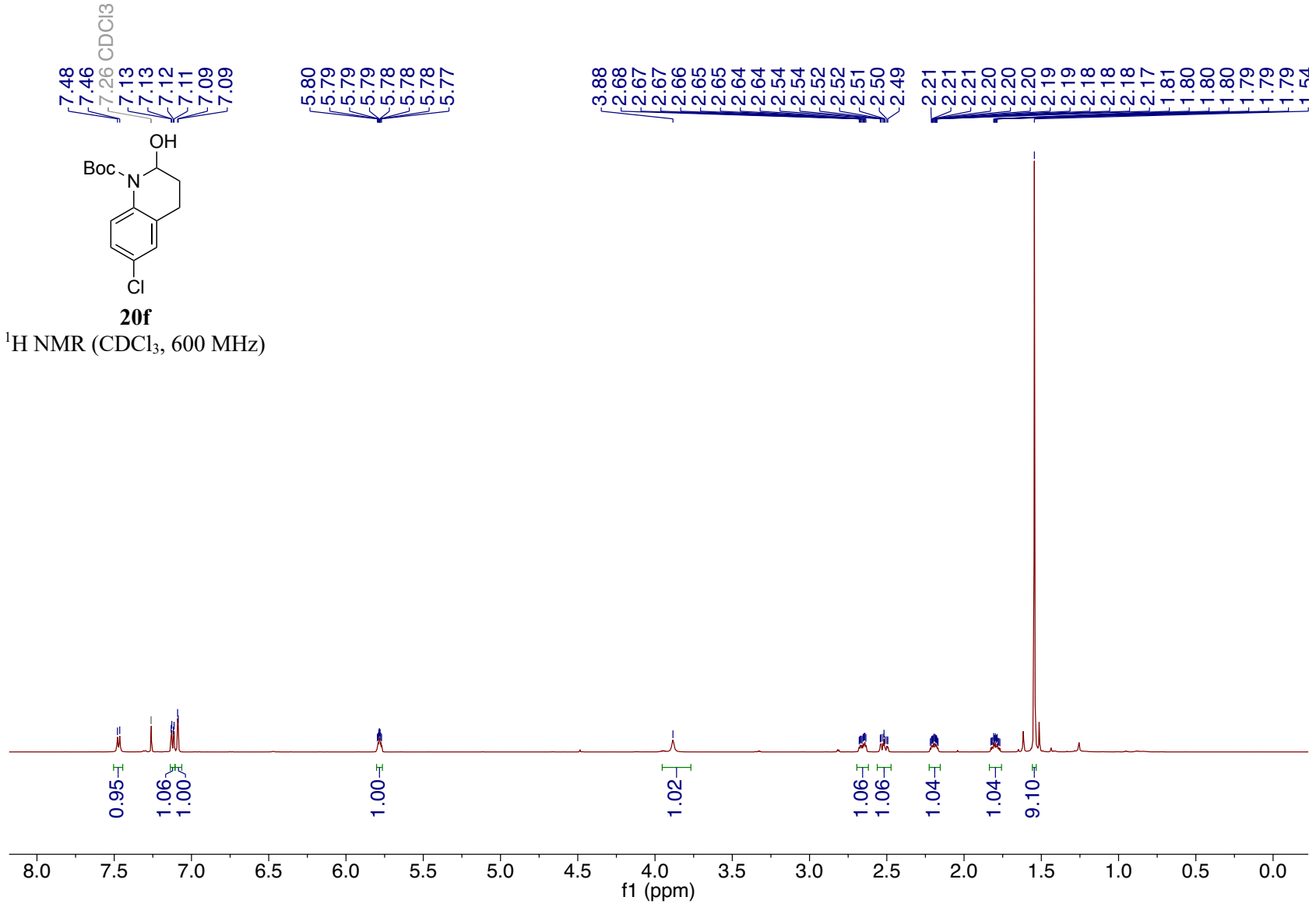
20e

^{1}H NMR ($CDCl_3$, 600 MHz)



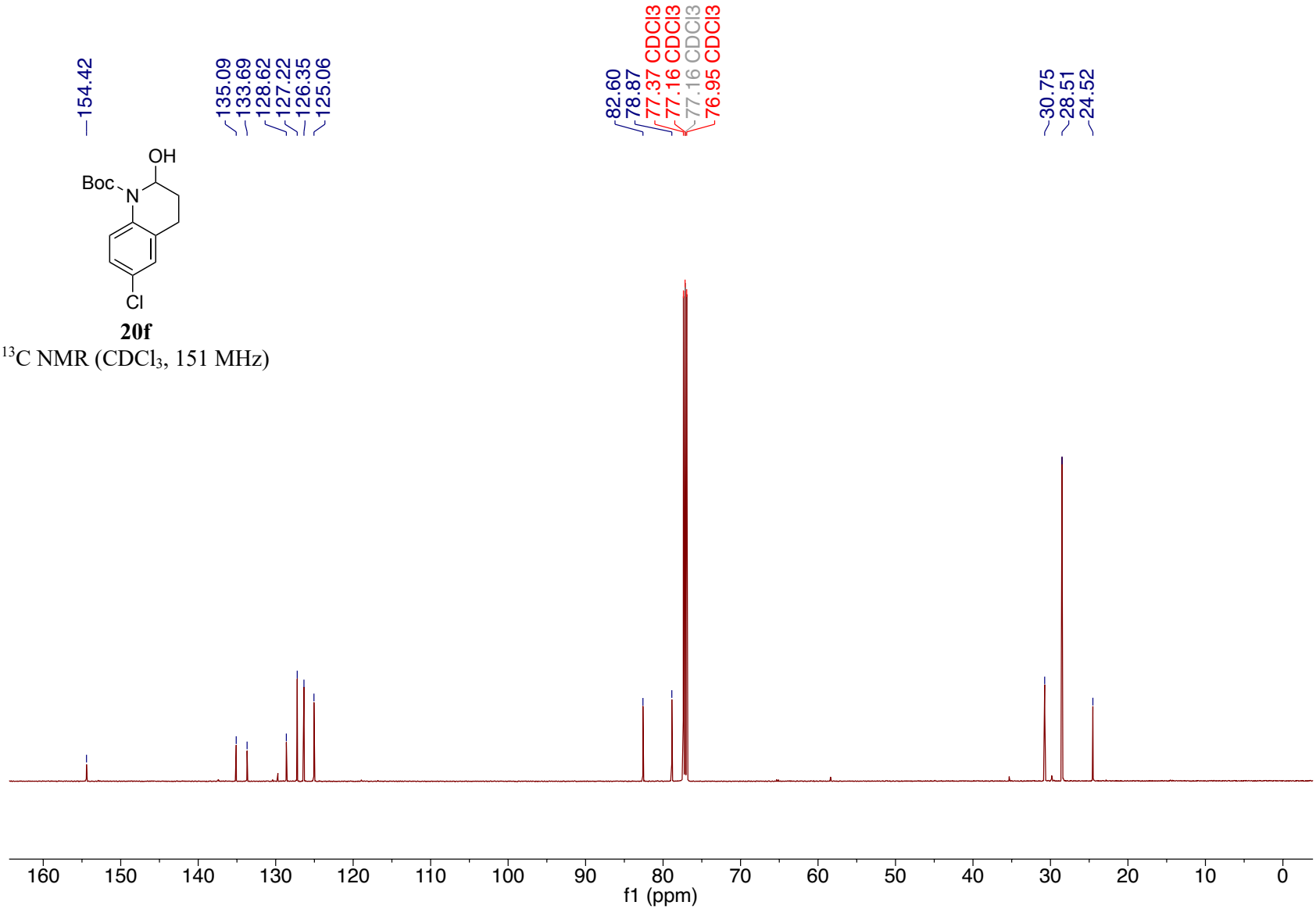
20e

^{13}C NMR ($CDCl_3$, 151 MHz)



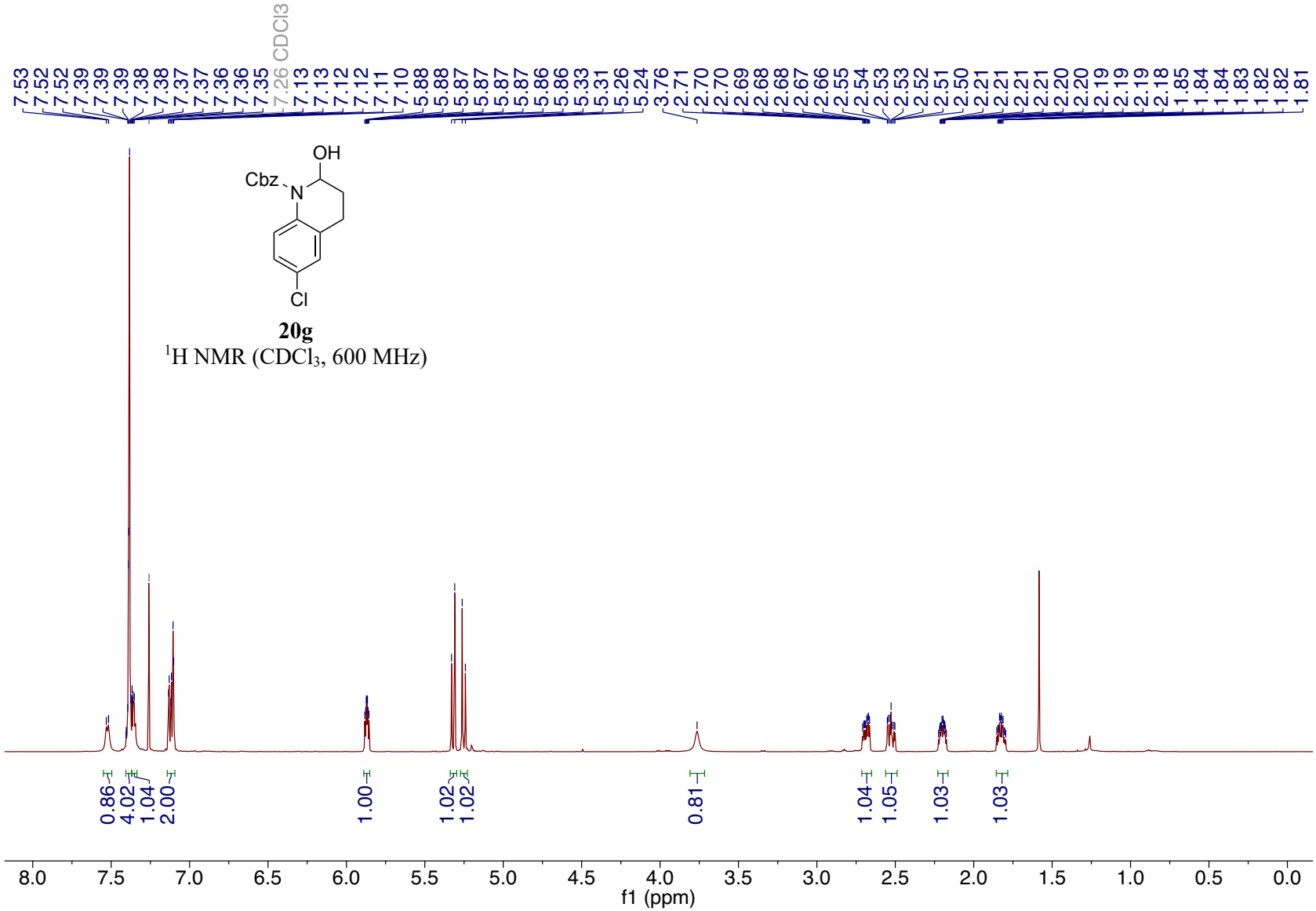
20f

^{1}H NMR ($CDCl_3$, 600 MHz)



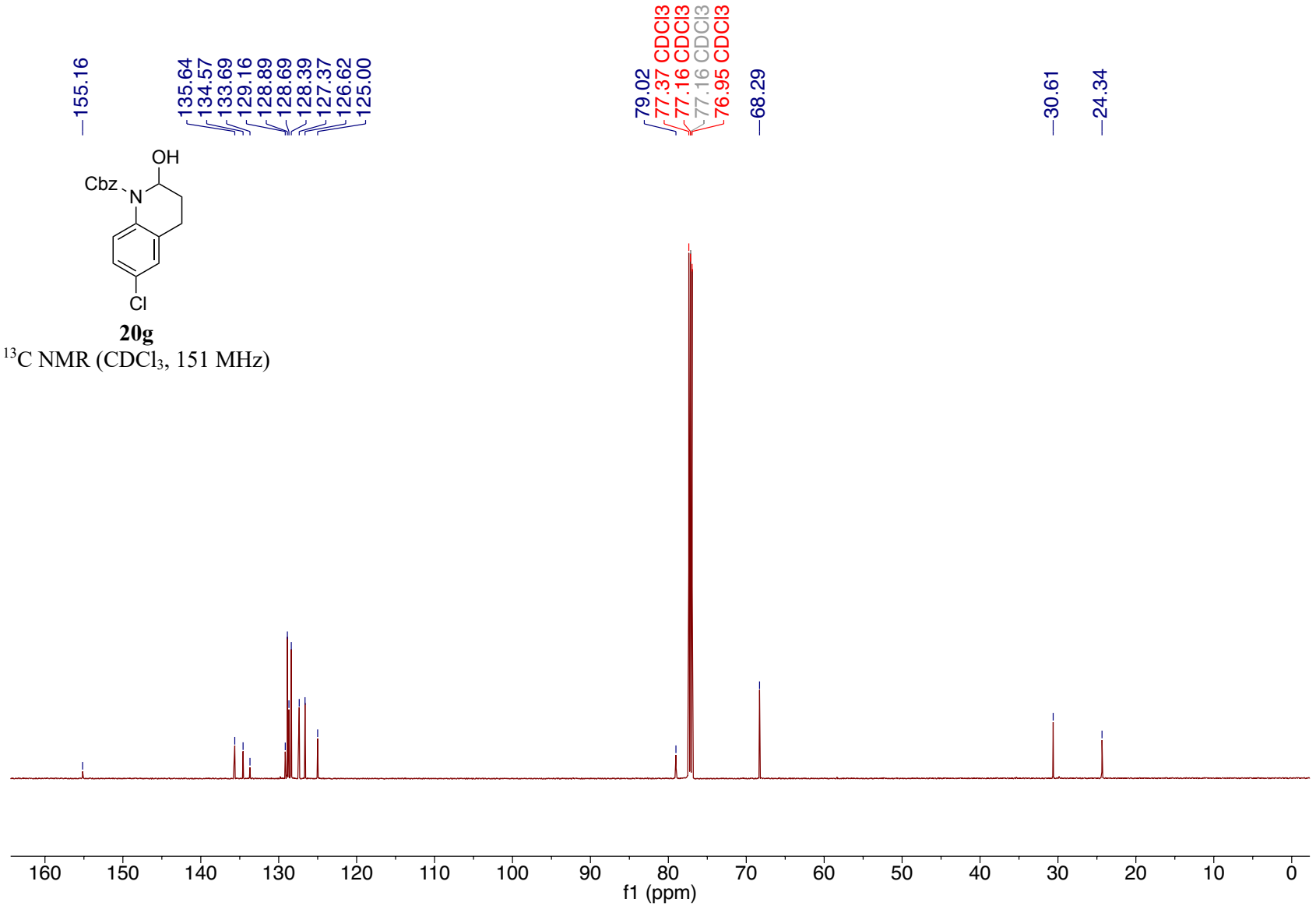
20f

^{13}C NMR ($CDCl_3$, 151 MHz)



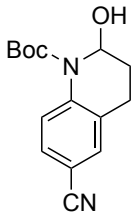
20g

^{1}H NMR ($CDCl_3$, 600 MHz)



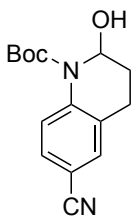
20g

^{13}C NMR ($CDCl_3$, 151 MHz)



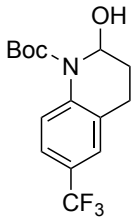
20h

^{1}H NMR ($CDCl_3$, 600 MHz)



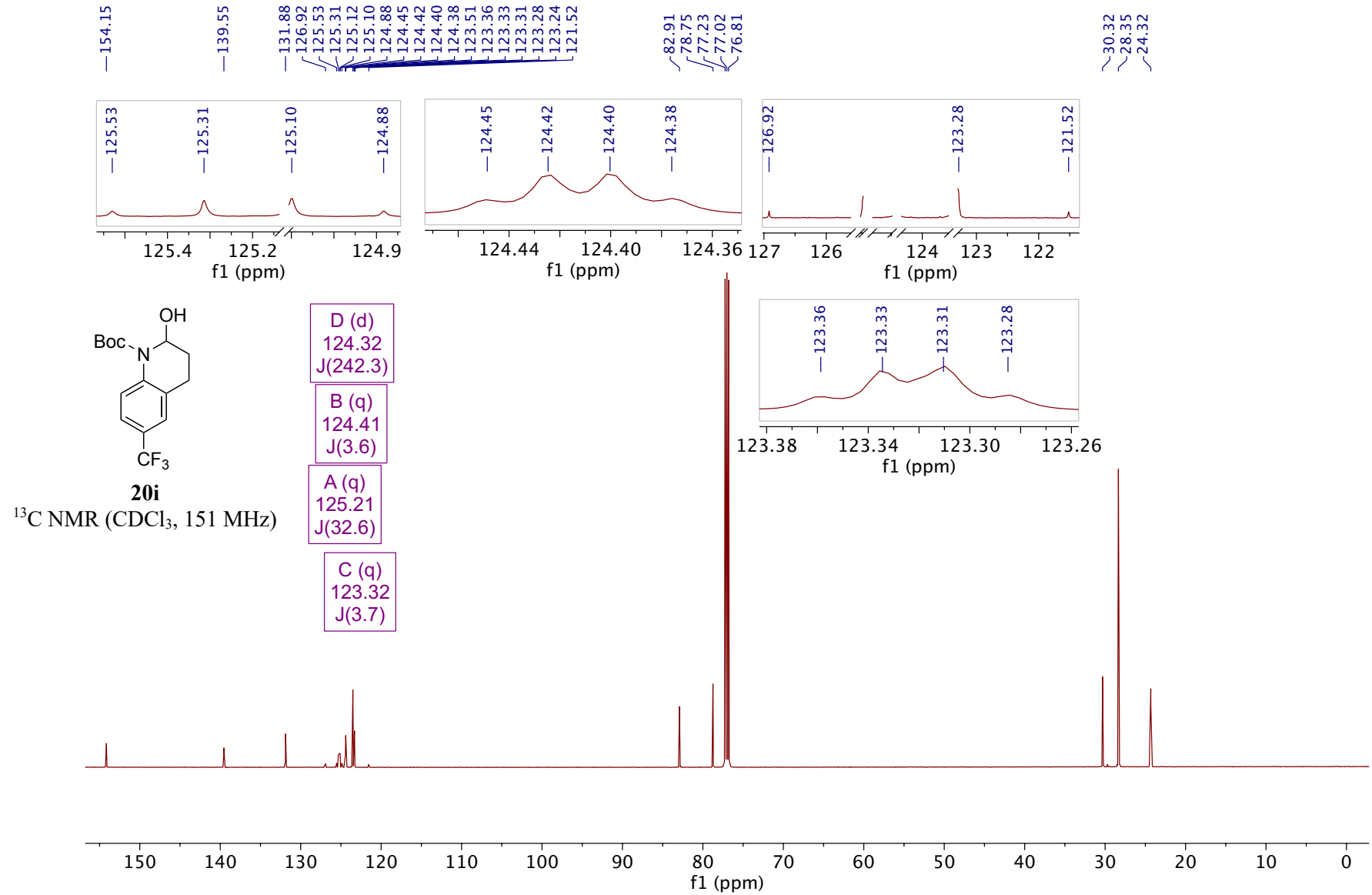
20h

^{13}C NMR ($CDCl_3$, 151 MHz)



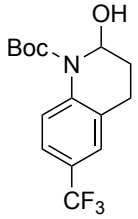
20i

^{1}H NMR ($CDCl_3$, 600 MHz)



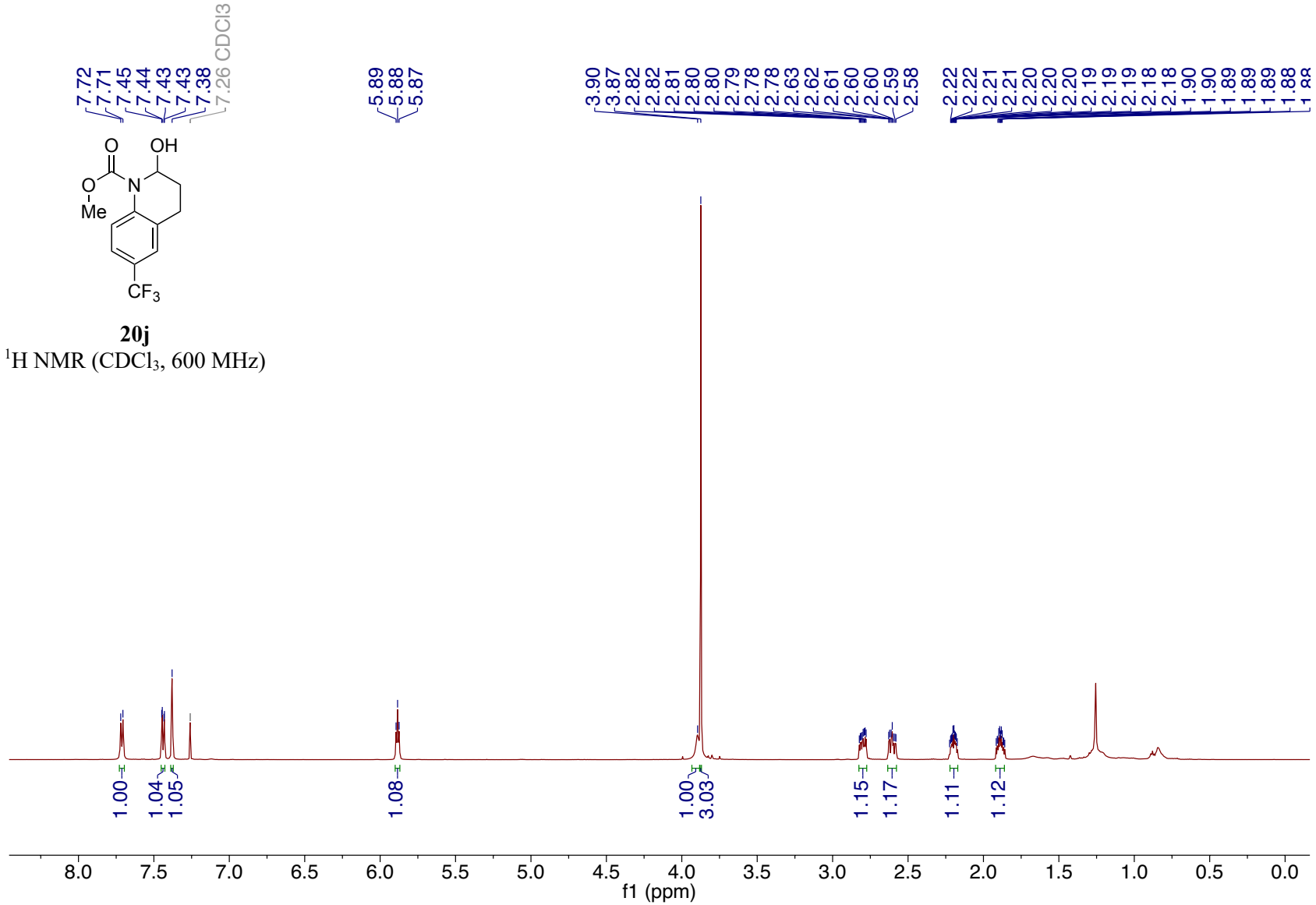
20i

^{13}C NMR ($CDCl_3$, 151 MHz)



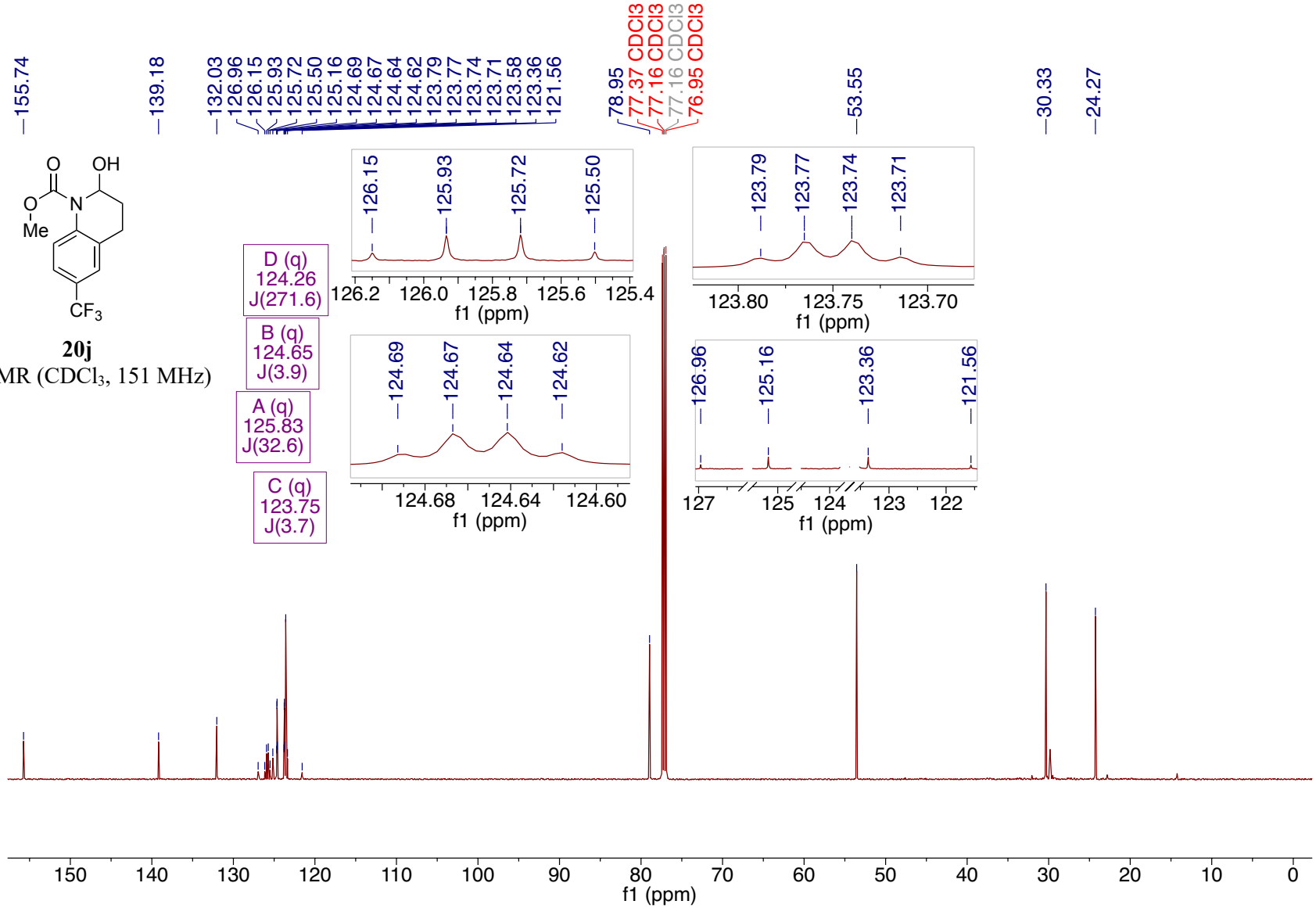
20i

^{19}F NMR ($CDCl_3$, 471 MHz)



20j

^{1}H NMR ($CDCl_3$, 600 MHz)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123.77
123.74
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77.16 CDCl3
77.16 CDCl3
76.95 CDCl3
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30.33
24.27
O
OH
O
N
Me
CF3
20j
13C NMR (CDCl3, 151 MHz)
D (q)
124.26
J(271.6)
B (q)
124.65
J(3.9)
A (q)
125.83
J(32.6)
C (q)
123.75
J(3.7)
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125.4
f1 (ppm)
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123.70
f1 (ppm)
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124
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f1 (ppm)
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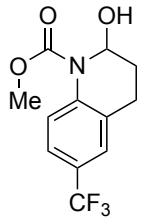
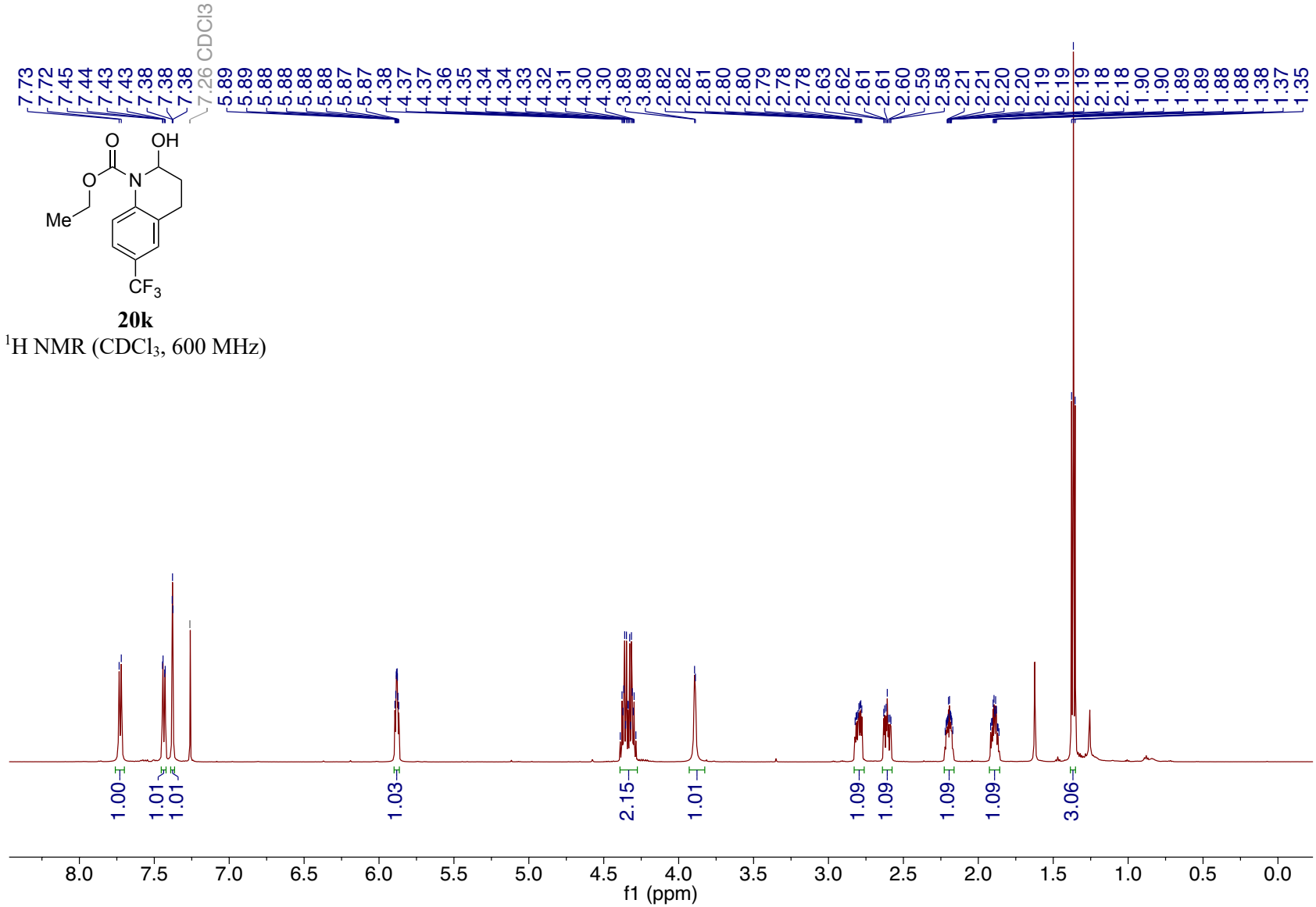
f1 (ppm)



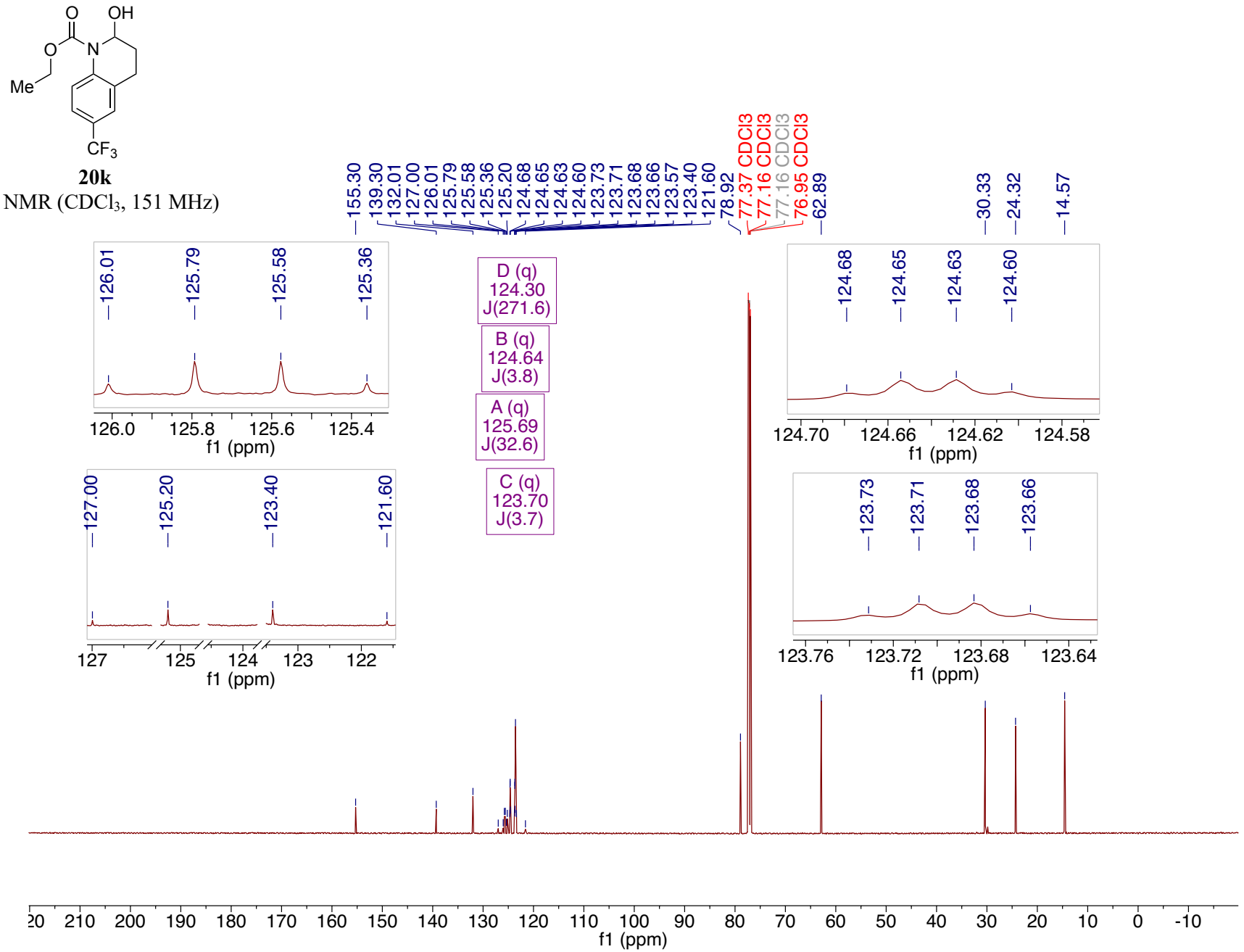
20j

^{19}F NMR ($CDCl_3$, 471 MHz)



20k

^{1}H NMR ($CDCl_3$, 600 MHz)


O
OH
O
N
Me
CF3
20k
13C NMR (CDCl3, 151 MHz)
155.30
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132.01
127.00
126.01
125.79
125.58
125.36
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124.68
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123.57
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121.60
78.92
77.37 CDCl3
77.16 CDCl3
77.16 CDCl3
76.95 CDCl3
62.89
30.33
24.32
14.57
D (q)
124.30
J(271.6)
B (q)
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J(3.8)
A (q)
125.69
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f1 (ppm)
f1 (ppm)
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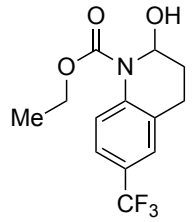
f1 (ppm)
f1 (ppm)



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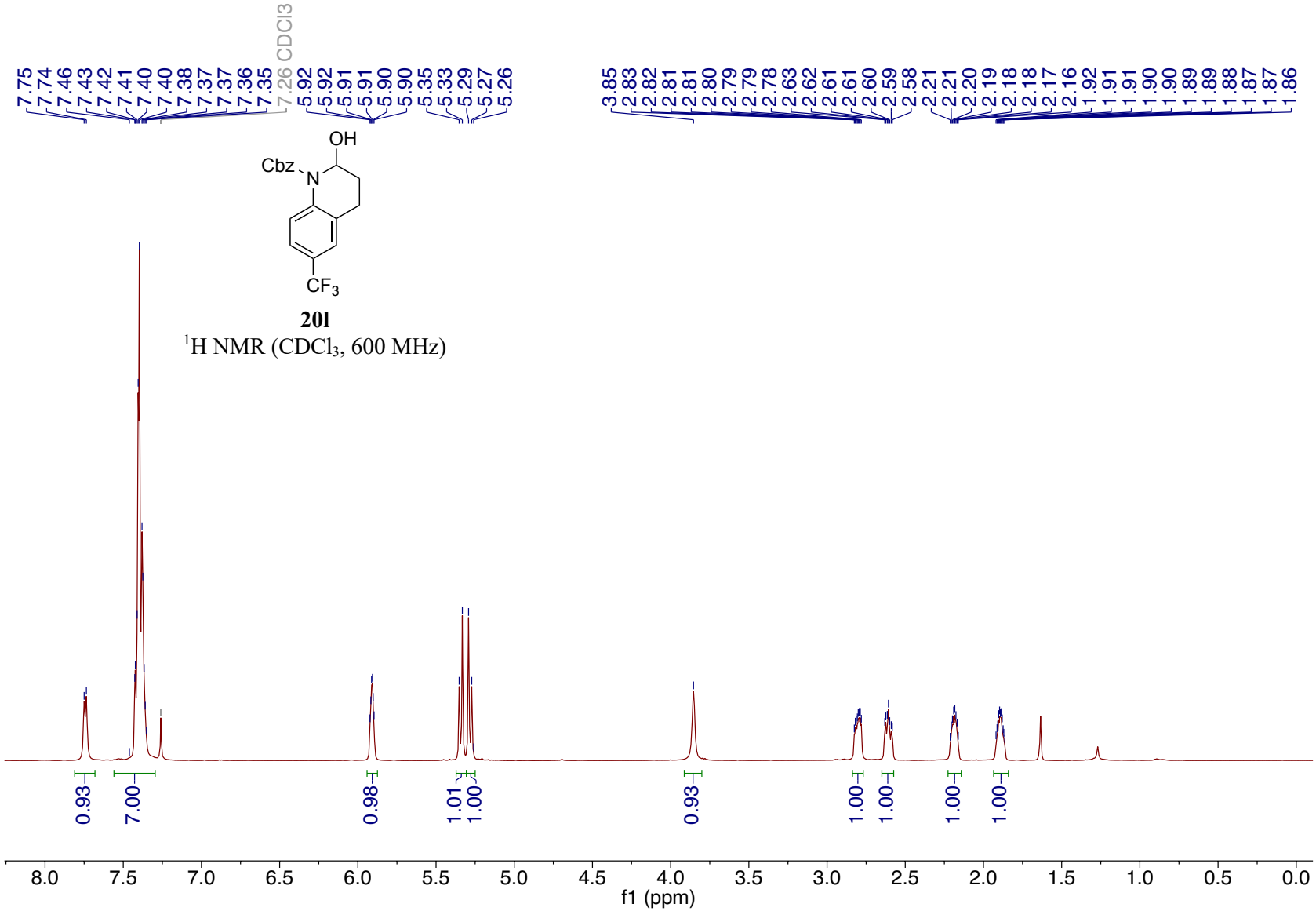
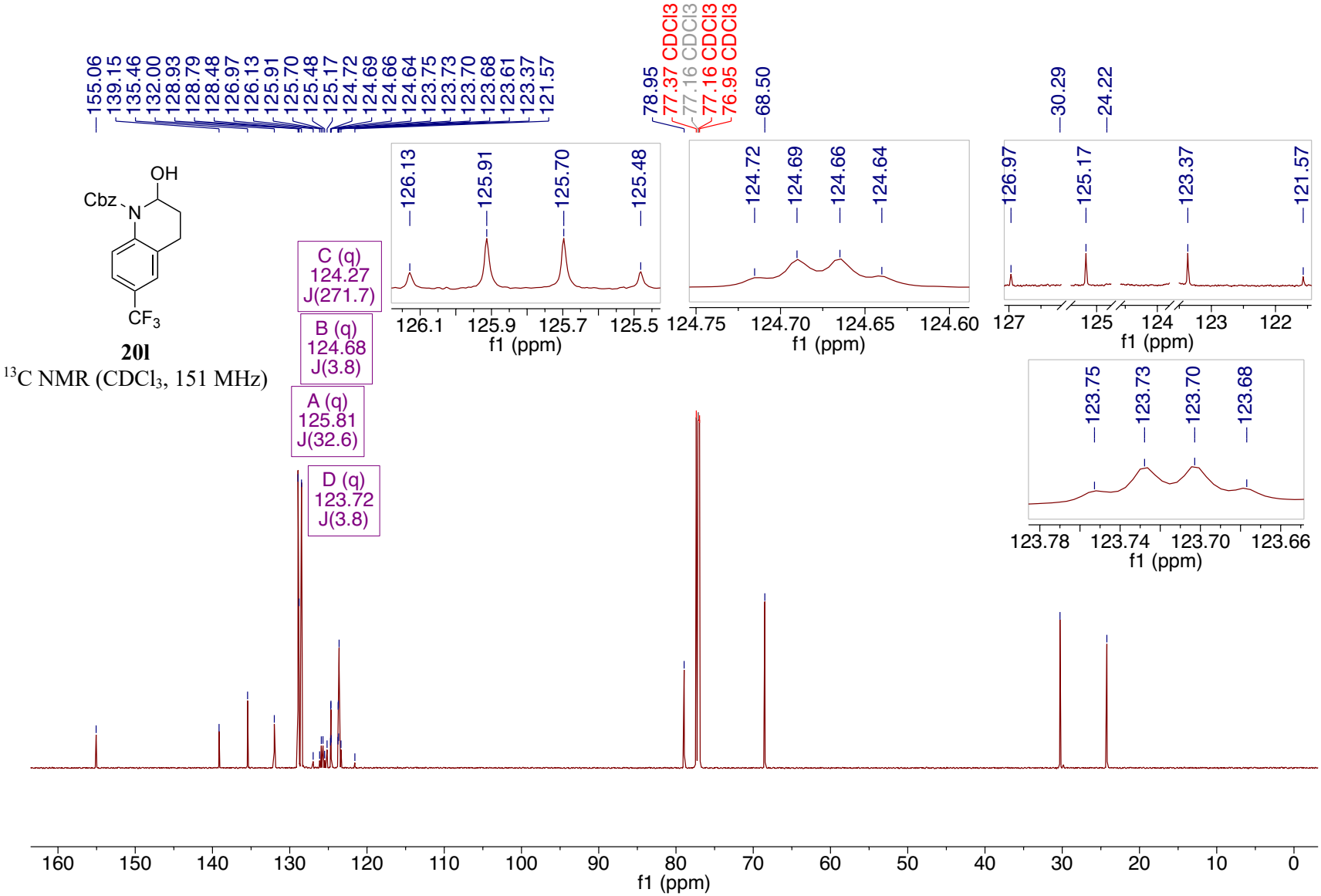
^{19}F NMR ($CDCl_3$, 471 MHz)



20l

^{1}H NMR ($CDCl_3$, 600 MHz)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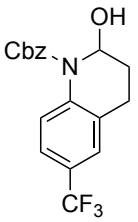
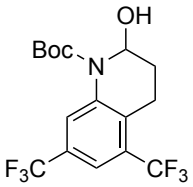
77.16 CDCl3
77.16 CDCl3
76.95 CDCl3
68.50
30.29
24.22
OH
Cbz
N
CF3
20l
13C NMR (CDCl3, 151 MHz)
C (q)
124.27
J(271.7)
B (q)
124.68
J(3.8)
A (q)
125.81
J(32.6)
D (q)
123.72
J(3.8)
126.13
125.91
125.70
125.48
126.1
125.9
125.7
125.5
f1 (ppm)
124.72
124.69
124.66
124.64
124.75
124.70
124.65
124.60
f1 (ppm)
126.97
125.17
123.37
121.57
127
125
124
123
122
f1 (ppm)
123.75
123.73
123.70
123.68
123.78
123.74
123.70
123.66
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



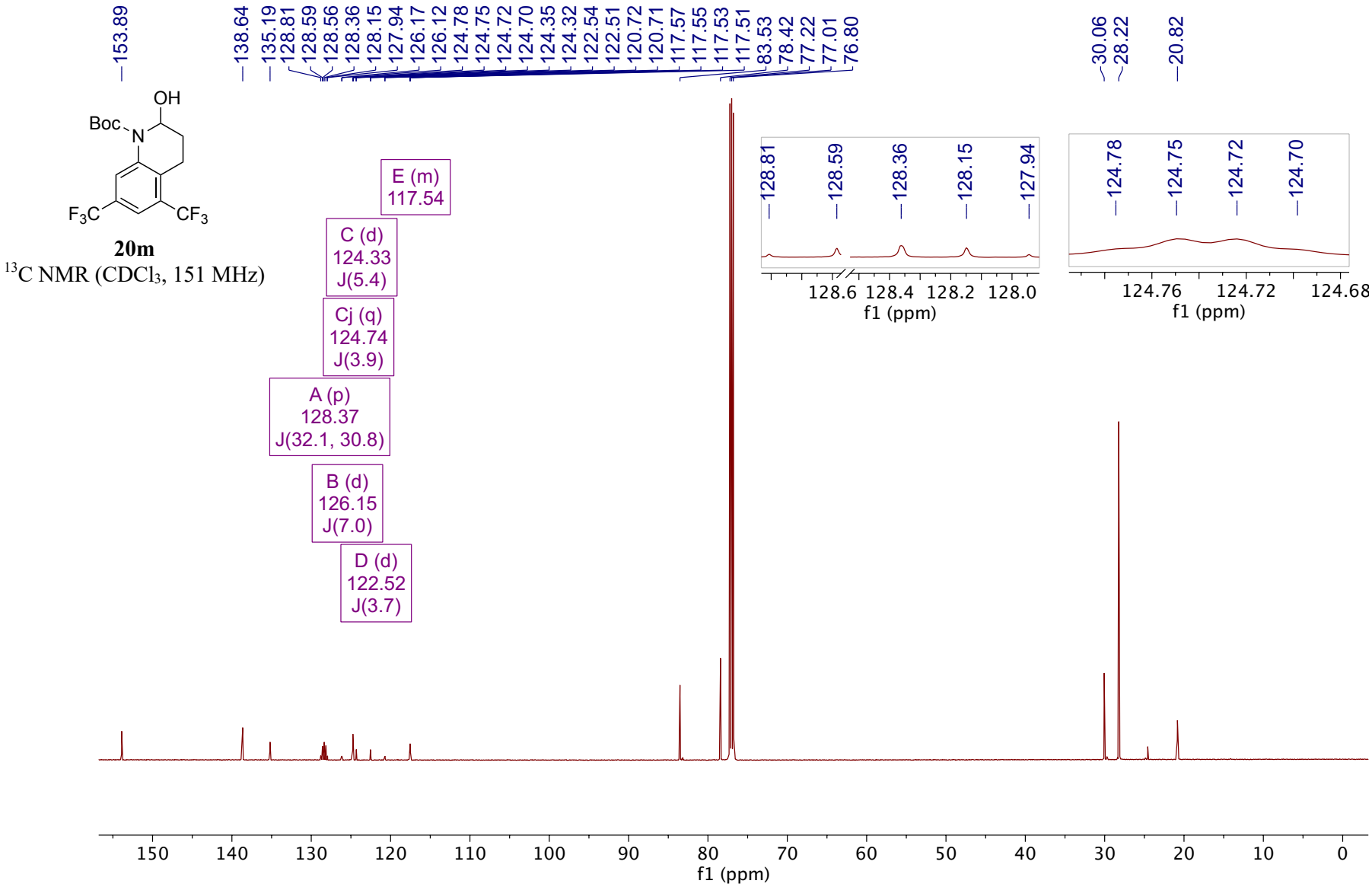
20l

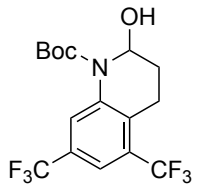
^{19}F NMR ($CDCl_3$, 471 MHz)



20m

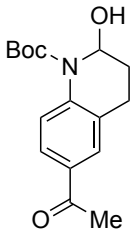
^{1}H NMR ($CDCl_3$, 600 MHz)


153.89
138.64
135.19
128.81
128.59
128.56
128.36
128.15
127.94
126.17
126.12
124.78
124.75
124.72
124.70
124.35
124.32
122.54
122.51
120.72
120.71
117.57
117.55
117.53
117.51
83.53
78.42
77.22
77.01
76.80
30.06
28.22
20.82
OH
Boc
N
F3C
CF3
20m
13C NMR (CDCl3, 151 MHz)
E (m)
117.54
C (d)
124.33
J(5.4)
Cj (q)
124.74
J(3.9)
A (p)
128.37
J(32.1, 30.8)
B (d)
126.15
J(7.0)
D (d)
122.52
J(3.7)
128.81
128.59
128.36
128.15
127.94
128.6 128.4 128.2 128.0
f1 (ppm)
124.78
124.75
124.72
124.70
124.76 124.72 124.68
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



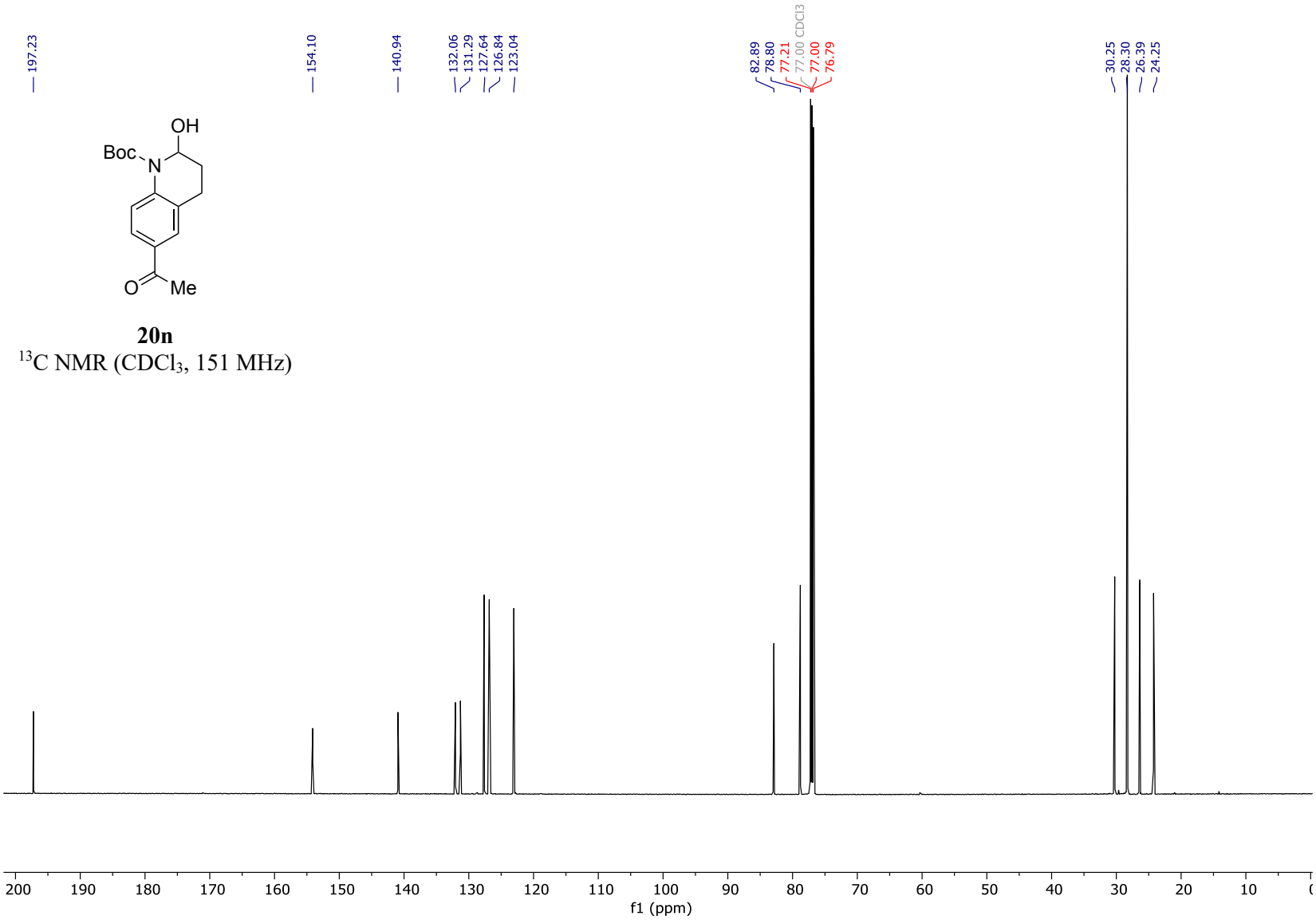
20m

^{19}F NMR ($CDCl_3$, 471 MHz)



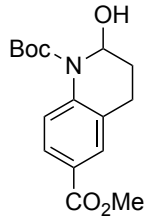
20n

^{1}H NMR ($CDCl_3$, 600 MHz)



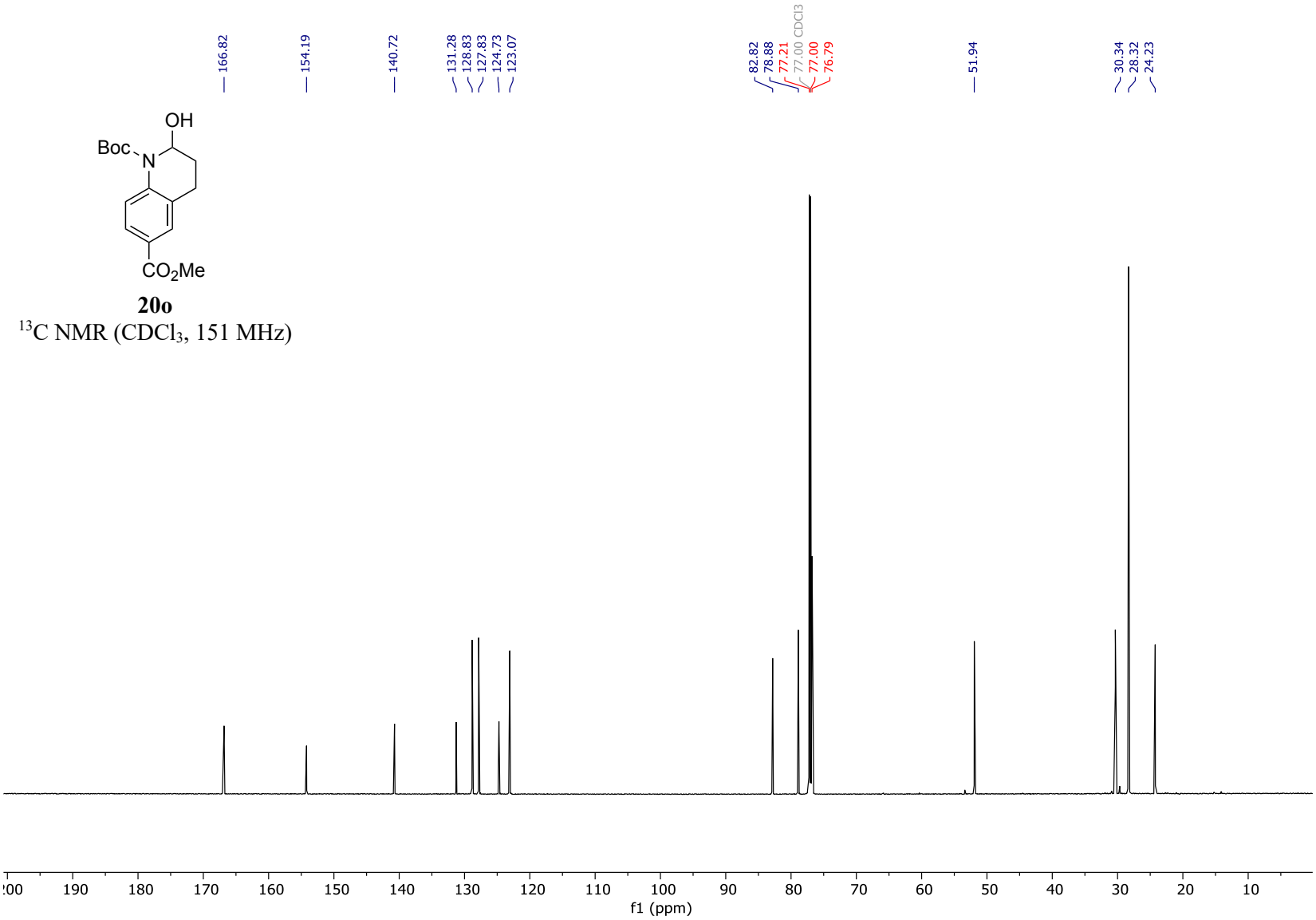
20n

^{13}C NMR ($CDCl_3$, 151 MHz)



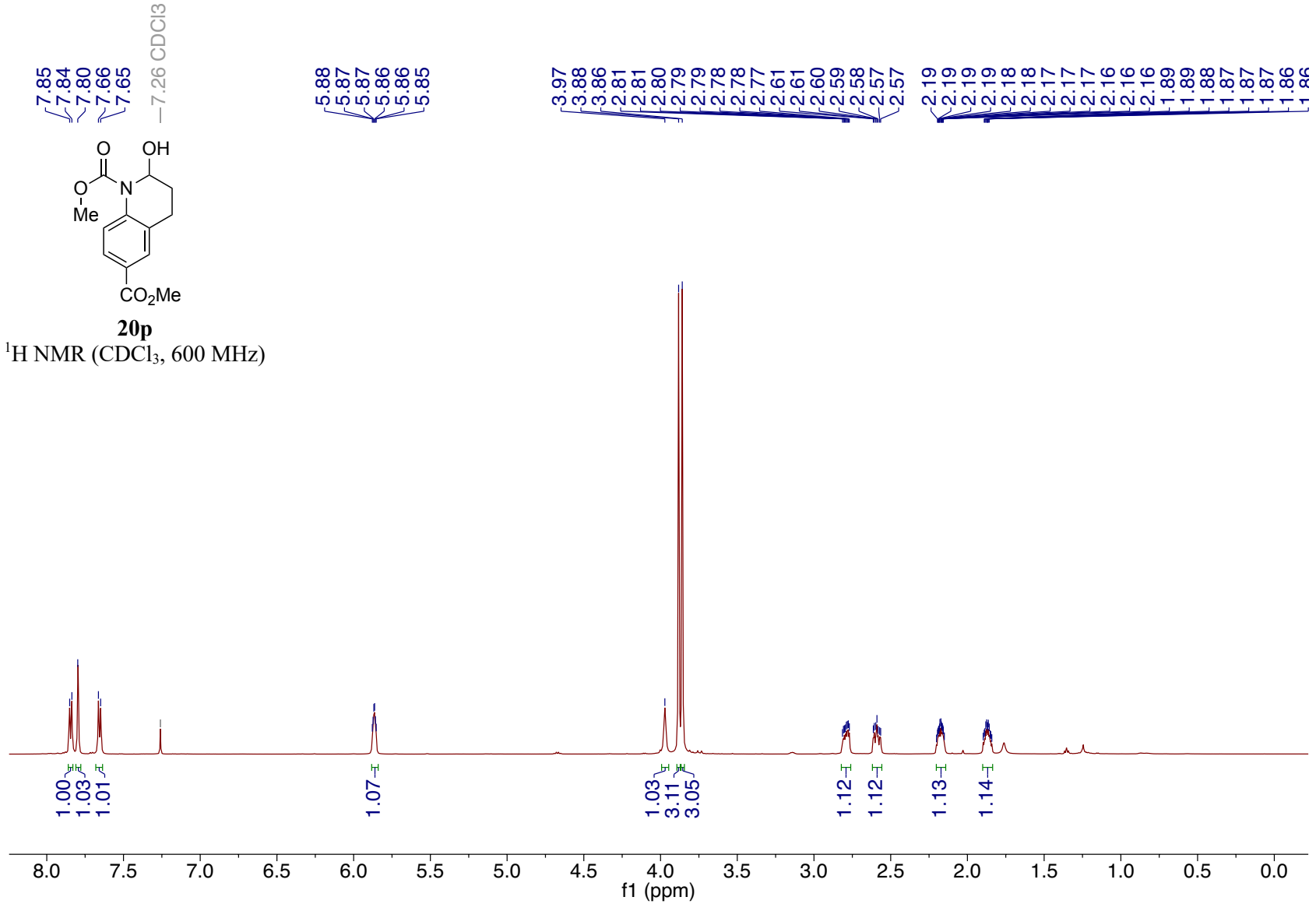
20o

^{1}H NMR ($CDCl_3$, 600 MHz)



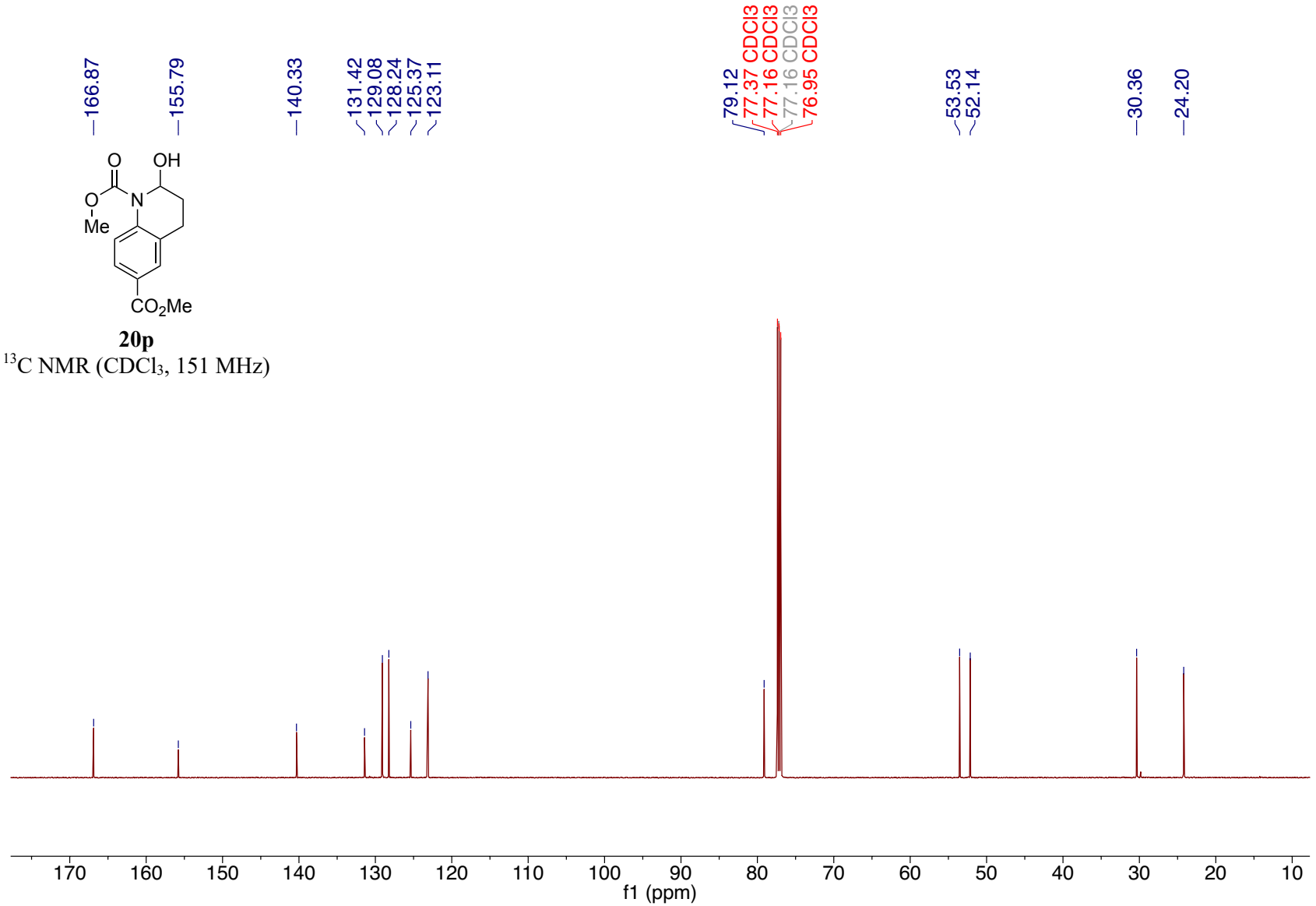
20o

^{13}C NMR ($CDCl_3$, 151 MHz)



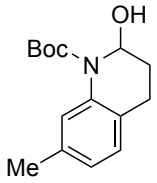
20p

^{1}H NMR ($CDCl_3$, 600 MHz)



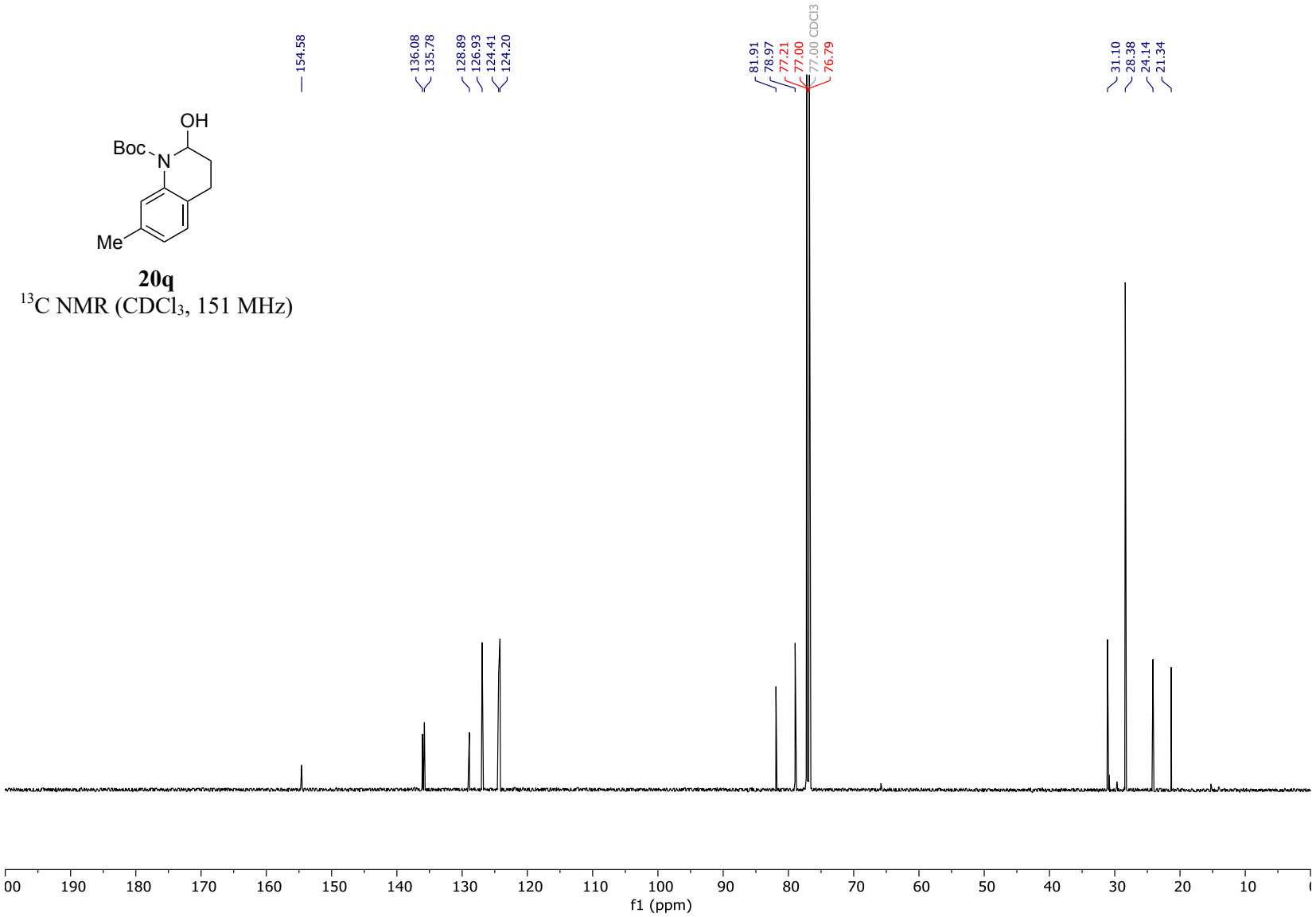
20p

^{13}C NMR ($CDCl_3$, 151 MHz)



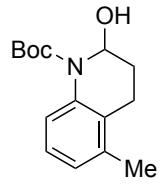
20q

^{1}H NMR ($CDCl_3$, 600 MHz)



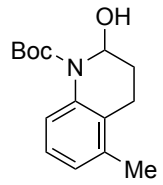
20q

^{13}C NMR ($CDCl_3$, 151 MHz)



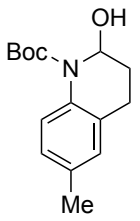
20r

^{1}H NMR ($CDCl_3$, 600 MHz)



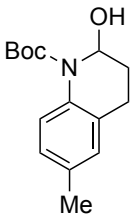
20r

^{13}C NMR ($CDCl_3$, 151 MHz)



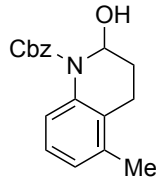
20s

^{1}H NMR ($CDCl_3$, 600 MHz)



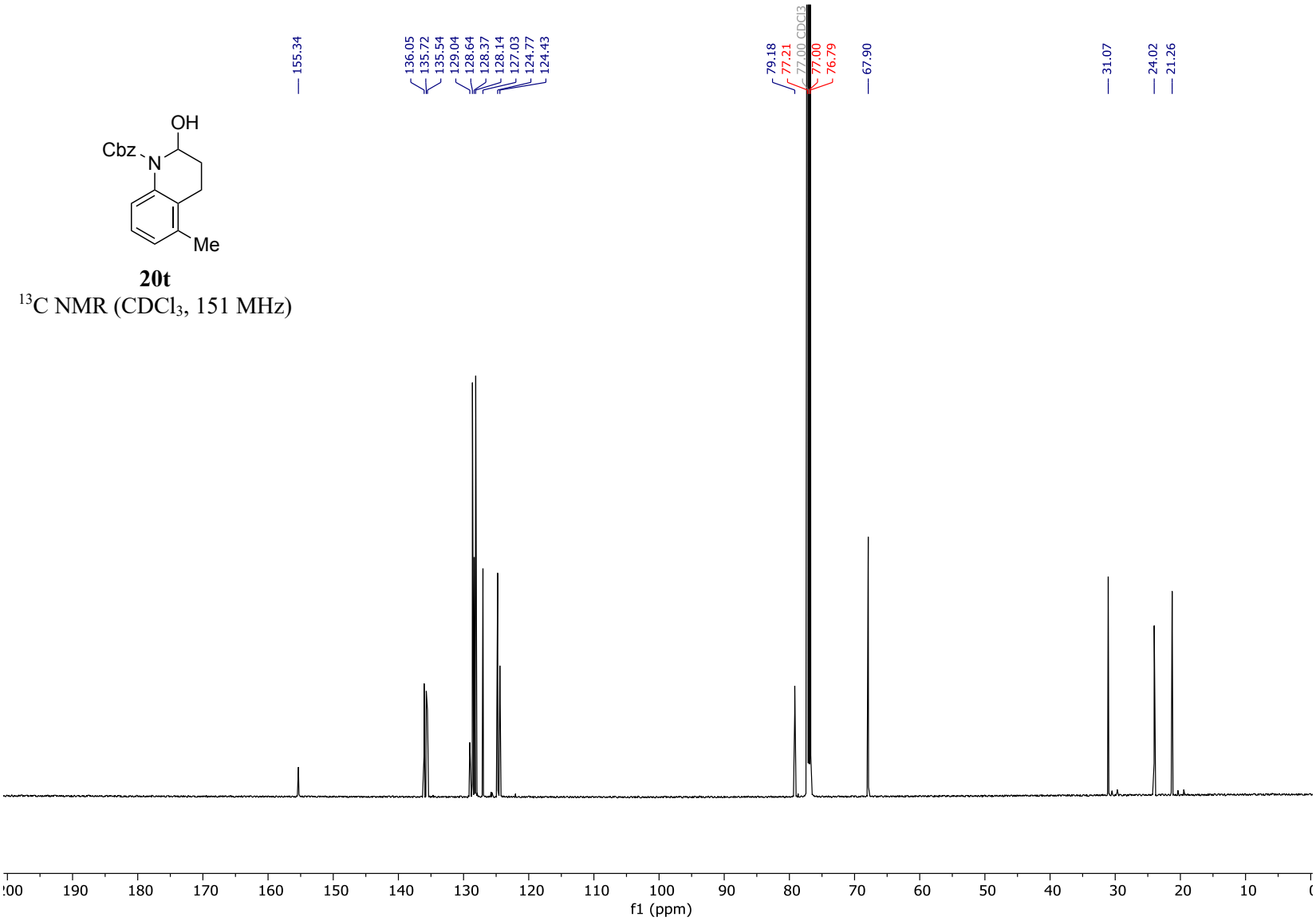
20s

^{13}C NMR ($CDCl_3$, 151 MHz)



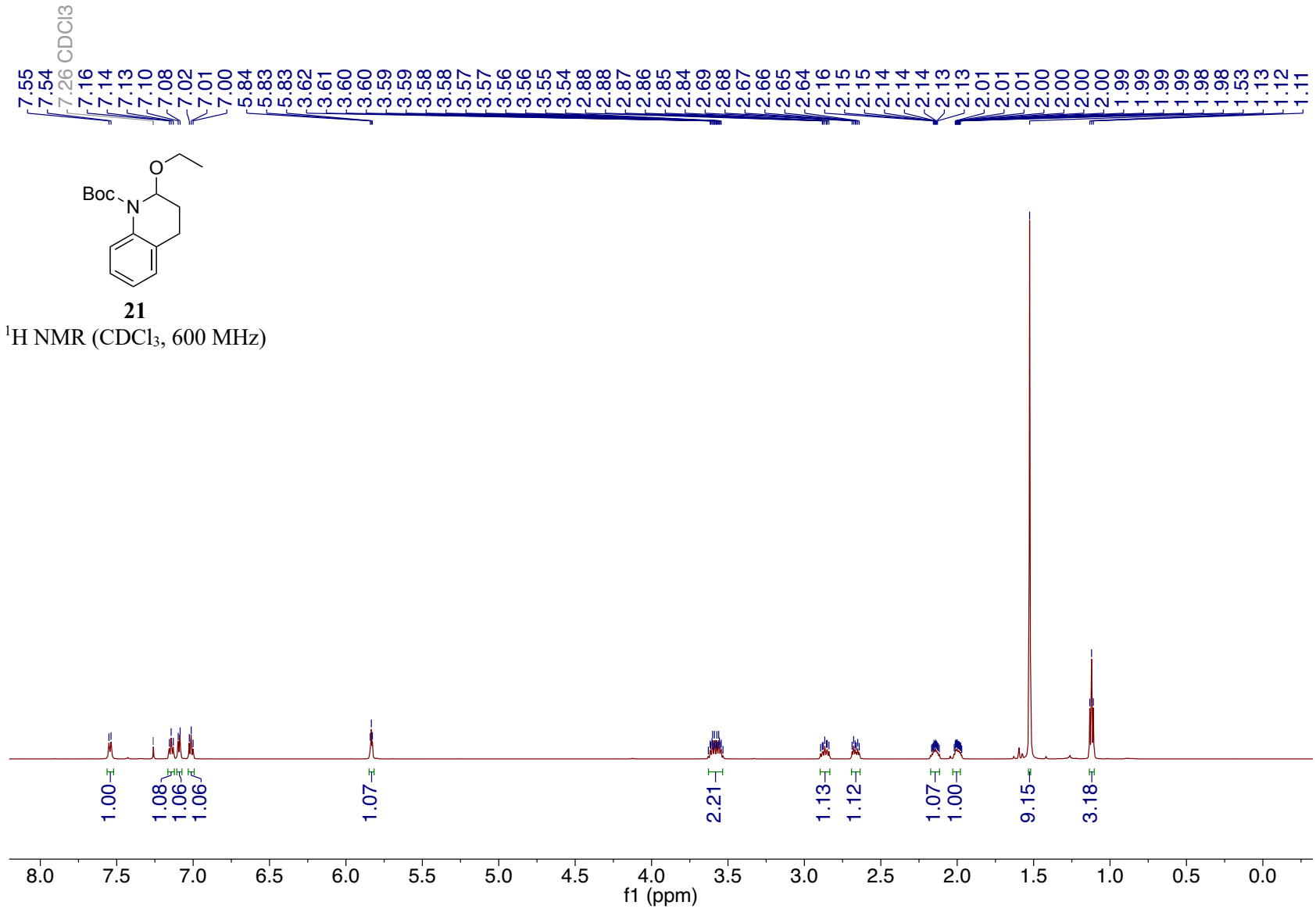
20t

^{1}H NMR ($CDCl_3$, 600 MHz)



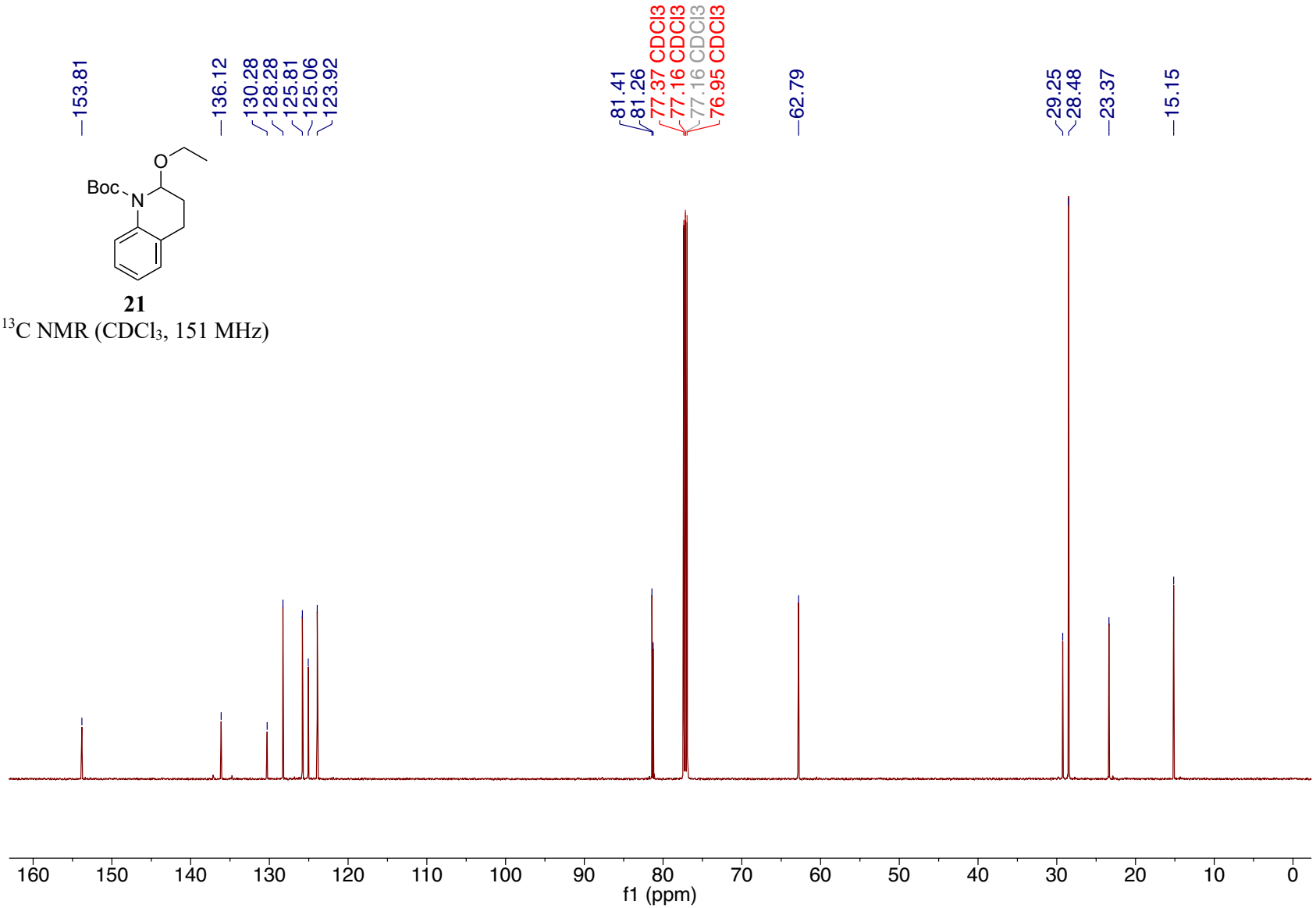
20t

^{13}C NMR ($CDCl_3$, 151 MHz)



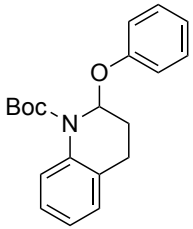
21

^{1}H NMR ($CDCl_3$, 600 MHz)



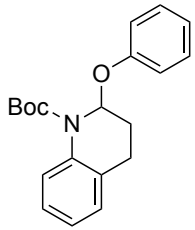
21

^{13}C NMR ($CDCl_3$, 151 MHz)



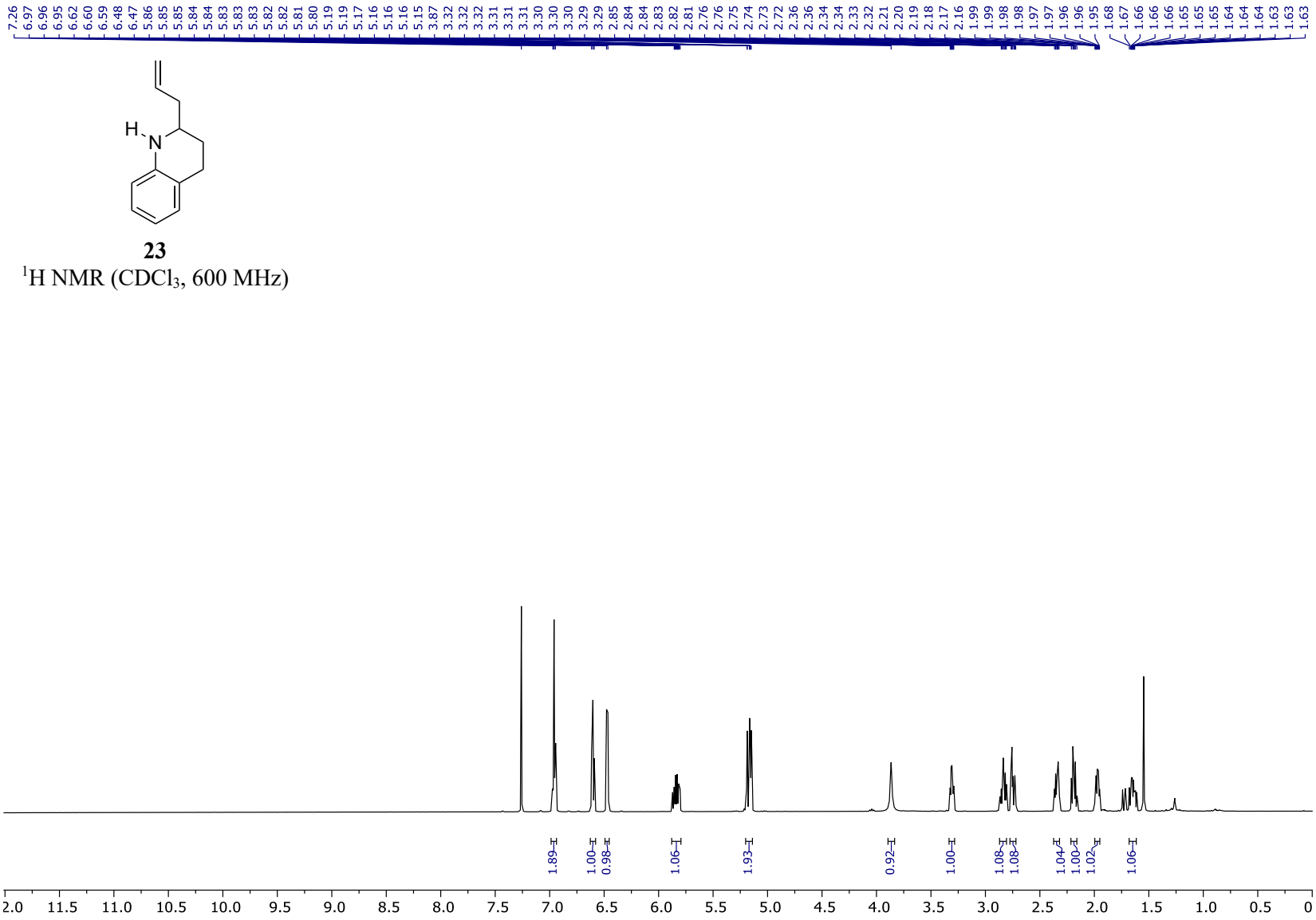
22

^{1}H NMR ($CDCl_3$, 600 MHz)



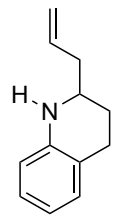
22

^{13}C NMR ($CDCl_3$, 151 MHz)



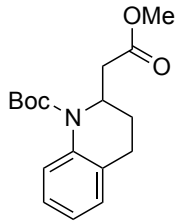
23

^{1}H NMR ($CDCl_3$, 600 MHz)



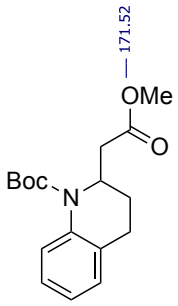
23

^{13}C NMR ($CDCl_3$, 151 MHz)



24

^{1}H NMR ($CDCl_3$, 600 MHz)



24

^{13}C NMR ($CDCl_3$, 151 MHz)