SUPPORTING INFORMATION

Practical Singly and Doubly Electrophilic Aminating Agents: A New, More Sustainable Platform for Carbon-Nitrogen Bond-Formation

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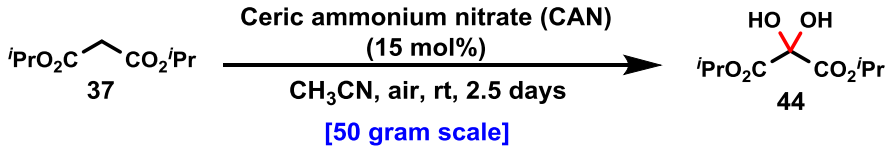
TABLE OF CONTENTS

1. General Experimental Procedures:

Reagents were purchased at the highest quality from the commercially available sources and used without further purification. Dichloromethane (DCM) and tetrahydrofuran (THF) for the reactions were obtained from pure process technology solvent system by passing the previously degassed solvents through an activated alumina column under argon. All reactions were carried out in flame-dried glass ware under an atmosphere of argon with magnetic stirring. All reactions were monitored by either ^{1}H NMR or thin layer chromatography (TLC) carried out on 0.25 mm pre-coated E. Merck silica plates (60F-254), using shortwave UV light as visualizing agent and $KMnO_4$ or phosphomolybdic acid (PMA) and heat as developing agents. Flash column chromatography was performed using Biotage Isolera One automated chromatograph with pre-packed KP-Sil cartridges. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer operating at 600 MHz for proton and 151 MHz for carbon nuclei and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR and 77.00 ppm ^{13}C NMR; DMSO-d_6: 2.50 ppm ^{1}H NMR and 39.52 ppm ^{13}C NMR). ^{19}F NMR spectra were recorded on a Bruker 500 UltraShield spectrometer operating at 471 MHz and the chemical shifts were relative to $CF^{35}Cl_3$ defined as 0 ppm.. For reporting NMR peak multiplicities, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent UHPLC TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) or chemical ionization time-of-flight (CI-TOF) reflectron experiments. Melting points and ranges were recorded on Mettler Toledo MP50 melting point system.

2. Gram-scale preparation of diisopropyl 2,2-dihydroxymalonate (44)



In a 3 L three-necked round bottom flask, diisopropyl malonate (50 g, 265.64 mmol, 1equiv) was first dissolved in acetonitrile (1.32 L, 0.2M) and to the resulting solution

ceric ammonium nitrate (CAN; 21.84 g, 15 mol%) was added in one portion under constant stirring. The reaction vessel was fitted with gas dispenser and a slow stream of air was bubbled through the reaction mixture under constant stirring. Progress of the reaction was monitored by checking the crude ^{1}H-NMR of the reaction mixture. After 2.5 days, the starting material was totally consumed. **Important:** During the course of the reaction, there is a decrease in the amount of solvent due to purging and based on the amount of solvent lost, the same amount of solvent is added to the reaction mixture as needed. After confirming the consumption of the starting material, water (1.5L) was added to the reaction mixture and stirred until the reaction mixture became colorless (e.g., usually an overnight period was allowed to hydrate all the ketomalonate in the reaction mixture). Next, the reaction mixture was extracted with ethyl acetate thrice (3 X 1L). The combined organic layers were washed with brine (1L), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was obtained as a thick slurry which was then triturated with hexanes (100 mL) and filtered (i.e., a white crystalline solid). During the filtration, some additional product crystallized from the mother liquor which was then recovered by filtration. The combined filtrates were washed with hexanes (3 X 50 mL) three times to afford **44** as white crystalline solid (43g, 73%) that requires no further purification.

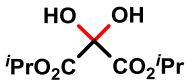
Synthesis of 44 on 400 g scale

Diisopropyl 2,2-dihydroxymalonate **44** was synthesized on 400 g scale (by largely adapting the above procedure) in a 10 L ChemGlass jacketed reactor that is outfitted with a large gas disperser as well as overhead mechanical stirring (see pictures). First, diisopropyl malonate (400 g, 2.12 mol, 1 equiv) was dissolved in acetonitrile (9 L) under constant stirring and to this solution ceric ammonium nitrate (CAN; 174.77 g, 15 mol%) was added in one portion. Next, a slow stream of air was introduced via the gas disperser and over the next 2 h period the temperature of the reaction mixture increased by 2 °C (22.5 °C to 24.6 °C). After continued vigorous stirring (at 200 rpm) overnight, the temperature remained at 24.7 °C. Progress of the reaction was monitored by ^{1}H-NMR and after 2.5 days of stirring the reaction was totally complete. At this point the bubbling of air was stopped and 4 L of deionized water was added to the reaction mixture under constant stirring (i.e., the 10 L reactor has > 3 L of overhead space to allow extra volume

during workup). During the workup the temperature initially dropped from 24 °C to 16 °C and stirring continued overnight (~15 h). At this point the reaction mixture was colorless and temperature of the reaction mixture was 24 °C. After draining through the bottom reactor valve, acetonitrile was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate thrice (3 x 3 L). The combined organic layers were dried over anhydrous Na_2SO_4 (150 g) and concentrated. The slurry that was formed after concentration was triturated with 300 mL of hexanes and filtered. The solid was washed repeatedly with another 500 mL of hexanes to afford a pure white crystalline solid (320 g, 68%).

Note: Repeated washing of the above product with hexanes is important for obtaining the pure product.

Diisopropyl 2,2-dihydroxymalonate (44)



44

Yield: 68%

Physical State: white crystalline solid (m.p. = 56 – 61 °C);

R_f = 0.23 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.15 (hept, *J* = 6.3 Hz, 2H), 4.80 (s, 2H), 1.30 (d, *J* = 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.0, 89.8, 71.6, 21.3;

HRMS (ESI-TOF): calc'd for $C_9H_{16}O_6$ $[M+Na]^+$ 243.0839; found 243.0840.

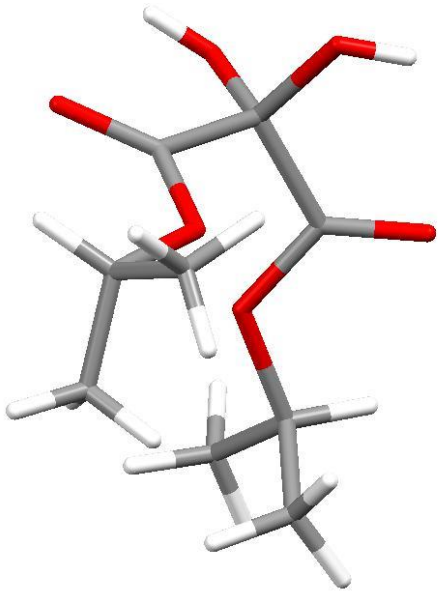


Figure S1. X-Ray crystal structure of diisopropyl 2,2-dihydroxymalonate (**44**)

Table S1. X-ray crystal data and structure refinement for **44**

Table 1.

Identification code	pvk19_0m_a	
Empirical formula	C9 H16 O6	
Formula weight	220.22	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.406(2) Å	α= 90°.
	b = 13.924(3) Å	β= 112.918(4)°.
	c = 10.168(3) Å	γ = 90°.
Volume	1226.5(5) $Å^3$	
Z	4	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	472	

Crystal size	0.150 x 0.100 x 0.050 mm^3
Theta range for data collection	2.505 to 28.522°.
Index ranges	-12<=h<=10, -18<=k<=18, -13<=l<=13
Reflections collected	9598
Independent reflections	3110 [R(int) = 0.0718]
Completeness to theta = 25.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.453
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3110 / 18 / 143
Goodness-of-fit on F^2	1.767
Final R indices [I>2sigma(I)]	R1 = 0.0926, wR2 = 0.2729
R indices (all data)	R1 = 0.1912, wR2 = 0.2956
Extinction coefficient	0.015(7)
Largest diff. peak and hole	0.497 and -0.431 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pvk19_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7849(3)	6286(2)	3173(2)	89(1)
O(2)	4836(3)	7209(2)	2834(2)	86(1)
O(3)	4028(2)	5372(2)	1506(3)	100(1)
O(4)	6075(3)	4772(2)	3505(3)	100(1)
O(5)	6598(3)	5765(2)	933(3)	106(1)
O(6)	4848(4)	6215(2)	4562(3)	104(1)
C(1)	5423(4)	5588(3)	2646(4)	76(1)
C(2)	6682(4)	5891(3)	2146(4)	74(1)
C(3)	9175(5)	6614(4)	2887(5)	110(2)
C(4)	9224(8)	7589(6)	2956(9)	208(3)
C(5)	10526(7)	6266(6)	4081(9)	231(4)
C(6)	5012(4)	6359(3)	3477(4)	74(1)
C(7)	4439(6)	8039(3)	3495(5)	96(1)
C(8)	5798(7)	8570(4)	4303(7)	169(3)

C(9)	3257(8)	8597(5)	2428(8)	180(3)

Table 3. Bond lengths [Å] and angles [°] for pvk19_0m_a.

O(1)-C(2)	1.306(4)
O(1)-C(3)	1.460(5)
O(2)-C(6)	1.330(4)
O(2)-C(7)	1.457(5)
O(3)-C(1)	1.404(3)
O(3)-H(3)	0.8200
O(4)-C(1)	1.418(4)
O(4)-H(4)	0.8200
O(5)-C(2)	1.217(4)
O(6)-C(6)	1.190(4)
C(1)-C(6)	1.507(5)
C(1)-C(2)	1.519(5)
C(3)-C(4)	1.359(9)
C(3)-C(5)	1.456(8)
C(3)-H(3A)	0.9800
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(7)-C(8)	1.428(7)
C(7)-C(9)	1.441(7)
C(7)-H(7)	0.9800
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600

C(2)-O(1)-C(3)	119.3(3)
C(6)-O(2)-C(7)	119.0(3)
C(1)-O(3)-H(3)	109.5
C(1)-O(4)-H(4)	109.5
O(3)-C(1)-O(4)	112.2(3)
O(3)-C(1)-C(6)	104.7(3)
O(4)-C(1)-C(6)	111.7(3)
O(3)-C(1)-C(2)	112.5(3)
O(4)-C(1)-C(2)	102.9(3)
C(6)-C(1)-C(2)	113.1(3)
O(5)-C(2)-O(1)	125.0(3)
O(5)-C(2)-C(1)	123.2(3)
O(1)-C(2)-C(1)	111.8(3)
C(4)-C(3)-C(5)	106.7(6)
C(4)-C(3)-O(1)	108.4(5)
C(5)-C(3)-O(1)	105.4(4)
C(4)-C(3)-H(3A)	112.0
C(5)-C(3)-H(3A)	112.0
O(1)-C(3)-H(3A)	112.0
C(3)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(3)-C(5)-H(5A)	109.5
C(3)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(3)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
O(6)-C(6)-O(2)	124.7(3)
O(6)-C(6)-C(1)	123.6(4)
O(2)-C(6)-C(1)	111.6(3)
C(8)-C(7)-C(9)	114.2(5)
C(8)-C(7)-O(2)	110.1(4)

C(9)-C(7)-O(2)	110.0(4)
C(8)-C(7)-H(7)	107.4
C(9)-C(7)-H(7)	107.4
O(2)-C(7)-H(7)	107.4
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for pvk19_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	70(2)	116(2)	75(1)	-20(2)	20(1)	-34(2)
O(2)	116(2)	57(2)	82(2)	2(1)	37(1)	10(1)
O(3)	67(2)	105(2)	115(2)	-40(2)	23(1)	-18(1)
O(4)	106(2)	65(2)	137(2)	14(2)	56(2)	15(2)
O(5)	105(2)	125(3)	82(2)	-27(2)	31(2)	-20(2)
O(6)	135(2)	84(2)	103(2)	7(2)	56(2)	-3(2)
C(1)	66(2)	68(2)	84(2)	-11(2)	20(2)	-5(2)
C(2)	74(2)	65(2)	72(2)	-7(2)	16(2)	-8(2)
C(3)	86(3)	133(4)	106(3)	-25(3)	33(2)	-43(3)
C(4)	169(4)	172(5)	305(6)	56(4)	117(4)	-17(4)
C(5)	112(4)	225(7)	347(8)	85(6)	81(5)	-12(4)

C(6)	73(2)	71(3)	71(2)	1(2)	21(2)	-5(2)
C(7)	127(3)	65(3)	99(3)	-5(2)	47(3)	5(3)
C(8)	151(5)	122(5)	182(5)	-52(4)	9(4)	12(4)
C(9)	146(5)	138(5)	212(6)	-35(5)	23(5)	51(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for pvk19_0m_a.

	x	y	z	U(eq)
H(3)	4208	5177	825	149
H(4)	5796	4756	4175	150
H(3A)	9145	6376	1969	131
H(4A)	9640	7787	3938	312
H(4B)	8200	7841	2489	312
H(4C)	9867	7826	2491	312
H(5A)	11256	6006	3729	346
H(5B)	10220	5775	4580	346
H(5C)	10993	6788	4720	346
H(7)	4005	7798	4165	115
H(8A)	6599	8135	4857	253
H(8B)	5577	9007	4929	253
H(8C)	6132	8926	3665	253
H(9A)	2989	9136	2875	270
H(9B)	2361	8204	1968	270
H(9C)	3634	8823	1732	270

Table 6. Torsion angles [°] for pvk19_0m_a.

Pictorial representations for the synthesis of 44 on bulk scale

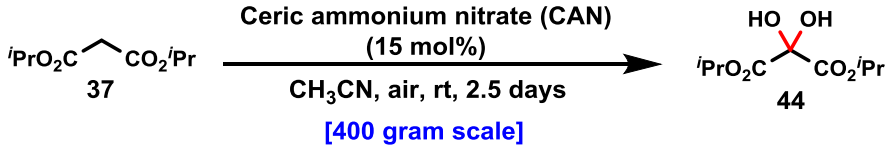


Figure S2. Reaction mixture after adding ceric ammonium nitrate (CAN)

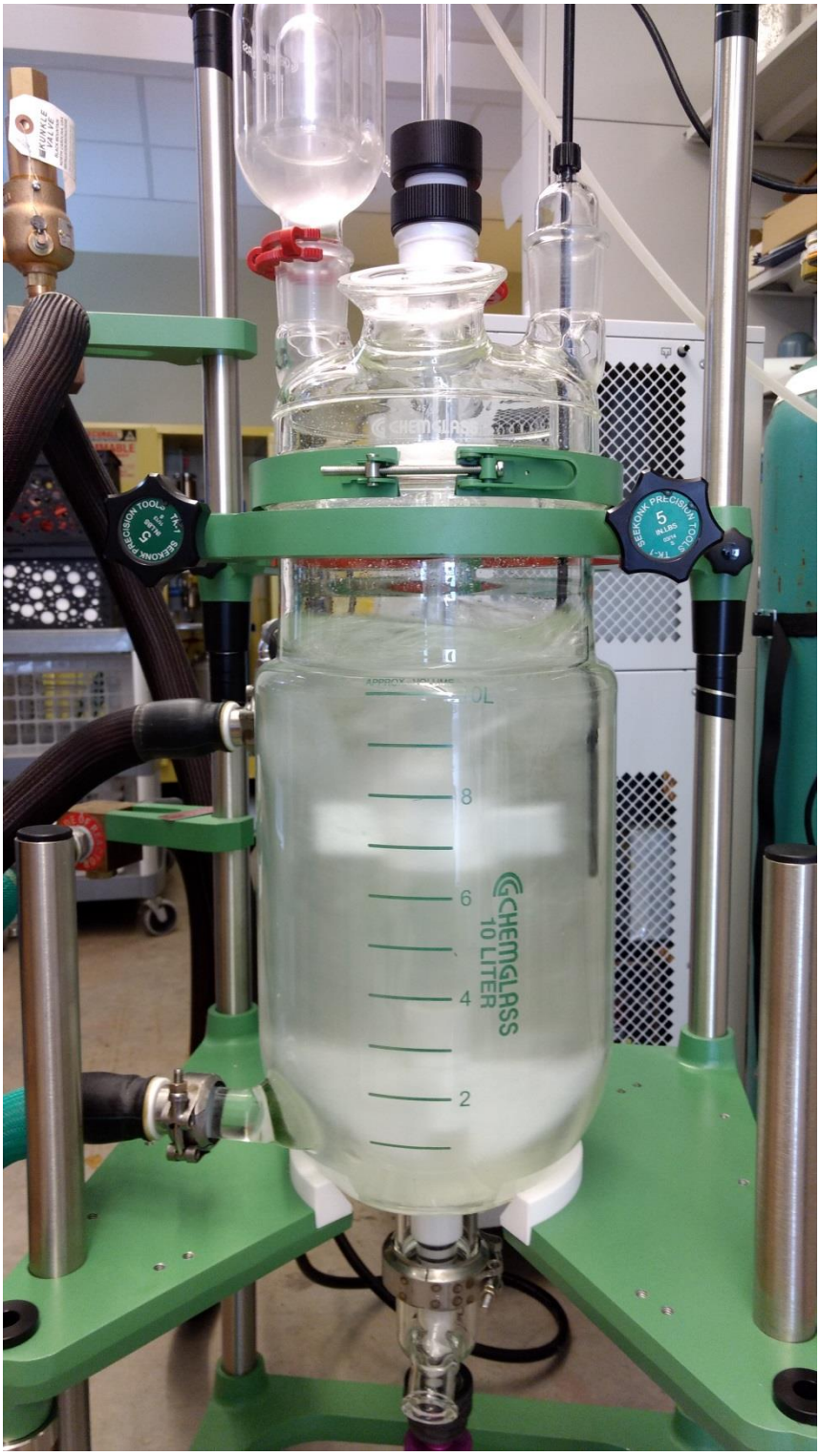


Figure S3. Reaction mixture after quenching with water

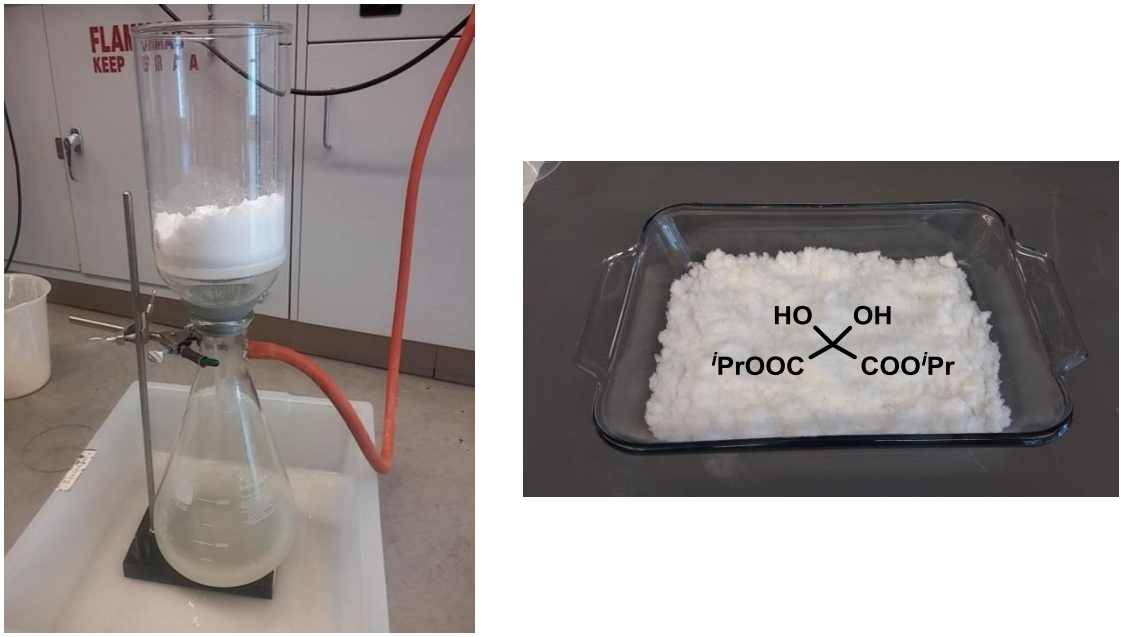
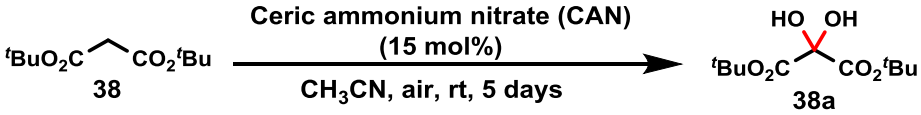


Figure S4. Filtration of crystalline product **44** after trituration

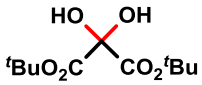
3. Preparation of di-*tert*-butyl 2,2-dihydroxymalonate (38a)



Compound **38a** was prepared according to the procedure described for the preparation of **44**. Di-*tert*-butyl malonate (**38**; 10 g, 46.23 mmol, 1equiv) was first dissolved in acetonitrile (232 mL, 0.2M) and to this solution ceric ammonium nitrate (CAN; 3.8 g, 15 mol%) was added in one portion under constant stirring. The three-necked round bottom flask was fitted with gas dispenser and a slow stream of air was bubbled through the reaction mixture under constant stirring. Progress of the reaction was monitored by checking the crude ^{1}H-NMR of the reaction mixture. After 5 days the NMR analysis indicated total consumption of the starting material (**38**). Any solvent lost during the course of the reaction due to the constant bubbling of air was replaced as needed. After confirming the completion of reaction, deionized water (250 mL) was added and stirring continued until the brownish yellow color of the reaction mixture turned colorless. Next,

the reaction mixture was extracted with ethyl acetate thrice (3 X 250 mL). The combined organic layers were washed with brine (300 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was obtained as thick slurry. This slurry was then triturated with hexanes (25 mL) and filtered. During the filtration process some of the product crystallized in the filtrate – these crystals were then recovered. The combined crops were washed with hexanes (3 X 20 mL) three times to afford **38a** as white crystalline solid (5.9 g, 52%) that requires no further purification.

Di-*tert*-butyl 2,2-dihydroxymalonate (38a)



38a

Yield: 52%

Physical State: white solid (m.p. 140 – 147 °C);

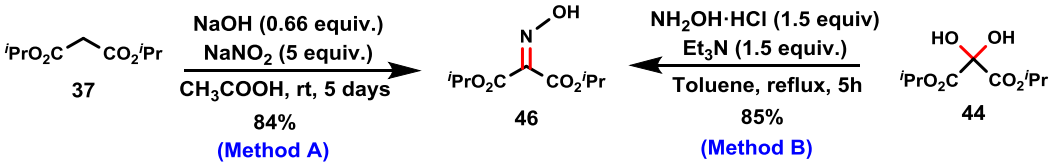
R_f = 0.20 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.60 (s, 1H), 1.51 (s, 18H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.7, 89.9, 84.4, 27.6;

HRMS (ESI-TOF): calc'd for $C_{11}H_{20}O_6$ $[M+Na]^+$ 271.1152; found 271.1152.

4. Preparation of diisopropyl 2-(hydroxyimino)malonate (46) (Methods A & B)

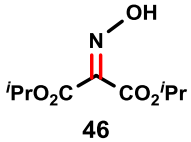


Method A: This procedure was adapted from literature reports[1-3]. Sodium hydroxide (0.997 g, 24.93 mmol, 0.66 equiv) was dissolved in glacial acetic acid (7.55 mL) under constant stirring. A thick, white slurry was formed. Then, a solution of diisopropyl malonate (7.1 g, 37.77 mmol, 1 equiv) in glacial acetic acid (2.11 mL) was added dropwise to the ice bath-cooled slurry (0 ^oC) over a period of 5 minutes. After this addition was complete, a 0 ^oC solution of sodium nitrite (13.03 g, 188.87 mmol, 5 equiv)

in water (23.61 mL) was added dropwise over a period of one hour (!) to the reaction mixture by means of an addition funnel, maintaining the temperature of the reaction mixture at 0 ^{o}C. After the addition of sodium nitrite was complete, the addition funnel was replaced with a septum fitted with an empty balloon and the reaction mixture was allowed to warm to room temperature and stirred for 5 days. After 5 days, the reaction mixture was saturated with solid sodium chloride and extracted with ethyl acetate thrice (3 X 75 mL). The combined organic extracts were washed with a 1:1 mixture of saturated aqueous solution of $NaHCO_3$ and brine until the pH of the aqueous layer becomes basic (pH 8-9). Then the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography to afford the **46** as a colorless viscous oily liquid (6.85 g, 84%). **Note:** In this method, the reaction goes to 85% completion only and 15% of the starting material was recovered during the chromatographic purification.

Method B: Diisopropyl 2,2-dihydroxymalonate **44** (20 g, 90.81 mmol, 1 equiv) was dissolved in toluene (227 mL) and to this solution hydroxylamine hydrochloride (9.46g, 136.22 mmol, 1.5 equiv) was added followed by triethylamine (18.98 mL, 136.22 mmol, 1.5 equiv) at room temperature under constant stirring. Then the reaction mixture was heated to reflux under Dean-Stark conditions for 5 h. Progress of the reaction was monitored by ^{1}H-NMR. After confirming the completion of the reaction by crude NMR, heating was stopped and the reaction mixture was allowed to cool to room temperature. Next, the precipitated triethylamine hydrochloride salt was filtered and washed with ethyl acetate thrice (3 X 25 mL). The combined organic layers were washed once with saturated aqueous $NaHCO_3$ solution (150 mL) followed by brine, dried over anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography to afford the product **46** as colorless viscous oily liquid (16.8 g, 85%).

Diisopropyl 2-(hydroxyimino)malonate (46)



46

Yield: 85% (**Method B**)

Physical State: colorless viscous oily liquid;

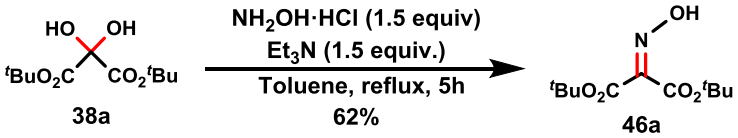
R_f = 0.45 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.41 (s, 1H), 5.22 (hept, *J* = 6.3 Hz, 1H), 5.15 (hept, *J* = 6.2 Hz, 1H), 1.29 (dd, *J* = 17.2, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.0, 159.3, 144.3, 70.5, 70.3, 21.2, 21.1;

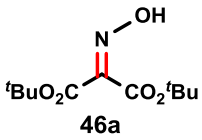
HRMS (ESI-TOF): calc'd for $C_9H_{15}NO_5$ $[M+Na]^+$ 240.0842; found 240.0843.

5. Preparation of di-*tert*-butyl 2-(hydroxyimino)malonate



Di-*tert*-butyl 2-(hydroxyimino)malonate was prepared on 1 gram scale according to the procedure described in **Method B** for the preparation of **46**. The product was obtained as colorless viscous oily liquid (614 mg, 62% yield).

Di-*tert*-butyl 2-(hydroxyimino)malonate (46a)



Yield: 62%

Physical State: colorless oily liquid;

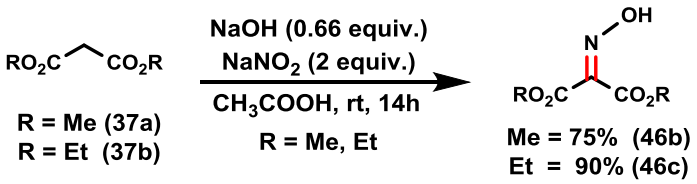
R_f = 0.24 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.58 (s, 1H), 1.49 (d, *J* = 17.0 Hz, 18H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.8, 158.9, 145.3, 84.3, 84.0, 27.8, 27.7;

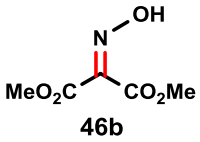
HRMS (ESI-TOF): calc'd for $C_{11}H_{19}NO_5$ $[M+Na]^+$ 268.1155; found 168.1155.

6. Preparation of dimethyl and diethyl oximinomalonates (46b, 46c)



Both the dimethyl and diethyl oximinomalonates were prepared according to literature reported procedures[1-3]. First, sodium hydroxide (3.99 g, 99.91 mmol, 0.66 equiv) was dissolved in glacial acetic acid (30 mL) under constant stirring. A thick white slurry was formed. Then, a solution of dimethyl malonate (20 g, 151.38 mmol, 1 equiv) in glacial acetic acid (8.4 mL) was added dropwise over a period of 5 minutes to the ice bath-cooled slurry. After this addition was complete, a 0 ^{o}C solution of sodium nitrite (20.89 g, 302.77 mmol, 2 equiv) in water (160 mL) was added dropwise over a period of 1 h to the reaction mixture by means of an addition funnel, while carefully maintaining the temperature of the reaction mixture at 0 ^{o}C. After the addition of $NaNO_2$ solution was completed, the addition funnel was replaced with a septum fitted with an empty balloon and the reaction mixture was allowed to warm to room temperature and stirred overnight (14h). After overnight stirring, the reaction mixture was saturated with sodium chloride and extracted with ethyl acetate thrice (3 X 100 mL). The combined organic extracts were washed with a 1:1 mixture of saturated aqueous solution of $NaHCO_3$ and brine until the pH of the aqueous layer was basic (pH 8-9). Next, the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography to afford the pure dimethyl oximinomalonate as a colorless viscous oily liquid which became a white solid (18.2 g, 75%) upon standing in the refrigerator. The diethyl oximinomalonate was also prepared by this same procedure: pale yellow colored viscous oily liquid (90% yield). The characterization data for these oximinomalonates is consistent with the literature reported data.

Dimethyl 2-(hydroxyimino)malonate (46b)



46b

Yield: 75%

Physical State: White solid;

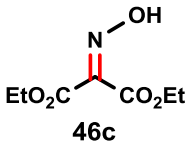
R_f = 0.12 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.73 (s, 1H), 3.86 (d, *J* = 17.8 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.9, 160.4, 143.5, 53.2, 52.9;

Spectral data is in accordance with the literature report[2].

Diethyl 2-(hydroxyimino)malonate (46c)



46c

diethyl 2-(hydroxyimino)malonate

Yield: 90%

Physical State: Pale yellow colored viscous oily liquid;

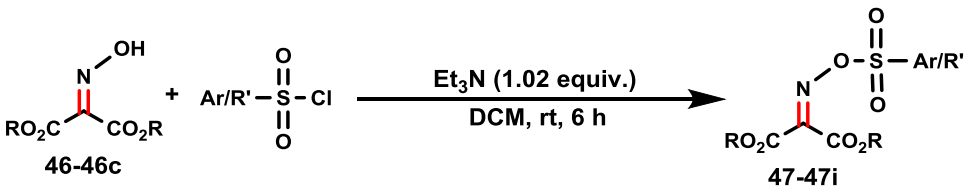
R_f = 0.2 (20% EtOAc/hexanes);

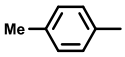
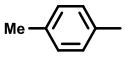
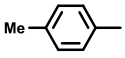
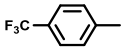
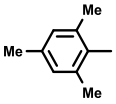
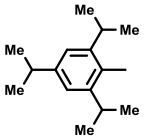
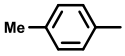
^{1}H NMR (600 MHz, $CDCl_3$): δ 10.47 (s, 1H), 4.33 (dq, *J* = 25.4, 7.1 Hz, 4H), 1.30 (dt, *J* = 14.1, 7.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.5, 159.9, 144.0, 62.6, 62.4, 13.79, 13.75;

Spectral data is in accordance with the literature report[2].

7. Table S2. Activation of oximinomalonates with different sulfonyl chlorides



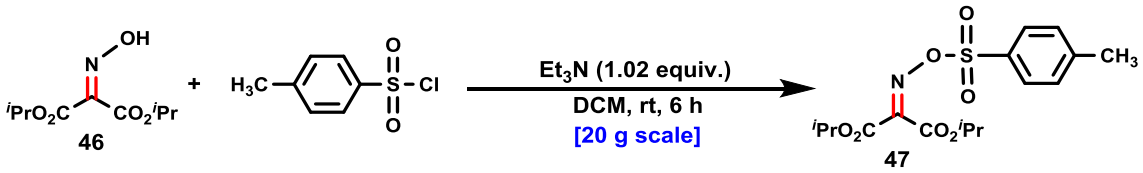
Entry	R	Ar/R'	Yield(%)
1	Me	Me	93
2	Me		83
3	Et	Me	82
4	Et		72
5	^{i}Pr	Me	70
6	^{i}Pr		72
7	^{i}Pr		76
8	^{i}Pr		74
9	^{i}Pr		85
10	^{t}Bu		79

8. Standard procedure for oximinomalonate activation with sulfonyl chlorides

This procedure was adapted from the literature[3] with small changes. To a solution of hydroxyimino malonate (1 equiv) and sulfonyl chloride (1 equiv) in DCM (0.56 M) under argon, was added neat Et_3N (1.02 equiv) in one portion at room temperature under constant stirring. The reaction mixture was stirred at room temperature for 6 hours. After confirming the complete consumption of starting material by thin layer chromatography (TLC), the reaction mixture was diluted with DCM (two volumes of the reaction mixture)

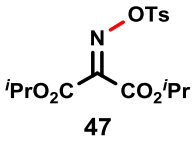
and washed with water thrice. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

9. General procedure for the synthesis of diisopropyl 2-((tosyloxy)imino)malonate (47)



To a solution of diisopropyl 2-(hydroxyimino) malonate **46** (20 g, 92.07 mmol, 1 equiv) and tosyl chloride (17.55 g, 92.07 mmol, 1 equiv) in DCM (165 mL) under argon, was added a solution of Et_3N (13.08 mL, 93.91 mmol, 1.02 equiv) in DCM (41 mL) in 2 minutes at room temperature under constant stirring. The reaction mixture was stirred at room temperature for 6 hours. After confirming the complete consumption of starting material by TLC, the reaction mixture was diluted with DCM (200 mL) and washed with water thrice (3 X 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography to afford the product as a white crystalline solid (28 g, 81%). All the oximinomalonates listed in **Table S2** (page S28) were activated with different sulfonyl chlorides by this procedure.

Diisopropyl 2-((tosyloxy)imino)malonate (47)



Yield: 81%

Physical State: white crystalline solid (m.p. 82 – 87 °C);

R_f = 0.20 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.24 (hept, *J* = 6.1 Hz, 1H), 5.12 (hept, *J* = 6.0 Hz, 1H), 2.45 (s, 3H), 1.31 (dd, *J* = 24.3, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.5, 157.3, 150.2, 146.1, 131.1, 129.8, 129.1, 71.8, 71.7, 21.7, 21.44, 21.41;

HRMS (ESI-TOF): calc'd for $C_{16}H_{21}NO_7S$ $[M+H]^+$ 372.1111; found 372.1119.

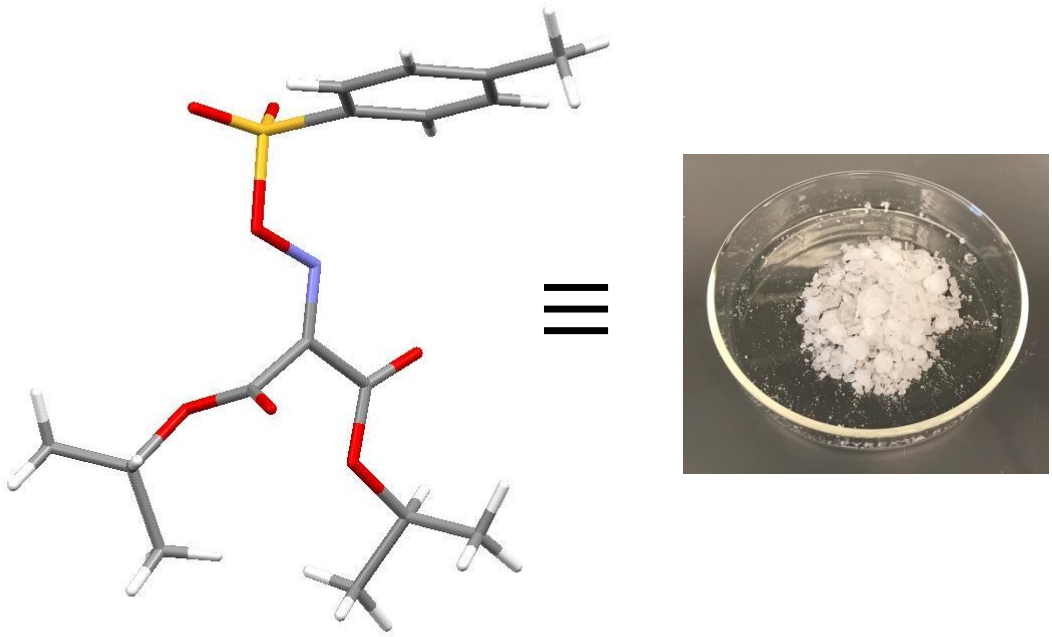


Figure S5. X-Ray crystal structure of diisopropyl 2-((tosyloxy)imino)malonate (**47**)

Table S3. X-Ray crystal data and structure refinement for **47**

Table 1.

Identification code	pvk127_0m_a	
Empirical formula	C16 H21 N O7 S	
Formula weight	371.40	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.2805(16) Å	α = 90°.
	b = 11.437(2) Å	β = 109.858(2)°.
	c = 10.852(2) Å	γ = 90°.
Volume	966.6(3) $Å^3$	
Z	2	

Density (calculated)	1.276 Mg/m^3
Absorption coefficient	0.202 mm^{-1}
F(000)	392
Crystal size	0.400 x 0.350 x 0.250 mm^3
Theta range for data collection	1.995 to 33.070°.
Index ranges	-12<=h<=12, -17<=k<=17, -16<=l<=16
Reflections collected	13160
Independent reflections	6721 [R(int) = 0.0173]
Completeness to theta = 25.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.651
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6721 / 7 / 231
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1108
R indices (all data)	R1 = 0.0447, wR2 = 0.1154
Absolute structure parameter	0.054(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.339 and -0.359 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pvk127_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4131(1)	6076(1)	9696(1)	43(1)
O(1)	2922(2)	5311(2)	9941(2)	59(1)
O(2)	5375(2)	6674(2)	10741(2)	57(1)
O(3)	5368(2)	5300(1)	9108(2)	47(1)
O(4)	5505(2)	2348(2)	6395(2)	56(1)
O(5)	2853(2)	2811(2)	6350(2)	68(1)
O(6)	8084(2)	3253(2)	9007(2)	56(1)
O(7)	7795(3)	4638(2)	7482(2)	75(1)
N(1)	4345(2)	4486(1)	8162(2)	44(1)
C(1)	3113(2)	7040(2)	8422(2)	40(1)

C(2)	3770(3)	8167(2)	8474(2)	48(1)
C(3)	2944(3)	8945(2)	7483(2)	54(1)
C(4)	1509(3)	8619(2)	6437(2)	53(1)
C(5)	882(3)	7481(2)	6409(2)	54(1)
C(6)	1658(3)	6690(2)	7393(2)	50(1)
C(7)	660(4)	9479(3)	5361(3)	76(1)
C(8)	5310(2)	3845(2)	7750(2)	39(1)
C(9)	4368(3)	2943(2)	6748(2)	44(1)
C(10)	4826(4)	1457(2)	5366(3)	67(1)
C(11)	6212(9)	544(4)	5662(7)	141(2)
C(12)	4423(7)	2016(4)	4055(4)	99(1)
C(13)	7223(3)	3970(2)	8076(2)	44(1)
C(14)	9958(3)	3179(4)	9278(3)	87(1)
C(15)	10752(5)	2926(6)	10673(5)	112(1)
C(16)	10194(7)	2240(8)	8355(7)	170(3)

Table 3. Bond lengths [Å] and angles [°] for pvk127_0m_a.

S(1)-O(1)	1.4208(19)
S(1)-O(2)	1.4223(16)
S(1)-O(3)	1.6393(15)
S(1)-C(1)	1.745(2)
O(3)-N(1)	1.430(2)
O(4)-C(9)	1.319(2)
O(4)-C(10)	1.475(3)
O(5)-C(9)	1.189(3)
O(6)-C(13)	1.308(2)
O(6)-C(14)	1.481(3)
O(7)-C(13)	1.196(3)
N(1)-C(8)	1.273(2)
C(1)-C(2)	1.393(3)
C(1)-C(6)	1.395(3)
C(2)-C(3)	1.383(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.387(3)

C(3)-H(3)	0.9300
C(4)-C(5)	1.398(3)
C(4)-C(7)	1.505(3)
C(5)-C(6)	1.381(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(13)	1.508(3)
C(8)-C(9)	1.510(3)
C(10)-C(12)	1.490(5)
C(10)-C(11)	1.504(6)
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(14)-C(15)	1.459(5)
C(14)-C(16)	1.526(8)
C(14)-H(14)	0.9800
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600

O(1)-S(1)-O(2)	120.78(11)
O(1)-S(1)-O(3)	108.25(10)
O(2)-S(1)-O(3)	101.07(9)
O(1)-S(1)-C(1)	110.86(11)
O(2)-S(1)-C(1)	110.60(10)
O(3)-S(1)-C(1)	103.38(8)

N(1)-O(3)-S(1)	109.57(12)
C(9)-O(4)-C(10)	116.7(2)
C(13)-O(6)-C(14)	116.64(19)
C(8)-N(1)-O(3)	109.72(16)
C(2)-C(1)-C(6)	121.14(19)
C(2)-C(1)-S(1)	118.45(15)
C(6)-C(1)-S(1)	120.40(15)
C(3)-C(2)-C(1)	118.72(18)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(2)-C(3)-C(4)	121.6(2)
C(2)-C(3)-H(3)	119.2
C(4)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	118.4(2)
C(3)-C(4)-C(7)	120.3(2)
C(5)-C(4)-C(7)	121.3(2)
C(6)-C(5)-C(4)	121.5(2)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.64(18)
C(5)-C(6)-H(6)	120.7
C(1)-C(6)-H(6)	120.7
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(1)-C(8)-C(13)	126.73(17)
N(1)-C(8)-C(9)	114.48(17)
C(13)-C(8)-C(9)	118.57(16)
O(5)-C(9)-O(4)	126.7(2)
O(5)-C(9)-C(8)	124.85(19)
O(4)-C(9)-C(8)	108.44(17)
O(4)-C(10)-C(12)	109.3(2)
O(4)-C(10)-C(11)	104.5(3)

C(12)-C(10)-C(11)	114.2(4)
O(4)-C(10)-H(10)	109.6
C(12)-C(10)-H(10)	109.6
C(11)-C(10)-H(10)	109.6
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(7)-C(13)-O(6)	127.2(2)
O(7)-C(13)-C(8)	120.7(2)
O(6)-C(13)-C(8)	112.02(16)
C(15)-C(14)-O(6)	106.9(3)
C(15)-C(14)-C(16)	115.3(5)
O(6)-C(14)-C(16)	105.6(3)
C(15)-C(14)-H(14)	109.6
O(6)-C(14)-H(14)	109.6
C(16)-C(14)-H(14)	109.6
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5

H(16B)-C(16)-H(16C) 109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for pvk127_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

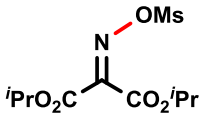
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	45(1)	40(1)	42(1)	-6(1)	12(1)	2(1)
O(1)	66(1)	53(1)	64(1)	1(1)	31(1)	-3(1)
O(2)	59(1)	57(1)	45(1)	-13(1)	4(1)	4(1)
O(3)	44(1)	42(1)	51(1)	-10(1)	11(1)	4(1)
O(4)	56(1)	54(1)	64(1)	-22(1)	26(1)	-5(1)
O(5)	44(1)	87(1)	63(1)	-21(1)	5(1)	1(1)
O(6)	35(1)	72(1)	59(1)	20(1)	14(1)	2(1)
O(7)	72(1)	70(1)	90(1)	28(1)	38(1)	1(1)
N(1)	46(1)	39(1)	41(1)	-5(1)	8(1)	7(1)
C(1)	38(1)	37(1)	42(1)	-7(1)	10(1)	2(1)
C(2)	49(1)	43(1)	48(1)	-8(1)	10(1)	-7(1)
C(3)	57(1)	41(1)	60(1)	-1(1)	14(1)	-6(1)
C(4)	50(1)	49(1)	55(1)	1(1)	12(1)	4(1)
C(5)	44(1)	53(1)	53(1)	-3(1)	1(1)	0(1)
C(6)	45(1)	40(1)	55(1)	-7(1)	5(1)	-5(1)
C(7)	70(2)	67(2)	77(2)	20(1)	5(1)	5(1)
C(8)	43(1)	36(1)	36(1)	2(1)	10(1)	6(1)
C(9)	47(1)	45(1)	37(1)	-2(1)	10(1)	4(1)
C(10)	86(2)	50(1)	75(2)	-26(1)	40(1)	-18(1)
C(11)	164(5)	86(3)	152(4)	-56(3)	28(4)	39(3)
C(12)	151(4)	88(2)	66(2)	-29(2)	45(2)	-40(3)
C(13)	48(1)	41(1)	45(1)	0(1)	17(1)	0(1)
C(14)	33(1)	132(3)	94(2)	41(2)	19(1)	-2(1)
C(15)	61(2)	161(3)	103(2)	24(2)	16(2)	-3(2)
C(16)	75(3)	248(8)	195(6)	-28(6)	55(4)	56(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for pvk127_0m_a.

	x	y	z	U(eq)
H(2)	4744	8393	9160	58
H(3)	3360	9704	7521	65
H(5)	-80	7252	5713	65
H(6)	1219	5939	7370	59
H(7A)	689	10245	5731	114
H(7B)	-511	9250	4923	114
H(7C)	1261	9491	4745	114
H(10)	3780	1112	5441	81
H(11A)	7229	879	5572	211
H(11B)	5831	-96	5060	211
H(11C)	6462	266	6542	211
H(12A)	3654	2661	3984	149
H(12B)	3890	1453	3383	149
H(12C)	5464	2294	3953	149
H(14)	10381	3931	9077	104
H(15A)	10551	3566	11175	168
H(15B)	11965	2821	10878	168
H(15C)	10262	2225	10882	168
H(16A)	11377	2215	8413	255
H(16B)	9488	2420	7472	255
H(16C)	9868	1493	8600	255

Table 6. Torsion angles [°] for pvk127_0m_a.

Diisopropyl 2-(((methylsulfonyl)oxy)imino)malonate (47a)



47a

Yield: 70%

Physical State: off-white solid (m.p. = 50 – 55 °C);

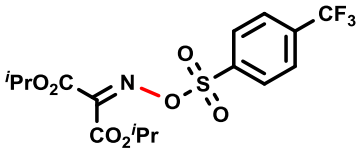
R_f = 0.26 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.28 (hept, *J* = 6.3 Hz, 1H), 5.21 (hept, *J* = 6.4 Hz, 1H), 3.24 (s, 3H), 1.35 (t, *J* = 6.0 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.3, 157.1, 150.9, 72.2, 72.0, 36.9, 21.3;

HRMS (ESI-TOF): calc'd for $C_{10}H_{17}NO_7S$ $[M+K]^+$ 334.0357; found 334.0368.

Diisopropyl 2-((((4-(trifluoromethyl)phenyl)sulfonyl)oxy)imino)malonate (47b)



47b

Yield: 76%

Physical State: white solid (m.p. = 73 – 78 °C);

R_f = 0.29 (10% EtOAc/hexanes);

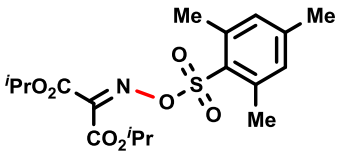
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 5.26 (hept, *J* = 6.2 Hz, 1H), 5.13 (hept, *J* = 6.2 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 6H), 1.29 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.2, 156.9, 151.0, 137.7, 136.5, 136.3, 136.1, 135.9, 129.7, 126.37, 126.35, 125.6, 123.8, 121.9, 120.1, 72.1, 72.0, 21.4, 21.3;

^{19}F NMR (471 MHz, $CDCl_3$): δ –63.4 (s);

HRMS (ESI-TOF): calc'd for $C_{16}H_{18}F_3NO_7S$ $[M+Na]^+$ 448.0648; found 448.0663.

Diisopropyl 2-(((mesitylsulfonyl)oxy)imino)malonate (47c)



47c

Yield: 74%

Physical State: white solid (m.p. 73 – 78 °C);

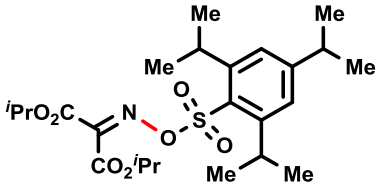
R_f = 0.48 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.99 (s, 2H), 5.27 (hept, *J* = 6.3 Hz, 1H), 5.10 (hept, *J* = 6.2 Hz, 1H), 2.64 (s, 6H), 2.32 (s, 3H), 1.35 (d, *J* = 6.3 Hz, 6H), 1.27 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 157.5, 149.5, 144.5, 141.4, 131.8, 129.3, 71.7, 71.6, 22.7, 21.5, 21.4, 21.1;

HRMS (ESI-TOF): calc'd for $C_{18}H_{25}NO_7S$ $[M+H]^+$ 400.1424; found 400.1315.

Diisopropyl 2-((((2,4,6-triisopropylphenyl)sulfonyl)oxy)imino)malonate (47d)



47d

Yield: 85%

Physical State: white solid (m.p. 74 – 78 °C);

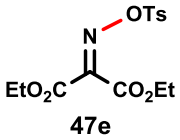
R_f = 0.37 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (s, 2H), 5.28 (p, *J* = 6.2 Hz, 1H), 5.11 (p, *J* = 6.3 Hz, 1H), 4.12 (hept, *J* = 6.8 Hz, 2H), 2.92 (p, *J* = 6.9 Hz, 1H), 1.36 (d, *J* = 6.4 Hz, 6H), 1.27 (t, *J* = 5.2 Hz, 24H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.8, 157.7, 154.8, 152.2, 149.3, 128.0, 124.0, 71.69, 71.68, 34.2, 29.9, 24.6, 23.4, 21.5, 21.4;

HRMS (ESI-TOF): calc'd for $C_{24}H_{37}NO_7S$ $[M+H]^+$ 484.2363; found 484.2349.

Diethyl 2-((tosyloxy)imino)malonate (47e)



47e

Yield: 72%

Physical State: white solid (m.p. 63 – 68 °C);

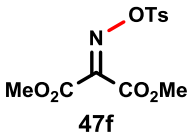
R_f = 0.44 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.33 (dt, *J* = 20.1, 7.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.99, 157.95, 149.7, 146.2, 131.1, 129.8, 129.1, 63.4, 63.2, 21.7, 13.9, 13.8;

HRMS (ESI-TOF): calc'd for $C_{14}H_{17}NO_7S$ $[M+H]^+$ 344.0798 $[M+Na]^+$ 366.0618; found 344.0799, 366.0623.

Dimethyl 2-((tosyloxy)imino)malonate (47f)



47f

Yield: 83%

Physical State: off-white solid (m.p. 91 – 96 °C);

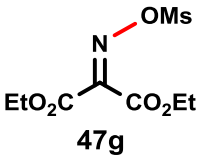
R_f = 0.21 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.4, 158.3, 149.1, 146.3, 130.9, 129.9, 129.1, 53.8, 53.6, 21.7;

HRMS (ESI-TOF): calc'd for $C_{12}H_{13}NO_7S$ $[M+H]^+$ 316.0485 $[M+Na]^+$ 338.0305; found 316.0482, 338.0317.

Diethyl 2-(((methylsulfonyl)oxy)imino)malonate (47g)



47g

Yield: 82%

Physical State: white solid (m.p. = 52 – 56 °C);

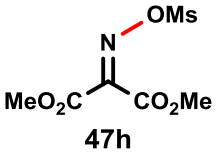
R_f = 0.21 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.38 (dq, *J* = 14.5, 7.1 Hz, 4H), 3.22 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 157.6, 150.2, 63.6, 63.4, 36.9, 13.77, 13.75;

HRMS (CI-TOF): calc'd for $C_8H_{13}NO_7S$ $[M+H]^+$ 268.0491; found 268.0486.

Dimethyl 2-(((methylsulfonyl)oxy)imino)malonate (47h)



47h

Yield: 93%

Physical State: off-white solid (m.p. = 68 – 73 °C);

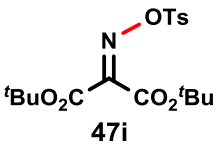
R_f = 0.20 (30% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.91 (d, *J* = 7.8 Hz, 6H), 3.22 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.1, 157.9, 149.6, 53.9, 53.6, 36.9;

HRMS (CI-TOF): calc'd for $C_6H_9NO_7S$ $[M+H]^+$ 240.0178; found 240.0176.

Di-*tert*-butyl 2-((tosyloxy)imino)malonate (47i)



47i

Yield: 79%

Physical State: white solid (m.p. 72 – 77 °C);

R_f = 0.43 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H), 1.51 (s, 9H), 1.46 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.1, 156.4, 151.1, 145.9, 131.1, 129.6, 128.9, 85.8, 85.2, 27.7, 27.5, 21.5;

HRMS (ESI-TOF): calc'd for $C_{18}H_{25}NO_7S$ $[M+Na]^+$ 422.1244; found 422.1240.

10. Preparation of diisopropyl and diethyl iminomalonates (51a-v)

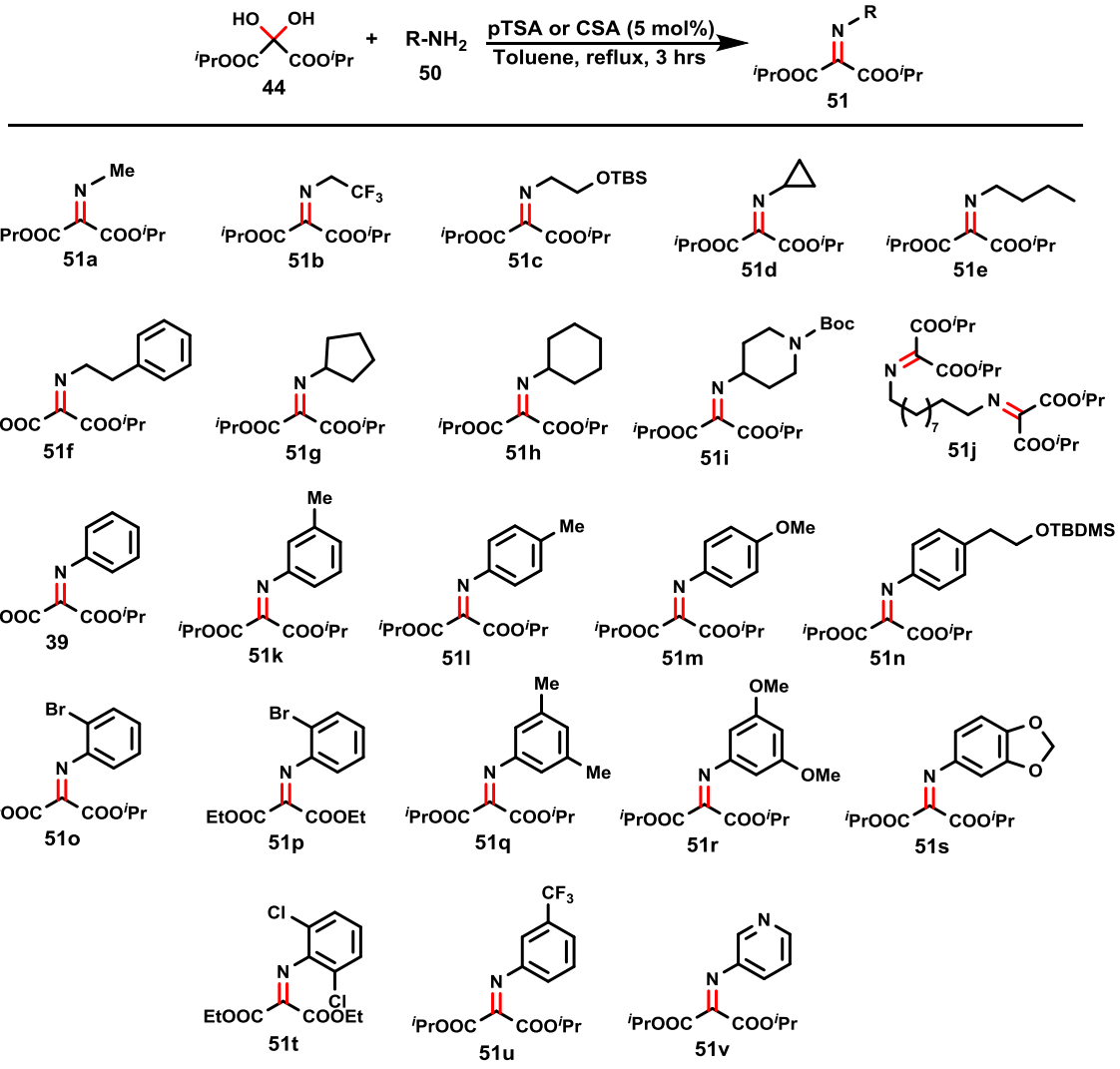


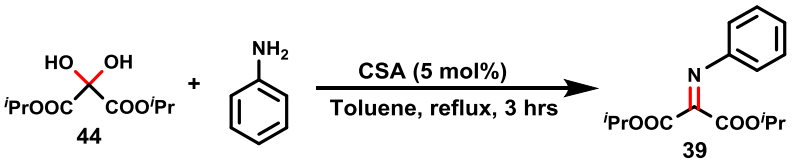
Table S4. List of diisopropyl and diethyl iminomalonates

Standard procedure for the preparation of iminomalonates presented above

Diisopropyl 2,2-dihydroxymalonate **44** (1 equiv) was taken in a flame dried flask and to this aliphatic or aromatic amine (1 equiv) was added followed by pTSA or CSA (5 mol%). To this mixture 5 Å molecular sieves were added followed by dry toluene (0.2 M) and heated to reflux using a Dean-Stark adapter for 3 h. Progress of the reaction was monitored by TLC. After confirming the completion of the reaction, heating was stopped and the reaction mixture was allowed to cool to room temperature. Toluene was removed under reduced pressure and the crude product was purified by column chromatography.

Note: One can use either pTSA or CSA and both are equally efficient in catalyzing the imine-formation reaction. The reaction also proceeds in the absence of catalyst but it takes twice as long. It is always better to purify the crude imine immediately after the reaction in order to obtain better yields. The imines are stable for 3 to 4 days in the freezer (–20 ^{o}C). Aliphatic imines are generally more stable and can be stored for longer periods of time compared to aromatic imines. All the above mentioned imines (**39** to **51v**) were prepared according to this standard procedure.

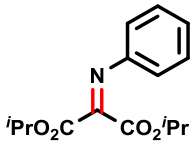
General procedure for the synthesis of diisopropyl 2-(phenylimino)malonate (39)



Diisopropyl 2,2-dihydroxymalonate **44** (500 mg, 2.27 mmol, 1 equiv) was taken in a flame dried flask and to this aniline (0.20 mL, 2.27 mmol, 1 equiv) was added followed by camphor sulfonic acid (CSA) (26.4 mg, 5 mol%). To this mixture 5 Å molecular sieves were added followed by dry toluene (0.2 M, 11.4 mL) and heated to reflux using a Dean-Stark adapter for 3 h or until the complete consumption of the starting material. Progress of the reaction was monitored TLC. After confirming the completion of the reaction, heating was stopped and the reaction mixture was allowed to cool to room temperature. Toluene was removed under reduced pressure and the crude product was purified by column chromatography to afford **39** as yellow viscous oil (420 mg, 67%).

11. Characterization data of the iminomalonate substrates (as displayed in Table S4)

1. Diisopropyl 2-(phenylimino)malonate (39)



39

Standard procedure described above was followed for converting 4.54 mmol of **44** and aniline to **39**

Yield: 67%

Physical State: yellow colored viscous oily liquid;

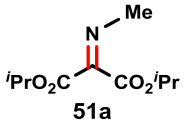
R_f = 0.37 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 5.18 (hept, *J* = 6.2 Hz, 1H), 4.94 (hept, *J* = 6.2 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 6H), 0.99 (d, *J* = 6.5 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.6, 160.1, 153.0, 147.5, 128.4, 126.1, 119.1, 70.6, 69.8, 21.2, 20.9;

HRMS (CI-TOF): calc'd for $C_{15}H_{19}NO_4$ $[M]^+$ 277.1314; found 277.1314.

2. Diisopropyl 2-(methylimino)malonate (51a)



51a

Standard procedure described above was followed for converting 9.08 mmol of **44** and methyl amine to **51a**.

Yield: 33%

Physical State: pale yellow colored oily liquid;

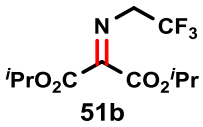
R_f = 0.26 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.02 (hept, *J* = 6.4 Hz, 1H), 4.96 (hept, *J* = 6.4 Hz, 1H), 3.25 (s, 3H), 1.11 (dd, *J* = 8.1, 6.4 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.0, 159.8, 155.0, 69.7, 69.4, 41.5, 21.0, 20.9;

HRMS (ESI-TOF): calc'd for $C_{10}H_{17}NO_4$ $[M+H]^+$ 216.1230; found 216.1233.

3. Diisopropyl 2-((2,2,2-trifluoroethyl)imino)malonate (51b)



51b

Standard procedure described above was followed for converting 2.27 mmol of **44** and trifluoroethyl amine to **51b**.

Yield: 42%

Physical State: pale beige colored oily liquid;

R_f = 0.19 (10% EtOAc/hexanes);

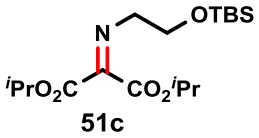
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.21 (dhept, *J* = 18.7, 6.1 Hz, 2H), 4.20 (q, *J* = 9.1 Hz, 2H), 1.33 (dd, *J* = 6.2, 2.0 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.5, 159.4, 157.2, 126.6, 124.7, 122.9, 121.1, 71.1, 71.0, 55.2, 55.0, 54.7, 54.5, 21.5, 21.4;

^{19}F NMR (471 MHz, $CDCl_3$): δ -70.44 (d, *J* = 7.5 Hz);

HRMS (ESI-TOF): calc'd for $C_{11}H_{16}F_3NO_4$ $[M+Na]^+$ 306.0924; found 306.0939.

4. Diisopropyl 2-((2-((*tert*-butyldimethylsilyl)oxy)ethyl)imino)malonate (51c)



51c

Standard procedure described above was followed for converting 3.80 mmol of **44** and TBDMS protected ethanolamine to **51c**.

Yield: 26%

Physical State: pale yellow colored oily liquid;

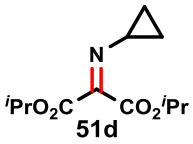
R_f = 0.34 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.19 (dp, *J* = 29.1, 6.3 Hz, 2H), 3.92 (t, *J* = 6.1 Hz, 2H), 3.70 (t, *J* = 6.1 Hz, 2H), 1.32 – 1.28 (m, 12H), 0.84 (s, 9H), 0.02 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.6, 160.5, 154.9, 70.3, 70.0, 62.1, 57.4, 25.7, 21.59, 21.50, 18.2, –5.3;

HRMS (CI-TOF): calc'd for $C_{17}H_{33}NO_5Si$ $[M+H]^+$ 360.2206; found 360.2208.

5. Diisopropyl 2-(cyclopropylimino)malonate (51d)



Standard procedure described above was followed for converting 2.27 mmol of **44** and cyclopropyl amine to **51d**.

Yield: 94%

Physical State: colorless viscous oily liquid;

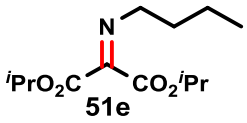
R_f = 0.41 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.22 (hept, *J* = 6.3 Hz, 1H), 5.13 (hept, *J* = 6.3 Hz, 1H), 3.13 (tt, *J* = 6.5, 3.1 Hz, 1H), 1.30 (d, *J* = 6.3 Hz, 6H), 1.26 (d, *J* = 6.3 Hz, 6H), 1.18 (p, J = 4.2, 3.5 Hz, 2H), 1.10 (dt, *J* = 6.6, 3.6 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.2, 160.5, 151.7, 69.9, 69.7, 37.3, 21.5, 21.4, 11.8;

HRMS (ESI-TOF): calc'd for $C_{12}H_{19}NO_4$ $[M+H]^+$ 242.1387; found 242.1343.

6. Diisopropyl 2-(butylimino)malonate (51e)



Standard procedure described above was followed for converting 4.54 mmol of **44** and n-butyl amine to **51e**.

Yield: 53%

Physical State: colorless oily liquid;

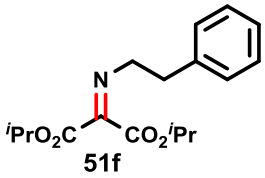
R_f = 0.45 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.22 (dq, *J* = 12.6, 6.1 Hz, 1H), 5.16 (dq, *J* = 12.4, 6.2 Hz, 1H), 3.55 (t, *J* = 7.1 Hz, 2H), 1.68 (p, *J* = 7.2 Hz, 2H), 1.38 – 1.25 (m, 14H), 0.89 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1, 160.4, 153.9, 70.3, 69.9, 55.2, 31.8, 21.5, 21.4, 20.4, 13.6;

HRMS (ESI-TOF): calc'd for $C_{13}H_{23}NO_4$ $[M+H]^+$ 258.1700; found 258.1702.

7. Diisopropyl 2-(phenethylimino)malonate (51f)



51f

Standard procedure described above was followed for converting 4.54 mmol of **44** and phenethyl amine to **51f**.

Yield: 77%

Physical State: pale yellow colored oily liquid;

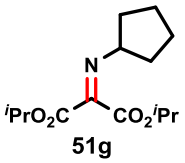
R_f = 0.32 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 9.5, 5.6 Hz, 2H), 7.19 – 7.14 (m, 3H), 5.18 (pd, *J* = 6.3, 2.5 Hz, 2H), 4.01 – 3.69 (m, 2H), 3.15 – 2.88 (m, 2H), 1.28 (dd, *J* = 22.7, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.5, 160.2, 154.1, 138.6, 128.4, 128.2, 126.1, 70.2, 69.8, 56.8, 36.1, 21.3, 21.3;

HRMS (CI-TOF): calc'd for $C_{17}H_{23}NO_4$ $[M+H]^+$ 306.1705; found 306.1711.

8. Diisopropyl 2-(cyclopentylimino)malonate (51g)



51g

Standard procedure described above was followed for converting 4.54 mmol of **44** and cyclopentyl amine to **51g**.

Yield: 84%

Physical State: pale yellow colored oily liquid;

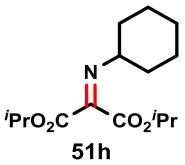
R_f = 0.43 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.04 (ddt, *J* = 39.8, 12.1, 6.0 Hz, 2H), 3.98 – 3.44 (m, 1H), 1.76 – 1.64 (m, 4H), 1.58 (dq, *J* = 14.2, 8.1, 7.4 Hz, 2H), 1.47 (t, *J* = 5.8 Hz, 2H), 1.16 (dd, *J* = 10.8, 6.5 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.0, 160.0, 151.8, 69.7, 69.3, 65.0, 33.8, 24.5, 21.2, 21.1;

HRMS (ESI-TOF): calc'd for $C_{14}H_{23}NO_4$ $[M+H]^+$ 270.1700; found 270.1712.

9. Diisopropyl 2-(cyclohexylimino)malonate (51h)



51h

Standard procedure described above was followed for converting 2.27 mmol of **44** and cyclohexyl amine to **51h**.

Yield: 66%

Physical State: pale yellow colored oily liquid;

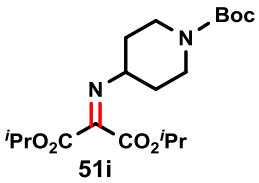
R_f = 0.36 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.24 (hept, *J* = 6.1 Hz, 1H), 5.18 (hept, *J* = 6.2 Hz, 1H), 3.33 (tt, *J* = 10.1, 4.0 Hz, 1H), 1.79 (d, *J* = 12.5 Hz, 2H), 1.68 (d, *J* = 10.7 Hz, 2H), 1.65 – 1.55 (m, 3H), 1.31 (t, *J* = 6.5 Hz, 12H), 1.23 (dq, *J* = 24.4, 12.3, 11.8 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.6, 160.5, 152.1, 70.3, 69.7, 64.6, 32.8, 25.1, 24.1, 21.6, 21.5;

HRMS (ESI-TOF): calc'd for $C_{15}H_{25}NO_4$ $[M+H]^+$ 284.1856; found 284.1869.

10. Diisopropyl 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)imino)malonate (51i)



51i

Standard procedure described above was followed for converting 4.54 mmol of **44** and boc protected 4-piperidinyl amine to **51i**.

Yield: 82%

Physical State: colorless oily liquid;

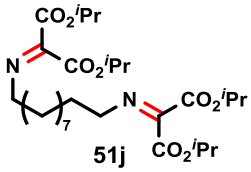
R_f = 0.57 (30% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.02 (hept, *J* = 6.0 Hz, 1H), 4.94 (hept, *J* = 6.1 Hz, 1H), 3.82 (s, 2H), 3.34 (dt, *J* = 9.4, 5.0 Hz, 1H), 2.67 (s, 2H), 1.57 – 1.49 (m, 2H), 1.45 (d, *J* = 10.2 Hz, 2H), 1.22 (s, 9H), 1.09 (dd, *J* = 9.0, 6.4 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.3, 159.7, 154.0, 152.5, 78.8, 69.8, 69.5, 61.3, 31.3, 27.8, 21.0, 20.9;

HRMS (ESI-TOF): calc'd for $C_{19}H_{32}N_2O_6$ $[M+Na]^+$ 407.2153; found 407.2168.

11. Tetraisopropyl 2,2'-(decane-1,10-diylbis(azanylylidene))dimalonate (51j)



51j

Standard procedure described above was followed for converting 8.0 mmol of **44** and 1,10-diaminodecane to **51j**.

Yield: 79%

Physical State: colorless oily liquid;

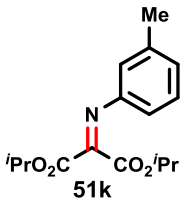
R_f = 0.27 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.29 – 5.09 (m, 4H), 3.54 (t, *J* = 7.2 Hz, 4H), 1.68 (p, *J* = 7.0 Hz, 4H), 1.29 (dd, *J* = 6.3, 2.8 Hz, 26H), 1.24 (d, *J* = 6.6 Hz, 10H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1, 160.4, 153.8, 70.3, 69.8, 55.5, 29.8, 29.3, 29.1, 27.2, 21.58, 21.50;

HRMS (ESI-TOF): calc'd for $C_{28}H_{48}N_2O_8$ $[M+Na]^+$ 563.3303; found 563.3317.

12. Diisopropyl 2-(*m*-tolylimino)malonate (51k)



51k

Standard procedure described above was followed for converting 4.54 mmol of **44** and m-toulidine to **51k**.

Yield: 72%

Physical State: yellow colored oily liquid;

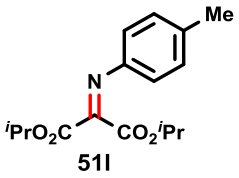
R_f = 0.41 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.25 (hept, *J* = 6.3 Hz, 1H), 5.04 (hept, *J* = 6.3 Hz, 1H), 2.30 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 6H), 1.09 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.0, 160.4, 152.9, 147.7, 138.5, 128.5, 127.2, 119.9, 116.5, 70.8, 70.0, 21.5, 21.2, 21.1;

HRMS (ESI-TOF): calc'd for $C_{16}H_{21}NO_4$ $[M+H]^+$ 292.1543; found 292.1556.

13. Diisopropyl 2-(*p*-tolylimino)malonate (51l)



51l

Standard procedure described above was followed for converting 2.27 mmol of **44** and p-toulidine to **51l**.

Yield: 78%

Physical State: yellow colored oily liquid;

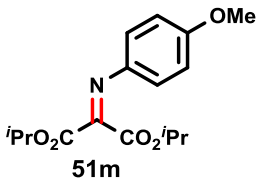
R_f = 0.40 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 2H), 5.15 (dt, *J* = 12.3, 6.1 Hz, 1H), 4.97 (dt, *J* = 12.4, 6.1 Hz, 1H), 2.21 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 6H), 1.02 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.9, 160.1, 152.2, 144.9, 136.3, 129.0, 119.5, 70.4, 69.7, 21.2, 20.9, 20.6;

HRMS (CI-TOF): calc'd for $C_{16}H_{21}NO_4$ $[M]^+$ 291.1471; found 291.1468.

14. Diisopropyl 2-((4-methoxyphenyl)imino)malonate (51m)



51m

Standard procedure described above was followed for converting 2.27 mmol of **44** and p-anisidine to **51m**.

Yield: 87%

Physical State: dark yellow colored viscous oily liquid;

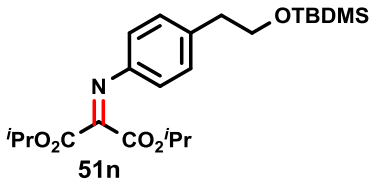
R_f = 0.35 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.03 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.23 (hept, *J* = 6.3 Hz, 1H), 5.10 (hept, *J* = 6.3 Hz, 1H), 3.76 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 6H), 1.14 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8, 160.5, 158.9, 151.1, 140.4, 122.3, 113.9, 70.6, 70.0, 55.3, 21.5, 21.2.

HRMS (ESI-TOF): calc'd for $C_{14}H_{18}N_2O_4$ $[M+H]^+$ 308.1492; found 308.1443.

15. Diisopropyl 2-((4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenyl)imino) malonate (51n)



51n

Standard procedure described above was followed for converting 3.80 mmol of **44** and 4-(2-((tert-butyldimethylsilyl)oxy)ethyl)aniline to **51n**.

Yield: 54%

Physical State: dark yellow colored oily liquid;

R_f = 0.39 (10% EtOAc/hexanes);

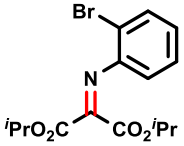
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.23 (hept, *J* = 6.2 Hz, 1H), 5.03 (hept, *J* = 6.3 Hz, 1H), 3.74 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* =

6.7 Hz, 2H), 1.34 (d, *J* = 6.4 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 6H), 0.82 (s, 9H), -0.08 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1, 160.3, 152.6, 145.7, 138.0, 129.4, 119.6, 70.7, 69.9, 64.0, 38.9, 25.7, 21.4, 21.2, 18.1, –5.5;

HRMS (ESI-TOF): calc'd for $C_{23}H_{37}NO_5Si$ $[M+H]^+$ 436.2514; found 436.2541.

16. Diisopropyl 2-((2-bromophenyl)imino)malonate (51o)



51o

Standard procedure described above was followed for converting 4.54 mmol of **44** and 2-bromo aniline to **51o**.

Yield: 52%

Physical State: pale yellow colored oily liquid;

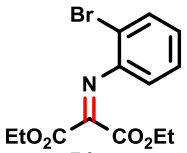
R_f = 0.35 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 6.99 (td, *J* = 7.8, 1.5 Hz, 1H), 6.74 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.24 (hept, *J* = 6.3 Hz, 1H), 4.94 (hept, *J* = 6.3 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 6H), 1.01 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.4, 160.0, 154.3, 146.8, 132.6, 127.4, 126.8, 118.6, 113.7, 71.0, 70.3, 21.4, 21.0;

HRMS (CI-TOF): calc'd for $C_{15}H_{18}BrNO_4$ $[M+H]^+$ 357.0399; found 357.0390.

17. Diethyl 2-((2-bromophenyl)imino)malonate (51p)



51p

Standard procedure described above was followed for converting 4.35 mmol of diethylketomalonate and 2-bromo aniline to **51p**.

Yield: 79%

Physical State: yellow colored oily liquid;

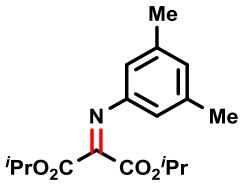
R_f = 0.50 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.19 (td, *J* = 7.7, 1.1 Hz, 1H), 6.99 (td, *J* = 7.9, 1.4 Hz, 1H), 6.76 – 6.69 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.7, 160.4, 153.5, 146.5, 132.6, 127.5, 127.0, 118.4, 113.7, 62.8, 61.9, 13.7, 13.4;

HRMS (ESI-TOF): calc'd for $C_{13}H_{14}BrNO_4$ $[M+H]^+$ 328.0179; found 328.0179.

18. Diisopropyl 2-((3,5-dimethylphenyl)imino)malonate (51q)



51q

Standard procedure described above was followed for converting 4.54 mmol of **44** and 3,5-dimethyl aniline to **51q**

Yield: 66%

Physical State: yellow colored oily liquid;

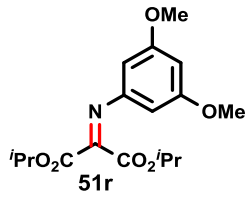
R_f = 0.40 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.80 (s, 1H), 6.59 (s, 2H), 5.24 (hept, *J* = 6.3 Hz, 1H), 5.05 (hept, *J* = 6.3 Hz, 1H), 2.25 (s, 6H), 1.35 (d, *J* = 6.3 Hz, 6H), 1.11 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.0, 160.4, 152.6, 147.6, 138.3, 128.1, 117.1, 70.7, 69.9, 21.4, 21.1, 21.0;

HRMS (ESI-TOF): calc'd for $C_{17}H_{23}NO_4$ $[M+H]^+$ 306.1700; found 306.1789.

19. Diisopropyl 2-((3,5-dimethoxyphenyl)imino)malonate (51r)



51r

Standard procedure described above was followed for converting 2.27 mmol of **44** and 3,5-dimethoxy aniline to **51r**

Yield: 23%

Physical State: dark yellow colored viscous oily liquid;

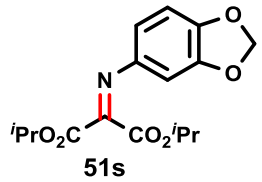
R_f = 0.38 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.21 (s, 1H), 6.06 (d, *J* = 2.0 Hz, 2H), 5.17 (hept, *J* = 6.2 Hz, 1H), 4.99 (hept, *J* = 6.2 Hz, 1H), 3.65 (s, 6H); 1.29 (d, *J* = 6.3 Hz, 6H), 1.05 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.6, 160.7, 160.0, 153.1, 149.3, 98.3, 97.5, 70.7, 70.0, 55.0, 21.3, 21.2, 21.0;

HRMS (ESI-TOF): calc'd for $C_{17}H_{23}NO_6$ $[M+Na]^+$ 360.1418; found 360.1418.

20. Diisopropyl 2-(benzo[*d*][1,3]dioxol-5-ylimino)malonate (51s)



51s

Standard procedure described above was followed for converting 4.54 mmol of **44** and 3,4-methylenedioxy)aniline to **51s**

Yield: 73%

Physical State: dark yellow colored oily liquid;

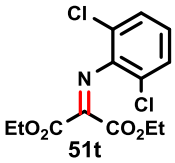
R_f = 0.24 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.72 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 2.1 Hz, 1H), 6.53 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.93 (s, 2H), 5.22 (hept, *J* = 6.3 Hz, 1H), 5.11 (hept, *J* = 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H), 1.16 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.5, 160.4, 151.6, 147.9, 146.8, 141.7, 114.2, 107.9, 102.2, 101.5, 70.7, 70.1, 21.4, 21.2;

HRMS (CI-TOF): calc'd for $C_{16}H_{19}NO_6$ $[M]^+$ 321.1212; found 321.1208.

21. Diethyl 2-((2,6-dichlorophenyl)imino)malonate (51t)



51t

Standard procedure described above was followed for converting 5.74 mmol of diethylketomalonate and 2,6-dichloro aniline to **51t**.

Yield: 83%

Physical State: yellow colored oily liquid;

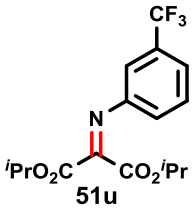
R_f = 0.45 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 8.1 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.8, 159.0, 155.7, 143.2, 127.8, 125.7, 123.0, 63.1, 62.4, 13.9, 13.4;

HRMS (ESI-TOF): calc'd for $C_{13}H_{13}Cl_2NO_4$ $[M+H]^+$ 318.0294; found 318.0294.

22. Diisopropyl 2-((3-(trifluoromethyl)phenyl)imino)malonate (51u)



51u

Standard procedure described above was followed for converting 2.27 mmol of **44** and m-trifluoromethyl aniline to **51u**

Yield: 81%

Physical State: yellow colored oily liquid;

R_f = 0.36 (10% EtOAc/hexanes);

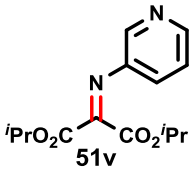
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 2H), 7.09 (s, 1H), 7.05 – 7.01 (m, 1H), 5.14 (hept, *J* = 6.3 Hz, 1H), 4.90 (hept, *J* = 6.2 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 6H), 0.95 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.8, 159.7, 154.4, 148.0, 131.3, 131.1, 130.9, 130.6, 129.2, 126.0, 124.2, 122.5, 120.6, 115.73, 115.70, 115.68, 115.65, 70.9, 70.3, 21.0, 20.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ –61.9 (s);

HRMS (ESI-TOF): calc'd for $C_{16}H_{18}F_3NO_4$ $[M+H]^+$ 346.1261; found 346.1261.

23. Diisopropyl 2-(pyridin-3-ylimino)malonate (51v)



51v

Standard procedure described above was followed for converting 4.54 mmol of **44** and 3-aminopyridine to **51v.**

Yield: 86%

Physical State: yellow colored oily liquid;

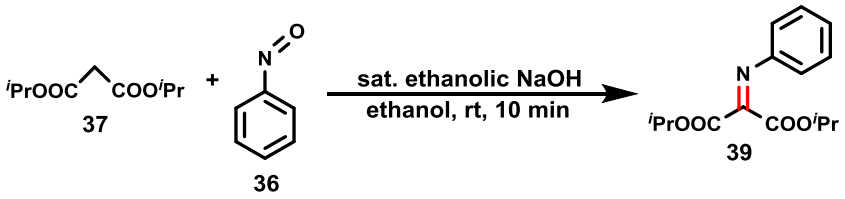
R_f = 0.28 (30% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 7.29 – 7.21 (m, 2H), 5.21 (hept, *J* = 6.3 Hz, 1H), 4.99 (hept, *J* = 6.3 Hz, 1H), 1.32 (d, *J* = 6.4 Hz, 6H), 1.04 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.9, 159.7, 154.7, 147.4, 143.7, 139.8, 126.7, 123.1, 71.2, 70.6, 21.3, 21.1;

HRMS (ESI-TOF): calc'd for $C_{14}H_{18}N_2O_4$ $[M+H]^+$ 279.1339; found 279.1336.

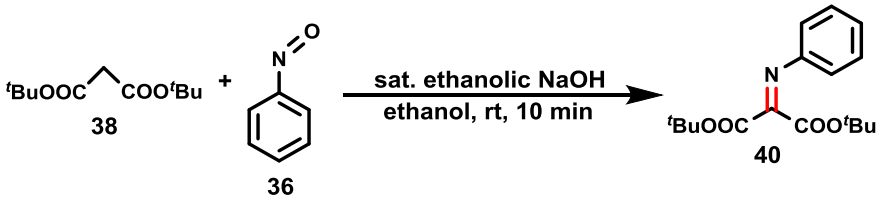
12(a). Procedure for the synthesis of 39 using nitroso benzene (This procedure was adapted from literature reported procedure)[4]



To a solution of diisopropyl malonate (500 mg, 2.65 mmol, 1 equiv) and nitroso benzene (313 mg, 2.92 mmol, 1 equiv) in absolute ethanol (1.25 mL, 2.2M), a saturated ethanolic solution of NaOH was added dropwise until the blue color of the solution turns pale brown. The reaction mixture was allowed to stir for 10 minutes and the solvent was removed under reduced pressure and the crude product was purified by column chromatography to afford **39** as viscous yellow colored oily liquid (492 mg, 67%).

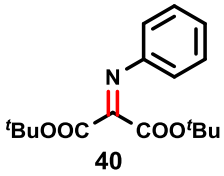
Note: The crude imine prepared by this method is very unstable and should be used immediately.

12(b). Procedure for the synthesis of 40 using nitroso benzene



The procedure described above for the synthesis of **39** was followed for converting 9.24 mmol of **38** to **40** as an yellow colored waxy solid (1.83g, 65%).

1. Characterization data of di-*tert*-butyl 2-(phenylimino)malonate (40)



Yield: 65%

Physical State: yellow colored waxy solid;

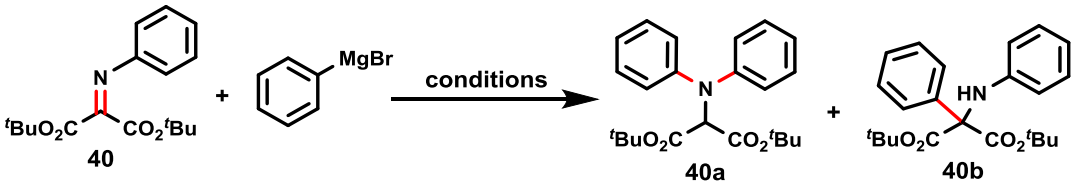
R_f = 0.28 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 1.59 (s, 9H), 1.29 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.6, 159.9, 154.6, 148.1, 128.6, 126.0, 119.4, 84.1, 27.9, 27.6;

HRMS (ESI-TOF): calc'd for $C_{17}H_{23}NO_4$ $[M+Na]^+$ 328.1519; found 328.1525.

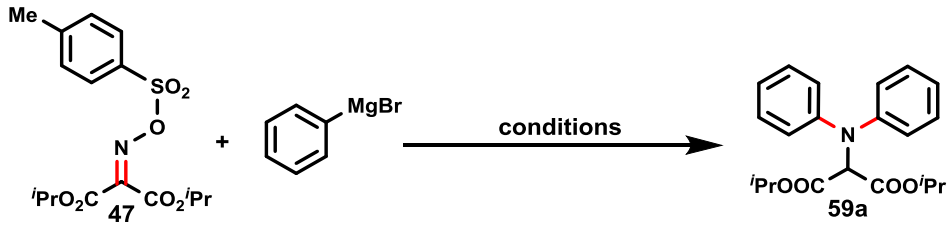
13. Screening of solvents for the amination using 40



Entry	Solvent (M)	PhMgBr (M)	Temperature (°C)	Time	Yield (%) (40a:40b)
1	DCM (0.1M)	0.84M in THF	–78 °C	1h	53:32
2	DME (0.1M)	0.84M in THF	–78 °C	1h	64:13
3	MTBE (0.1M)	0.84M in THF	–78 °C	1h	59:14
4	THF (0.1M)	1M in THF	–78 °C	1h	67:12
5	2-Me-THF (0.1M)	1M in THF	–78 °C	1h	56:10
6	Et_2O (0.1M)	1M in THF	–78 °C	1h	51:6

Table S5. Optimization of solvents for amination using 40

14. Optimization of the reaction conditions for amination using 47

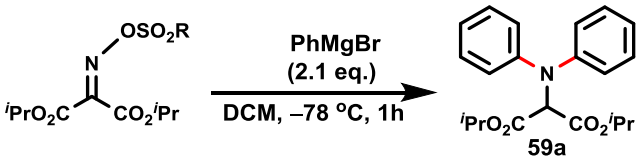


Entry	Solvent (M)	PhMgBr (M)	Temperature (°C)	Time	Yield (%)
1	THF (0.2M)	0.7M in THF	–78 °C	10 min	22
2	DCM (0.2M)	0.7M in THF	–78 °C (3h) to RT	Overnight	61
3	DME (0.2M)	0.76M in THF	–78 °C	3h	24

4	Et_2O (0.2M)	0.88M in THF	–78 °C	3h	(Starting material was not totally consumed)
5	DCE (0.2M)	0.26M in THF	–78 °C (3h) to RT	Overnight	22
6	Toluene (0.2M)	0.26M in THF	–78 °C (3h) to RT	Overnight	31
7	DCM (0.2M)	0.6M in THF	–78 °C	1h	30
8	DCE (0.2M)	0.6M in THF	–78 °C	1h	13
9	Toluene (0.2M)	0.6M in THF	–78 °C	1h	42
10	Toluene (0.2M)	0.74M in THF	–42 °C	1h 15min	45
11	DCM (0.2 M)	0.74M in THF	–42 °C	1h 15min	56
12	DCM (0.2M)	0.76M in THF	–78 °C	1h	63
13	**DCM (0.1M)**	**0.76M in THF**	**–78 °C**	**1h**	**75**
14	DCM (0.1M)	0.76M in THF	–42 °C	1h	63
15	DCM (0.1M)	1.6M in Et_2O	–78 °C	1h	(Reaction was messy with lot of spots on TLC)
16	DCM (0.05M)	1.6M in Et_2O	–78 °C	1h	(Reaction was messy with lot of spots on TLC)
17	DCM (0.1M)	0.66M in THF	–78 °C	1h	66
18	DCM (0.05M)	0.66M in THF	–78 °C	1h	66
19	DCM (0.1M)	0.88M in THF	–20 °C	1h	62
20	DCM (0.1M)	0.88M in THF	0 °C	1h	58
21	DCM (0.1M)	0.88M in THF	RT	1h	58

Table S6. Optimization of conditions for amination

15. Screening of different activating groups



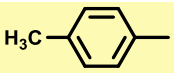
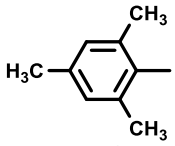
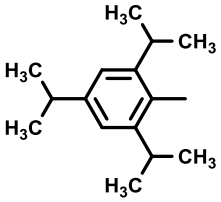
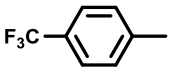
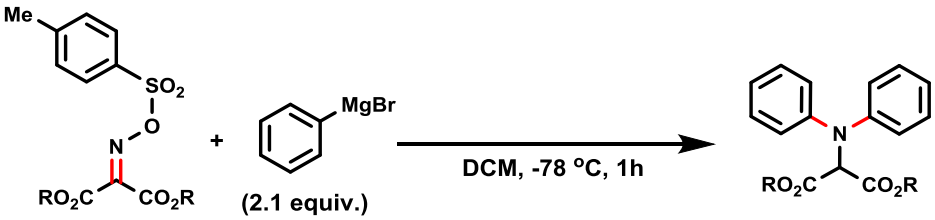
Entry	R	Yield(%)
1	—CH_3	68%
2		75%
3		67%
4		60%
5		62%

Table S7. Evaluation of different activating groups

16. Screening of different aminating agents



Entry	R	Yield (%)
1	Me	63
2	Et	62
3	^{i}Pr	75
4	^{t}Bu	55

Table S8. Evaluation of different aminating agents

17. General experimental procedures (Methods C through H)

Amination of aryl and alkyl metals using doubly electrophilic aminating agent 47

Method C: To a flame dried 25 mL round bottom flask, activated magnesium turnings (7.5 mmol, 1.5 equiv) were added under argon followed by 2.5 mL of anhydrous THF. To this mixture 2 drops of 1,2-dibromoethane were added under constant stirring. After 5 min, a solution of aryl or alkyl bromide (5.0 mmol, 1.0 equiv) in 2.5 mL of anhydrous THF was added dropwise over 10-15 minutes to the suspension. This reaction is slightly exothermic but no external cooling is required. After the flask cools to room temperature by itself, the Grignard reagent is titrated using the standard procedure[5] and the concentration is determined. Next, to a thick-walled flame dried reaction vial, aminating agent **47** (1.0 mmol, 1.0 equiv) followed by anhydrous DCM (10 mL, 0.1M) were added under argon. The resulting solution of **47** was cooled to −78 ^{o}C by means of dry ice/acetone bath and the freshly prepared Grignard reagent (2.1 mmol, 2.1 equiv) was added via syringe over a period of 1 min under constant stirring. After stirring for 1 hour at −78 ^{o}C, the reaction mixture was quenched using saturated NH_4Cl solution (3 mL) and allowed to warm to room temperature.

Workup and purification: After quenching, the reaction mixture was diluted with water (20 mL) and the organic layer was separated. The aqueous layer was then extracted with DCM twice (2 X 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method D: This procedure was adapted from the literature[6]. To a flame dried 25 mL round bottom flask, commercially available iPrMgCl·LiCl solution in THF (1.3M; 1.1 mmol, 1.1 eq) was added under argon. This mixture was cooled to −15 ^{o}C in case of aryl bromides and to −45 ^{o}C in case of aryl iodides and the corresponding solution of aryl bromide or iodide (1.0 mmol, 1.0 equiv) in THF was added in 1 min and stirred for 30 min. This turbo Grignard reagent was then titrated and the concentration was determined. To a thick-walled flame dried reaction vial, aminating agent (1.0 mmol, 1.0 equiv) followed by anhydrous DCM (10 mL, 0.1M) was added under argon. This reaction mixture was cooled to −78 ^{o}C by means of dry ice/acetone bath and the freshly prepared

Grignard reagent (2.1 mmol, 2.1 equiv) was added in 1 min under constant stirring. After stirring for 1 hour at –78 ^{o}C the reaction mixture was quenched using saturated NH_4Cl solution (3 mL) and allowed to warm to room temperature.

Workup and purification: After quenching, the reaction mixture was diluted with water (20 mL) and the organic layer was separated. The aqueous layer was then extracted with DCM twice (2 X 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method E (Amination using *N*-substituted diisopropyl iminomalonates):

To a flame dried 25 mL round bottom flask, activated magnesium turnings (7.5 mmol, 1.5 equiv) were added under argon followed by 2.5 mL of anhydrous THF. To this mixture 2 drops of 1,2-dibromoethane were added under constant stirring. After 5 min, a solution of aryl or alkyl bromide (5.0 mmol, 1.0 equiv) in 2.5 mL of anhydrous THF was added dropwise over 10-15 minutes to the suspension. This reaction is slightly exothermic but no external cooling is required. After the flask cools to room temperature by itself, the Grignard reagent is titrated using the standard procedure[5] and the concentration is determined. For making the turbo Grignard reagent, follow **Mehod D**. To a thick-walled flame dried reaction vial, iminomalonate (1.0 mmol, 1.0 equiv) dissolved in anhydrous DCM (10 mL, 0.1M) was added under argon. This reaction mixture was cooled to –78 ^{o}C by means of dry ice/acetone bath and the freshly prepared Grignard reagent (1.1 mmol, 1.1 equiv) was added over 1 min while mainatining constant stirring. After stirring for 1 hour at –78 ^{o}C the reaction was quenched using saturated NH_4Cl solution (3 mL) and allowed to warm to room temperature.

Workup and purification: After quenching, the reaction mixture was diluted with water (20 mL) and the organic layer was separated. The aqueous layer was then extracted with DCM twice (2 X 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method F: To a thick-walled flame dried reaction vial, iminomalonate (1.0 mmol, 1.0 equiv) dissolved in anhydrous THF (10 mL, 0.1M) was added under argon. This solution was cooled to –78 ^{o}C by means of dry ice/acetone bath and the commercially available

aryl or alkyl lithium solution in THF (1.1 mmol, 1.1 equiv) was added dropwise under constant stirring. After stirring for 1 hour at −78 ^{o}C the reaction was quenched using saturated NH_4Cl solution (3 mL).

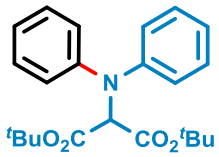
Method G: This procedure was adapted from the literature with slight modifications[7]. In a thick-walled flame dried reaction vial, methyl-2-bromo acetate (2.0 mmol, 2.0 equiv) was taken in anhydrous THF (10 mL, 0.2M) under argon and cooled to −78 ^{o}C using dry ice/acetone bath. To this cooled reaction mixture, commercially available LiHMDS (1M solution in THF) (2.1 mmol, 2.1 equiv) was added dropwise and stirred for 45 min. Then iminomalonate (1.0 mmol, 1.0 equiv) dissolved in anhydrous THF (10 mL, 0.1M) was added slowly dropwise to the enolate solution and continued stirring for 2 h. Then the reaction was quenched using saturated NH_4Cl solution (3 mL).

Workup and purification: After quenching, the reaction mixture was diluted with water (20 mL) and the organic layer was separated. The aqueous layer was then extracted with EtOAc twice (2 X 20 mL) and the combined organic layers were washed with brine (30 mL) once, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method H: In a thick-walled flame dried reaction vial, acetophenone (2.0 mmol, 2.0 equiv) was dissolved in anhydrous THF (5 mL, 0.4M) under argon and cooled to −78 ^{o}C using dry ice/acetone bath. To this cooled reaction mixture, commercially available LiHMDS (1M solution in THF) (2.1 mmol, 2.1 equiv) was added dropwise and stirred for 45 min. Then iminomalonate (1.0 mmol, 1.0 equiv) dissolved in anhydrous THF (5 mL, 0.2M) was added slowly dropwise to the enolate solution and continued stirring for 2 h at −78 ^{o}C. Then the reaction was quenched using saturated NH_4Cl solution (3 mL).

Workup and purification: After quenching, the reaction mixture was diluted with water (20 mL) and the organic layer was separated. The aqueous layer was then extracted with EtOAc twice (2 X 20 mL) and the combined organic layers were washed with brine (30 mL) once, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

18. Characterization data of di-*tert*-butyl 2-(diphenylamino)malonate (40a)



40a

Yield: 67% (**Method E, here THF was used as the solvent instead of DCM**)

Physical State: Brown colored solid (m.p. = 76 – 81 °C);

R_f = 0.53 (9:1 EtOAc : hexanes);

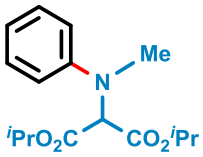
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (ddd, *J* = 7.5, 6.3, 1.8 Hz, 4H), 6.96 (d, *J* = 7.7 Hz, 4H), 6.92 (t, *J* = 7.3 Hz, 2H), 5.12 (s, 1H), 1.26 (s, 18H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.4, 146.2, 129.1, 122.5, 122.2, 82.5, 69.1, 27.7;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4$ $[M+Na]^+$ 406.1989; found 406.1990.

19. Characterization data of the products made using the singly- and doubly-electrophilic aminating agents (as displayed in Figs. 3-5)

1. Diisopropyl 2-(methyl(phenyl)amino)malonate (55a)



55a

Yield: 68% (**Method E**)

Physical State: dark purple colored waxy solid;

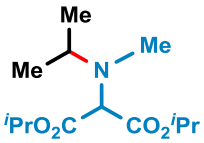
R_f = 0.52 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 2H), 6.86 – 6.80 (m, 3H), 5.16 (hept, *J* = 6.3 Hz, 2H), 5.08 (s, 1H), 3.11 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 149.0, 129.1, 118.3, 113.3, 69.5, 66.1, 35.7, 21.6, 21.5;

HRMS (ESI-TOF): calc'd for $C_{16}H_{23}NO_4$ $[M+H]^+$ 294.1700; found 294.1703.

2. Diisopropyl 2-(isopropyl(methyl)amino)malonate (55b)



55b

Yield: 80% (**Method E**)

Physical State: colorless oily liquid;

R_f = 0.62 (20% EtOAc/hexanes);

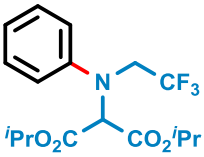
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97 (hept, *J* = 6.3 Hz, 2H), 4.06 (s, 1H), 2.90 (hept, *J* = 6.5 Hz, 1H), 2.37 (s, 3H), 1.15 (d, *J* = 6.4 Hz, 12H), 0.97 (d, *J* = 6.6 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.7, 68.2, 66.8, 52.8, 33.9, 21.29, 21.27, 19.5;

HRMS (ESI-TOF): calc'd for $C_{13}H_{25}NO_4$ $[M+H]^+$ 260.1856; found 260.1846.

Note: For this reaction to form **55b**, directly iPrMgCl·LiCl solution in THF was added on to the imine.

3. Diisopropyl 2-(phenyl(2,2,2-trifluoroethyl)amino)malonate (55c)



55c

Yield: 34% (**Method E**)

Physical State: orange colored waxy solid;

R_f = 0.59 (8:1 EtOAc : hexanes);

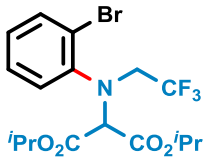
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 5.10 (hept, *J* = 6.2 Hz, 2H), 4.88 (s, 1H), 4.24 – 4.14 (m, 2H), 1.26 (dd, *J* = 16.6, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 148.2, 129.2, 127.8, 125.9, 124.1, 122.2, 121.9, 118.1, 70.1, 68.2, 51.2, 51.0, 50.8, 50.6, 21.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ –69.83 (t, *J* = 8.9 Hz);

HRMS (ESI-TOF): calc'd for $C_{17}H_{22}F_3NO_4$ $[M+H]^+$ 362.1574; found 362.1581.

4. Diisopropyl 2-((2-bromophenyl)(2,2,2-trifluoroethyl)amino)malonate (55d)



55d

Yield: 79% (**Method E**)

Physical State: colorless oily liquid;

R_f = 0.72 (20% EtOAc/hexanes);

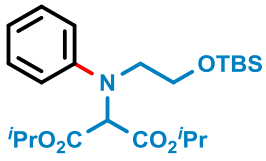
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.17 (m, 2H), 5.99 (d, *J* = 52.9 Hz, 1H), 5.14 (dt, *J* = 12.3, 6.0 Hz, 1H), 5.03 (s, 1H), 4.07 – 3.51 (m, 2H), 1.79 – 0.76 (m, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.2, 155.6, 155.4, 133.6, 133.3, 133.1, 130.7, 130.5, 130.4, 127.5, 126.6, 126.4, 124.8, 124.6, 122.9, 122.7, 121.0, 120.9, 70.5, 69.6, 63.5, 46.5, 46.3, 46.0, 45.8, 22.0, 21.8, 21.7, 21.6, 21.4.

^{19}F NMR (471 MHz, $CDCl_3$): δ –69.5 – –70.2 (m);

HRMS (ESI-TOF): calc'd for $C_{17}H_{21}BrF_3NO_4$ $[M+H]^+$ 440.0679; found 440.0674.

5. Diisopropyl 2-((2-((*tert*-butyldimethylsilyl)oxy)ethyl)(phenyl)amino)malonate (55e)



55e

Yield: 58% (**Method E**)

Physical State: dark yellow colored oily liquid;

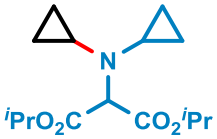
R_f = 0.53 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 5.11 (hept, *J* = 6.2 Hz, 2H), 5.00 (s, 1H), 3.80 (t, *J* = 7.3 Hz, 2H), 3.59 (t, *J* = 7.3 Hz, 2H), 1.27 (dd, *J* = 8.8, 6.3 Hz, 12H), 0.91 (s, 9H), 0.06 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 147.9, 129.0, 118.8, 114.4, 69.5, 67.1, 60.8, 51.6, 25.8, 21.5, 18.2;

HRMS (ESI-TOF): calc'd for $C_{23}H_{39}NO_5Si$ $[M+H]^+$ 438.2670; found 438.3076.

6. Diisopropyl 2-(dicyclopropylamino)malonate (55f)



55f

Yield: 89% (**Method E**)

Physical State: colorless oily liquid;

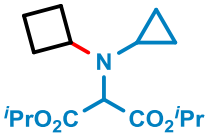
R_f = 0.21 (5% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.00 (hept, *J* = 6.2 Hz, 2H), 4.15 (s, 1H), 2.52 (tt, *J* = 6.8, 3.9 Hz, 2H), 1.18 (dd, *J* = 6.4, 3.2 Hz, 12H), 0.39 (p, *J* = 4.6, 3.8 Hz, 4H), 0.37 – 0.31 (m, 4H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 70.3, 68.4, 34.5, 21.5, 21.4, 6.3;

HRMS (ESI-TOF): calc'd for $C_{15}H_{25}NO_4$ $[M+H]^+$ 284.1856; found 284.1861.

7. Diisopropyl 2-(cyclobutyl(cyclopropyl)amino)malonate (55g)



55g

Yield: 85% (**Method E**)

Physical State: colorless oily liquid;

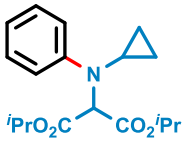
R_f = 0.39 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.00 (hept, *J* = 6.3 Hz, 2H), 4.10 (s, 1H), 3.58 (ddd, *J* = 16.8, 9.4, 7.4 Hz, 1H), 2.29 (tt, *J* = 6.7, 3.9 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.96 – 1.89 (m, 2H), 1.56 – 1.38 (m, 2H), 1.20 (dd, *J* = 6.5, 3.2 Hz, 12H), 0.49 – 0.43 (m, 2H), 0.42 – 0.35 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.7, 68.4, 67.5, 57.4, 30.9, 28.7, 21.47, 21.40, 14.5, 6.5;

HRMS (ESI-TOF): calc'd for $C_{16}H_{27}NO_4$ $[M+H]^+$ 298.2013; found 298.2024.

8. Diisopropyl 2-(cyclopropyl(phenyl)amino)malonate (55h)



55h

Yield: 73% (**Method E**)

Physical State: dark brown colored oily liquid;

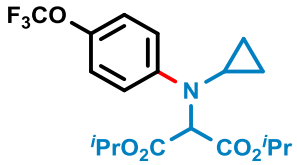
R_f = 0.63 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.11 (hept, *J* = 6.1 Hz, 2H), 4.91 (s, 1H), 2.87 – 2.76 (m, 1H), 1.27 (d, *J* = 6.2 Hz, 6H), 1.23 (d, *J* = 6.2 Hz, 6H), 0.87 – 0.81 (m, 2H), 0.78 (d, *J* = 6.6 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 148.7, 128.6, 118.8, 114.8, 69.5, 69.0, 31.6, 21.6, 21.5, 9.3;

HRMS (ESI-TOF): calc'd for $C_{18}H_{25}NO_4$ $[M+H]^+$ 320.1856; found 320.1865.

9. Diisopropyl 2-(cyclopropyl(4-(trifluoromethoxy)phenyl)amino)malonate (55i)



55i

Yield: 19% (**Method E**)

Physical State: beige colored viscous oily liquid;

R_f = 0.42 (10% EtOAc/hexanes);

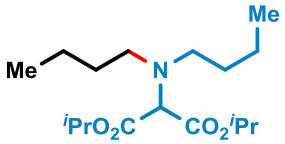
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 5.09 (hept, *J* = 6.3 Hz, 2H), 4.87 (s, 1H), 2.85 – 2.79 (m, 1H), 1.26 (d, *J* = 6.3 Hz, 6H), 1.19 (d, *J* = 6.3 Hz, 6H), 0.83 – 0.76 (m, 4H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 147.3, 141.7, 121.5, 115.6, 69.7, 69.2, 32.5, 21.58, 21.50, 9.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ –58.4 (s);

HRMS (ESI-TOF): calc'd for $C_{19}H_{24}F_3NO_5$ $[M+H]^+$ 404.1679; found 404.1680.

10. Diisopropyl 2-(dibutylamino)malonate (55j)



55j

Yield: 56% (**Method F**)

Physical State: colorless oily liquid;

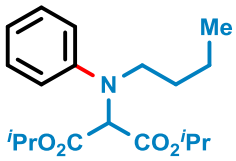
R_f = 0.53 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.06 (hept, *J* = 6.0 Hz, 2H), 4.13 (s, 1H), 2.66 – 2.61 (m, 4H), 1.42 (p, *J* = 7.5 Hz, 4H), 1.28 (dt, *J* = 15.0, 7.4 Hz, 4H), 1.23 (d, *J* = 6.3 Hz, 12H), 0.87 (t, *J* = 7.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.9, 68.6, 67.6, 52.0, 30.7, 21.6, 21.6, 20.2, 13.9;

HRMS (ESI-TOF): calc'd for $C_{17}H_{33}NO_4$ $[M+H]^+$ 316.2482; found 316.2489.

11. Diisopropyl 2-(butyl(phenyl)amino)malonate (55k)



55k

Yield: 94% (**Method E**)

Physical State: dark brown oily liquid;

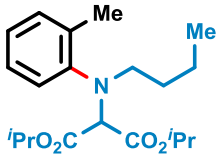
R_f = 0.66 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.85 – 6.78 (m, 3H), 5.12 (hept, *J* = 6.3 Hz, 2H), 4.98 (s, 1H), 3.50 – 3.35 (m, 2H), 1.63 (p, *J* = 7.8 Hz, 2H), 1.35 (h, *J* = 7.4 Hz, 2H), 1.27 (dd, *J* = 11.1, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 147.9, 128.9, 118.5, 114.8, 69.4, 67.3, 49.2, 30.0, 21.5, 20.1, 13.8;

HRMS (ESI-TOF): calc'd for $C_{19}H_{29}NO_4$ $[M+H]^+$ 336.2169; found 336.2180.

12. Diisopropyl 2-(butyl(*o*-tolyl)amino)malonate (55l)



55l

Yield: 83% (**Method E**)

Physical State: colorless oily liquid;

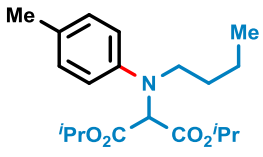
R_f = 0.51 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 5.10 (hept, *J* = 6.2 Hz, 2H), 4.27 (s, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 3H), 1.30 (dd, *J* = 14.7, 5.2 Hz, 4H), 1.25 (dd, *J* = 8.1, 6.4 Hz, 12H), 0.82 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 147.3, 134.8, 130.8, 125.8, 124.1, 124.0, 69.8, 68.5, 48.3, 30.4, 21.4, 21.3, 19.9, 17.6, 13.7;

HRMS (ESI-TOF): calc'd for $C_{20}H_{31}NO_4$ $[M+H]^+$ 350.2326; found 350.2388.

13. Diisopropyl 2-(butyl(*p*-tolyl)amino)malonate (55m)



55m

Yield: 94% (**Method E**)

Physical State: brown colored viscous oily liquid;

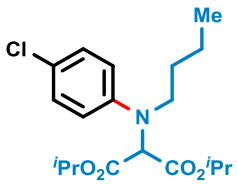
R_f = 0.60 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.05 (d, *J* = 7.7 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.16 – 5.07 (m, 2H), 4.93 (s, 1H), 3.46 – 3.33 (m, 2H), 2.26 (s, 3H), 1.59 (s, 2H), 1.33 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.32 – 1.23 (m, 12H), 0.93 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.5, 145.7, 129.5, 128.0, 115.5, 69.3, 67.9, 49.1, 30.2, 21.5, 20.2, 20.1, 13.8;

HRMS (ESI-TOF): calc'd for $C_{20}H_{31}NO_4$ $[M+H]^+$ 350.2326; found 350.2336.

14. Diisopropyl 2-(butyl(4-chlorophenyl)amino)malonate (55n)



55n

Yield: 86% (**Method E**)

Physical State: brown colored viscous oily liquid;

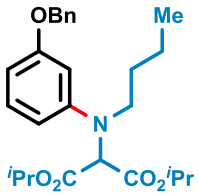
R_f = 0.58 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 5.09 (hept, *J* = 6.3 Hz, 2H), 4.87 (s, 1H), 3.43 – 3.31 (m, 2H), 1.57 (p, *J* = 7.7 Hz, 2H), 1.31 (h, *J* = 7.4 Hz, 2H), 1.25 (dd, *J* = 13.6, 6.3 Hz, 12H), 0.91 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 146.5, 128.7, 123.4, 116.1, 69.6, 67.5, 49.6, 29.9, 21.5, 20.0, 13.8;

HRMS (ESI-TOF): calc'd for $C_{19}H_{28}ClNO_4$ $[M+H]^+$ 370.1780; found 370.1785.

15. Diisopropyl 2-((3-(benzyloxy)phenyl)(butyl)amino)malonate (55o)



55o

Yield: 81% (**Method E**)

Physical State: pale yellow colored oily liquid;

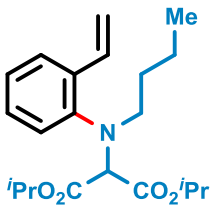
R_f = 0.50 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 1H), 6.54 – 6.44 (m, 3H), 5.16 (hept, *J* = 6.2 Hz, 2H), 5.09 (s, 2H), 5.02 (s, 1H), 3.47 – 3.42 (m, 2H), 1.65 (ddd, *J* = 15.6, 8.8, 6.8 Hz, 2H), 1.37 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.32 (dd, *J* = 9.7, 6.3 Hz, 12H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 159.7, 149.3, 137.1, 129.6, 128.4, 127.7, 127.3, 107.7, 104.3, 102.1, 69.8, 69.4, 67.2, 49.3, 30.0, 21.5, 20.1, 13.8;

HRMS (ESI-TOF): calc'd for $C_{26}H_{35}NO_5$ $[M+H]^+$ 442.2588; found 442.2624.

16. Diisopropyl 2-(butyl(2-vinylphenyl)amino)malonate (55p)



55p

Yield: 86% (**Method E**)

Physical State: pale yellow colored oily liquid;

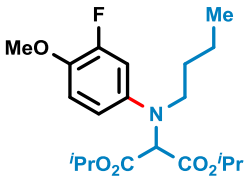
R_f = 0.49 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.9, 1.5 Hz, 1H), 7.15 (dd, *J* = 17.8, 11.0 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.66 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.23 (dd, *J* = 11.0, 1.4 Hz, 1H), 5.10 (hept, *J* = 6.3 Hz, 2H), 4.36 (s, 1H), 3.40 (t, *J* = 7.1 Hz, 2H), 1.36 (p, *J* = 7.7, 6.9 Hz, 2H), 1.30 (dt, *J* = 15.4, 7.2 Hz, 2H), 1.27 – 1.21 (m, 12H), 0.83 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.5, 146.4, 134.3, 133.8, 127.7, 126.6, 123.9, 123.2, 114.2, 70.6, 68.8, 47.8, 30.3, 21.58, 21.51, 20.0, 13.8;

HRMS (ESI-TOF): calc'd for $C_{21}H_{31}NO_4$ $[M+H]^+$ 362.2326; found 362.2382.

17. Diisopropyl 2-(butyl(3-fluoro-4-methoxyphenyl)amino)malonate (55q)



55q

Yield: 80% (**Method E**)

Physical State: dark brown colored viscous oily liquid;

R_f = 0.40 (8:1 EtOAc : hexanes);

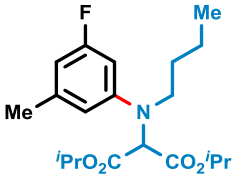
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.85 (t, *J* = 9.3 Hz, 1H), 6.68 (dd, *J* = 14.1, 2.9 Hz, 1H), 6.59 – 6.53 (m, 1H), 5.09 (hept, *J* = 6.3 Hz, 2H), 4.79 (s, 1H), 3.82 (s, 3H), 3.38 – 3.24 (m, 2H), 1.54 (p, *J* = 7.7 Hz, 2H), 1.32 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.26 (dd, *J* = 10.0, 6.3 Hz, 12H), 0.91 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 153.7, 152.1, 142.7, 142.6, 140.9, 140.8, 114.9, 114.8, 111.69, 111.68, 105.5, 105.3, 69.6, 68.4, 57.1, 49.9, 30.1, 21.63, 21.62, 20.1, 13.8;

^{19}F NMR (471 MHz, $CDCl_3$): δ –133.4 (ddd, *J* = 14.0, 9.7, 1.3 Hz);

HRMS (ESI-TOF): calc'd for $C_{20}H_{30}FNO_5$ $[M+H]^+$ 384.2181; found 384.2192.

18. Diisopropyl 2-(butyl(3-fluoro-5-methylphenyl)amino)malonate (55r)



55r

Yield: 96% (**Method E**)

Physical State: brown colored viscous oily liquid;

R_f = 0.60 (8:1 EtOAc : hexanes);

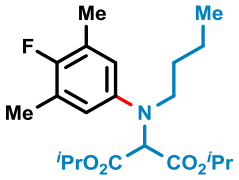
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.35 (s, 1H), 6.31 (d, *J* = 10.7 Hz, 2H), 5.11 (hept, *J* = 6.2 Hz, 2H), 4.91 (s, 1H), 3.42 – 3.34 (m, 2H), 2.27 (s, 3H), 1.61 (p, *J* = 7.8 Hz, 2H), 1.33 (dq, *J* = 14.9, 7.5 Hz, 2H), 1.27 (dd, *J* = 9.5, 6.3 Hz, 12H), 0.93 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.0, 164.5, 162.9, 149.4, 149.3, 140.39, 140.32, 110.6, 105.9, 105.7, 98.9, 98.7, 69.6, 67.1, 49.6, 29.9, 21.8, 21.7, 21.5, 20.0, 13.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ -113.5 (dd, *J* = 12.2, 9.2 Hz);

HRMS (ESI-TOF): calc'd for $C_{20}H_{30}FNO_4$ $[M+H]^+$ 368.2232; found 368.2240.

19. Diisopropyl 2-(butyl(4-fluoro-3,5-dimethylphenyl)amino)malonate (55s)



55s

Yield: 91% (**Method E**)

Physical State: dark brown colored oily liquid;

R_f = 0.67 (8:1 EtOAc : hexanes);

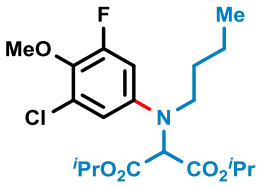
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.51 (d, *J* = 6.0 Hz, 2H), 5.10 (hept, *J* = 6.2 Hz, 2H), 4.82 (s, 1H), 3.42 – 3.25 (m, 2H), 2.20 (s, 6H), 1.53 (p, *J* = 7.7 Hz, 2H), 1.32 (dq, *J* = 15.0, 7.5 Hz, 2H), 1.26 (dd, *J* = 9.4, 6.3 Hz, 12H), 0.91 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 154.9, 153.3, 143.5, 143.5, 124.3, 124.2, 116.8, 116.8, 69.2, 68.6, 49.3, 30.2, 21.4, 20.0, 14.88, 14.85, 13.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ -133.5 (s);

HRMS (ESI-TOF): calc'd for $C_{21}H_{32}FNO_4$ $[M+H]^+$ 382.2388; found 382.2387.

20. Diisopropyl 2-(butyl(3-chloro-5-fluoro-4-methoxyphenyl)amino)malonate (55t)



55t

Yield: 54% (**Method E**)

Physical State: dark brown colored oily liquid;

R_f = 0.60 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.57 – 6.52 (m, 1H), 6.46 (dd, *J* = 13.6, 3.0 Hz, 1H), 5.10 (hept, *J* = 6.2 Hz, 2H), 4.77 (s, 1H), 3.83 (s, 3H), 3.36 – 3.27 (m, 2H), 1.56 (p, *J* =

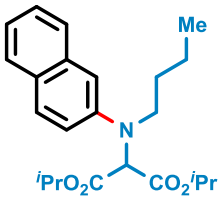
7.8 Hz, 2H), 1.35 – 1.28 (m, 2H), 1.26 (dd, *J* = 11.4, 6.3 Hz, 12H), 0.92 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 157.3, 155.7, 144.5, 144.4, 136.4, 136.3, 128.8, 128.8, 111.3, 102.4, 102.2, 69.9, 67.4, 61.56, 61.54, 50.0, 29.8, 21.55, 21.54, 20.0, 13.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ –126.9 – –127.6 (m)

HRMS (ESI-TOF): calc'd for $C_{20}H_{29}ClFNO_5$ $[M+H]^+$ 418.1791; found 418.1791.

21. Diisopropyl 2-(butyl(naphthalen-2-yl)amino)malonate (55u)



55u

Yield: 95% (**Method E**)

Physical State: dark reddish brown colored oily liquid;

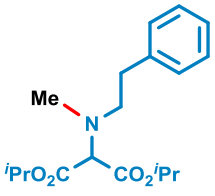
R_f = 0.56 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (t, *J* = 9.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.13 (d, *J* = 2.2 Hz, 1H), 5.18 (dq, *J* = 12.6, 6.3 Hz, 2H), 5.15 (s, 1H), 3.64 – 3.53 (m, 2H), 1.72 (p, *J* = 7.8 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 1.32 (dd, *J* = 12.2, 6.3 Hz, 12H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 145.7, 134.5, 128.7, 127.8, 127.3, 126.4, 126.1, 122.8, 117.8, 109.8, 69.5, 67.8, 49.3, 30.2, 21.6, 20.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{23}H_{31}NO_4$ $[M+H]^+$ 386.2326; found 386.2331.

22. Diisopropyl 2-(methyl(phenethyl)amino)malonate (55v)



55v

Yield: 39% (**Method F**)

Physical State: Pale yellow colored viscous oily liquid;

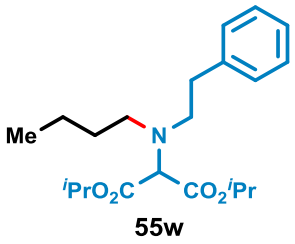
R_f = 0.29 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.26 (m, 3H), 5.20 (hept, *J* = 6.3 Hz, 2H), 4.21 (s, 1H), 3.02 – 2.97 (m, 2H), 2.92 (dd, *J* = 10.3, 5.4 Hz, 2H), 2.66 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 139.9, 139.2, 128.7, 128.2, 125.9, 70.2, 68.9, 56.8, 39.4, 34.8, 21.7, 21.6.

HRMS (ESI-TOF): calc'd for $C_{10}H_{17}NO_4$ $[M+H]^+$ 322.2013; found 322.2014.

23. Diisopropyl 2-(butyl(phenethyl)amino)malonate (55w)



55w

Yield: 60% (**Method F**)

Physical State: colorless oily liquid;

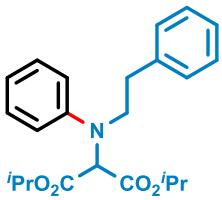
R_f = 0.53 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.17 (m, 3H), 5.11 (hept, *J* = 6.2 Hz, 2H), 4.22 (s, 1H), 3.00 – 2.94 (m, 2H), 2.83 – 2.78 (m, 2H), 2.78 – 2.73 (m, 2H), 1.47 (p, *J* = 7.5 Hz, 2H), 1.32 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.28 (dd, *J* = 6.3, 1.6 Hz, 12H), 0.92 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.7, 140.0, 128.6, 128.0, 125.7, 68.6, 67.7, 54.3, 52.2, 35.5, 30.6, 21.6, 21.5, 20.1, 13.9;

HRMS (ESI-TOF): calc'd for $C_{21}H_{33}NO_4$ $[M+H]^+$ 364.2482; found 364.2493.

24. Diisopropyl 2-(phenethyl(phenyl)amino)malonate (55x)



55x

Yield: 25% (M = Li), 54% (M = MgBr) (**Method F** for M = Li and **Method E** for M = MgBr)

Physical State: dark orange colored non-viscous liquid;

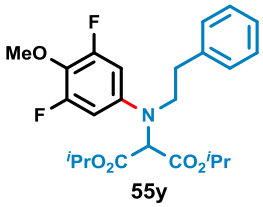
R_f = 0.42 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 4H), 7.25 – 7.19 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 5.10 (hept, *J* = 6.3 Hz, 2H), 5.02 (s, 1H), 3.73 – 3.61 (m, 2H), 3.00 – 2.86 (m, 2H), 1.26 (dd, *J* = 9.0, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 147.5, 139.5, 129.2, 128.6, 128.4, 126.1, 118.9, 69.6, 67.3, 50.9, 34.3, 21.6;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4$ $[M+H]^+$ 384.2169; found 384.2191.

25. Diisopropyl 2-((3,5-difluoro-4-methoxyphenyl)(phenethyl)amino)malonate (55y)



55y

Yield: 43% (**Method E**)

Physical State: colorless viscous oily liquid;

R_f = 0.35 (10% EtOAc/hexanes);

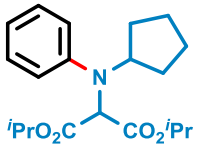
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 2H), 7.19 (d, *J* = 7.1 Hz, 3H), 6.38 (d, *J* = 10.8 Hz, 2H), 5.08 (hept, *J* = 6.2 Hz, 2H), 4.82 (s, 1H), 3.85 (s, 3H), 3.61 – 3.52 (m, 2H), 2.92 – 2.84 (m, 2H), 1.25 (dd, *J* = 11.2, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 157.3, 157.2, 155.7, 155.6, 143.5, 138.7, 128.5, 128.4, 126.3, 98.8, 98.6, 69.9, 67.2, 61.9, 51.6, 34.1, 21.5, 21.4;

^{19}F NMR (471 MHz, $CDCl_3$): δ –127.7 – –128.3 (m)

HRMS (ESI-TOF): calc'd for $C_{24}H_{29}F_2NO_5$ $[M+H]^+$ 450.2087; found 450.2110.

26. Diisopropyl 2-(cyclopentyl(phenyl)amino)malonate (55z)



55z

Yield: 82% (**Method E**)

Physical State: dark brown colored oily liquid;

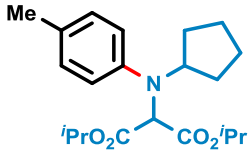
R_f = 0.73 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 – 7.14 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 5.02 (hept, *J* = 6.3 Hz, 2H), 4.74 (s, 1H), 4.12 (p, *J* = 8.3 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.77 – 1.68 (m, 2H), 1.58 (dh, *J* = 15.7, 7.6, 6.8 Hz, 4H), 1.22 (d, *J* = 6.3 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.2, 148.0, 128.5, 119.8, 118.0, 69.4, 65.2, 62.1, 29.8, 23.7, 21.5, 21.3;

HRMS (ESI-TOF): calc'd for $C_{20}H_{29}NO_4$ $[M+H]^+$ 348.2169; found 348.2180.

27. Diisopropyl 2-(cyclopentyl(*p*-tolyl)amino)malonate (56a)



56a

Yield: 66% (**Method E**)

Physical State: orange colored crystalline solid (m.p. = 51-55.2 °C);

R_f = 0.45 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.97 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.02 (hept, *J* = 6.2 Hz, 2H), 4.70 (s, 1H), 4.05 (p, *J* = 8.0 Hz, 1H), 2.23 (s, 3H), 1.95 (dd, *J* = 14.0, 5.5 Hz, 2H), 1.70 (s, 2H), 1.61 – 1.50 (m, 4H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.11 (d, *J* = 6.4 Hz, 6H);

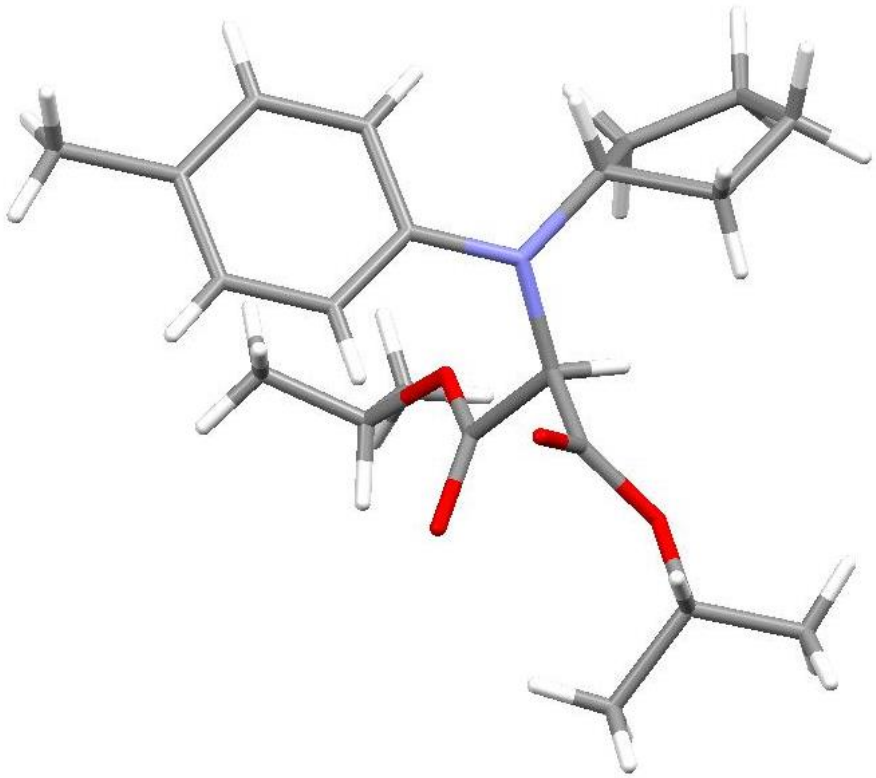


Figure S6. X-ray crystal structure of diisopropyl 2-(cyclopentyl(*p*-tolyl)amino)malonate **(56a)**

Table S9. X-Ray **c**rystal data and structure refinement for **56a**

Table 1.		
Identification code	pvk225c_0m_a	
Empirical formula	C21 H31 N O4	
Formula weight	361.47	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.048(8) Å	α = 90°.

	b = 10.848(8) Å	β = 90°.
	c = 20.346(16) Å	γ = 90°.
Volume	2218(3) $Å^3$	
Z	4	
Density (calculated)	1.083 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	784	
Crystal size	0.317 x 0.233 x 0.179 mm^3	
Theta range for data collection	2.002 to 28.332°.	
Index ranges	-13<=h<=13, -14<=k<=14, -27<=l<=27	
Reflections collected	23728	
Independent reflections	5507 [R(int) = 0.0396]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.949 and 0.887	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5507 / 24 / 240	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1992	
R indices (all data)	R1 = 0.1208, wR2 = 0.2379	
Absolute structure parameter	0.5(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.326 and -0.258 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pvk225c_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6056(3)	3980(3)	4085(1)	69(1)
O(2)	7051(3)	2140(3)	4100(2)	77(1)
O(3)	7713(3)	1668(3)	2651(2)	79(1)
O(4)	9616(3)	2513(3)	3011(2)	94(1)

N(1)	8108(3)	4759(3)	3221(2)	57(1)
C(1)	8732(4)	5182(4)	3794(2)	58(1)
C(2)	9413(4)	4390(4)	4206(2)	67(1)
C(3)	10026(5)	4806(5)	4775(3)	88(2)
C(4)	10035(7)	6039(6)	4944(3)	105(2)
C(5)	9368(8)	6833(6)	4526(3)	117(2)
C(6)	8726(6)	6422(4)	3964(3)	84(1)
C(7)	10678(11)	6482(8)	5576(4)	165(4)
C(8)	7669(4)	5633(4)	2715(2)	61(1)
C(9)	6236(5)	6129(5)	2784(3)	85(1)
C(10)	5804(6)	6505(9)	2104(3)	126(3)
C(11)	6770(10)	5972(11)	1665(4)	171(4)
C(12)	7731(5)	5146(5)	2014(2)	80(1)
C(13)	7509(4)	3545(3)	3210(2)	55(1)
C(14)	6865(4)	3129(4)	3853(2)	57(1)
C(15)	5383(6)	3740(5)	4709(2)	87(2)
C(16)	6112(11)	4361(13)	5202(4)	194(4)
C(17)	4025(8)	4215(12)	4654(4)	172(4)
C(18)	8429(4)	2520(4)	2953(2)	65(1)
C(19)	8400(5)	534(6)	2432(3)	102(2)
C(20)	8322(10)	-404(6)	2986(5)	143(3)
C(21)	7747(8)	137(10)	1837(5)	157(3)

Table 3. Bond lengths [Å] and angles [°] for pvk225c_0m_a.

O(1)-C(14)	1.317(5)
O(1)-C(15)	1.463(5)
O(2)-C(14)	1.199(5)
O(3)-C(18)	1.322(5)
O(3)-C(19)	1.479(6)
O(4)-C(18)	1.199(5)
N(1)-C(1)	1.402(5)
N(1)-C(13)	1.448(5)
N(1)-C(8)	1.467(5)
C(1)-C(2)	1.382(6)
C(1)-C(6)	1.389(6)

C(2)-C(3)	1.386(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.381(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(9)
C(4)-C(7)	1.518(8)
C(5)-C(6)	1.387(7)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-C(12)	1.522(6)
C(8)-C(9)	1.544(7)
C(8)-H(8)	0.9800
C(9)-C(10)	1.505(8)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.441(11)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.497(10)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.527(5)
C(13)-C(18)	1.538(6)
C(13)-H(13)	0.9800
C(15)-C(16)	1.412(11)
C(15)-C(17)	1.463(11)
C(15)-H(15)	0.9800
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600

C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(19)-C(21)	1.443(10)
C(19)-C(20)	1.522(10)
C(19)-H(19)	0.9800
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

C(14)-O(1)-C(15)	118.1(3)
C(18)-O(3)-C(19)	117.9(3)
C(1)-N(1)-C(13)	119.7(3)
C(1)-N(1)-C(8)	120.4(3)
C(13)-N(1)-C(8)	116.9(3)
C(2)-C(1)-C(6)	116.9(4)
C(2)-C(1)-N(1)	121.5(4)
C(6)-C(1)-N(1)	121.5(4)
C(1)-C(2)-C(3)	121.6(4)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
C(4)-C(3)-C(2)	121.7(5)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(3)-C(4)-C(5)	116.6(5)
C(3)-C(4)-C(7)	121.4(6)
C(5)-C(4)-C(7)	121.9(6)
C(4)-C(5)-C(6)	122.1(5)
C(4)-C(5)-H(5)	118.9
C(6)-C(5)-H(5)	118.9
C(5)-C(6)-C(1)	121.0(5)
C(5)-C(6)-H(6)	119.5
C(1)-C(6)-H(6)	119.5
C(4)-C(7)-H(7A)	109.5

C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(1)-C(8)-C(12)	114.8(4)
N(1)-C(8)-C(9)	116.3(3)
C(12)-C(8)-C(9)	104.1(4)
N(1)-C(8)-H(8)	107.0
C(12)-C(8)-H(8)	107.0
C(9)-C(8)-H(8)	107.0
C(10)-C(9)-C(8)	106.3(4)
C(10)-C(9)-H(9A)	110.5
C(8)-C(9)-H(9A)	110.5
C(10)-C(9)-H(9B)	110.5
C(8)-C(9)-H(9B)	110.5
H(9A)-C(9)-H(9B)	108.7
C(11)-C(10)-C(9)	105.5(5)
C(11)-C(10)-H(10A)	110.6
C(9)-C(10)-H(10A)	110.6
C(11)-C(10)-H(10B)	110.6
C(9)-C(10)-H(10B)	110.6
H(10A)-C(10)-H(10B)	108.8
C(10)-C(11)-C(12)	112.3(6)
C(10)-C(11)-H(11A)	109.1
C(12)-C(11)-H(11A)	109.1
C(10)-C(11)-H(11B)	109.1
C(12)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.9
C(11)-C(12)-C(8)	102.2(5)
C(11)-C(12)-H(12A)	111.3
C(8)-C(12)-H(12A)	111.3
C(11)-C(12)-H(12B)	111.3
C(8)-C(12)-H(12B)	111.3
H(12A)-C(12)-H(12B)	109.2
N(1)-C(13)-C(14)	115.6(3)

N(1)-C(13)-C(18)	114.4(3)
C(14)-C(13)-C(18)	109.4(3)
N(1)-C(13)-H(13)	105.5
C(14)-C(13)-H(13)	105.5
C(18)-C(13)-H(13)	105.5
O(2)-C(14)-O(1)	125.0(4)
O(2)-C(14)-C(13)	123.9(4)
O(1)-C(14)-C(13)	111.1(3)
C(16)-C(15)-O(1)	107.0(6)
C(16)-C(15)-C(17)	111.7(8)
O(1)-C(15)-C(17)	107.6(5)
C(16)-C(15)-H(15)	110.2
O(1)-C(15)-H(15)	110.2
C(17)-C(15)-H(15)	110.2
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(4)-C(18)-O(3)	125.6(4)
O(4)-C(18)-C(13)	124.7(4)
O(3)-C(18)-C(13)	109.7(3)
C(21)-C(19)-O(3)	106.8(6)
C(21)-C(19)-C(20)	113.5(7)
O(3)-C(19)-C(20)	108.0(5)
C(21)-C(19)-H(19)	109.5
O(3)-C(19)-H(19)	109.5
C(20)-C(19)-H(19)	109.5
C(19)-C(20)-H(20A)	109.5

C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for pvk225c_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	82(2)	64(2)	61(2)	8(1)	19(2)	8(1)
O(2)	91(2)	62(2)	78(2)	11(2)	10(2)	8(2)
O(3)	58(2)	80(2)	99(2)	-35(2)	9(2)	-5(1)
O(4)	58(2)	92(2)	134(3)	-35(2)	5(2)	-1(2)
N(1)	60(2)	58(2)	54(2)	5(1)	-5(2)	-6(2)
C(1)	56(2)	58(2)	61(2)	2(2)	-7(2)	-7(2)
C(2)	68(2)	60(2)	73(2)	3(2)	-14(2)	-9(2)
C(3)	88(3)	86(3)	89(3)	15(3)	-33(3)	-17(3)
C(4)	123(5)	100(4)	91(4)	-7(3)	-45(4)	-31(4)
C(5)	165(7)	74(3)	111(4)	-13(3)	-57(5)	-9(4)
C(6)	102(4)	61(3)	89(3)	-6(2)	-32(3)	2(3)
C(7)	235(11)	131(6)	129(6)	-21(5)	-99(7)	-33(7)
C(8)	59(2)	66(2)	60(2)	11(2)	0(2)	-4(2)
C(9)	68(3)	95(3)	92(3)	17(3)	-1(2)	13(3)
C(10)	79(3)	190(7)	111(5)	18(5)	-16(3)	29(4)
C(11)	160(7)	259(9)	93(4)	-6(5)	-48(5)	50(7)

C(12)	87(3)	96(3)	59(2)	7(2)	0(2)	-3(3)
C(13)	52(2)	58(2)	56(2)	-2(2)	0(2)	-6(2)
C(14)	55(2)	56(2)	60(2)	2(2)	-3(2)	-2(2)
C(15)	115(4)	89(3)	57(3)	6(2)	25(3)	23(3)
C(16)	169(6)	312(8)	100(4)	-41(6)	8(5)	-12(6)
C(17)	105(5)	303(12)	109(5)	12(7)	40(4)	-8(7)
C(18)	54(2)	70(3)	72(3)	-11(2)	9(2)	-6(2)
C(19)	64(3)	110(4)	132(5)	-61(4)	25(3)	-7(3)
C(20)	166(7)	76(4)	187(8)	16(5)	66(6)	13(4)
C(21)	108(5)	186(7)	177(7)	-98(6)	15(5)	11(5)

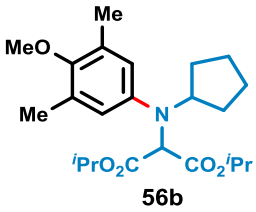
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for pvk225c_0m_a.

	x	y	z	U(eq)
H(2)	9462	3558	4099	80
H(3)	10442	4239	5050	105
H(5)	9349	7669	4626	140
H(6)	8285	6985	3697	101
H(7A)	11442	6977	5473	247
H(7B)	10948	5785	5834	247
H(7C)	10050	6966	5821	247
H(8)	8267	6346	2738	74
H(9A)	5651	5495	2956	102
H(9B)	6215	6832	3079	102
H(10A)	4920	6192	2009	152
H(10B)	5794	7395	2062	152
H(11A)	7258	6628	1448	205
H(11B)	6310	5501	1328	205
H(12A)	8621	5222	1834	96
H(12B)	7453	4291	1992	96
H(13)	6779	3598	2892	66
H(15)	5367	2853	4799	104
H(16A)	6094	3886	5600	290
H(16B)	5721	5155	5280	290

H(16C)	7016	4464	5060	290
H(17A)	4026	5088	4732	258
H(17B)	3468	3816	4973	258
H(17C)	3690	4054	4221	258
H(19)	9335	722	2337	123
H(20A)	8724	-66	3375	215
H(20B)	8786	-1140	2860	215
H(20C)	7407	-597	3074	215
H(21A)	6853	-115	1937	236
H(21B)	8226	-544	1650	236
H(21C)	7726	806	1528	236

Table 6. Torsion angles [°] for pvk225c_0m_a.

28. Diisopropyl 2-(cyclopentyl(4-methoxy-3,5-dimethylphenyl)amino)malonate (56b)



56b

Yield: 70% (**Method E**)

Physical State: off white waxy solid;

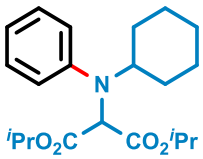
R_f = 0.47 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.66 (s, 2H), 5.06 – 4.93 (m, 2H), 4.63 (s, 1H), 4.05 – 3.92 (m, 1H), 3.60 (s, 3H), 2.18 (s, 6H), 1.91 (s, 2H), 1.66 (s, 2H), 1.60 – 1.41 (m, 4H), 1.18 (d, *J* = 6.5 Hz, 6H), 1.09 (d, *J* = 6.5 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.2, 150.8, 143.8, 130.0, 119.5, 68.8, 65.8, 62.0, 59.5, 30.0, 23.5, 21.3, 21.1, 16.1;

HRMS (ESI-TOF): calc'd for $C_{23}H_{35}NO_5$ $[M+H]^+$ 406.2588; found 406.2644.

29. Diisopropyl 2-(cyclohexyl(phenyl)amino)malonate (56c)



56c

Yield: 83% (**Method E**)

Physical State: dark brown colored oily liquid;

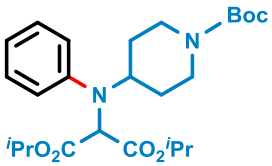
R_f = 0.60 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 8.8, 7.1 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 5.02 (hept, *J* = 6.2 Hz, 2H), 4.78 (s, 1H), 3.60 (td, *J* = 11.2, 3.2 Hz, 1H), 1.97 (d, *J* = 11.5 Hz, 2H), 1.84 (d, *J* = 12.7 Hz, 2H), 1.68 (d, *J* = 13.4 Hz, 1H), 1.36 (dp, *J* = 23.6, 12.6 Hz, 4H), 1.23 (d, *J* = 6.3 Hz, 6H), 1.18 – 1.10 (m, 1H), 1.05 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.3, 147.5, 128.4, 118.7, 116.2, 63.8, 59.0, 31.0, 25.9, 25.6, 21.4, 21.1;

HRMS (ESI-TOF): calc'd for $C_{21}H_{31}NO_4$ $[M+H]^+$ 362.2326; found 362.2335.

30. Diisopropyl 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)(phenyl)amino)malonate (56d)



56d

Yield: 48% (**Method E**)

Physical State: dark brownish yellow waxy solid;

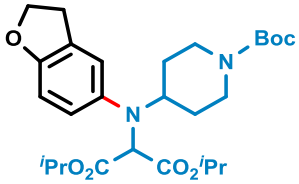
R_f = 0.47 (4:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (t, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 5.01 (hept, *J* = 6.1 Hz, 2H), 4.70 (s, 1H), 4.20 (s, 2H), 3.70 (t, *J* = 10.0 Hz, 1H), 2.77 (s, 2H), 1.90 (d, *J* = 12.2 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.45 (s, 9H), 1.22 (d, *J* = 6.3 Hz, 6H), 1.07 (d, *J* = 6.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.1, 154.6, 147.2, 128.6, 120.0, 117.8, 79.5, 69.4, 64.5, 57.8, 43.5, 30.4, 28.3, 21.5, 21.3;

HRMS (ESI-TOF): calc'd for $C_{25}H_{38}N_2O_6$ $[M+H]^+$ 463.2803; found 463.2812.

31. Diisopropyl 2-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)(2,3-dihydrobenzofuran-5-yl)amino)malonate (56e)



56e

Yield: 32% (**Method E**)

Physical State: pale yellow colored gummy substance;

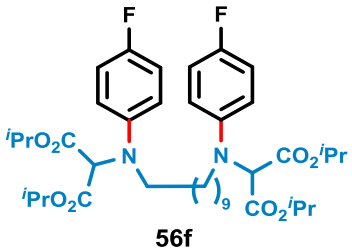
R_f = 0.30 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.00 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 4.99 (hept, *J* = 6.2 Hz, 2H), 4.57 (s, 1H), 4.47 (t, *J* = 8.6 Hz, 2H), 4.24 – 3.87 (m, 2H), 3.37 (tt, *J* = 11.4, 3.4 Hz, 1H), 3.09 (t, *J* = 8.6 Hz, 2H), 2.69 (s, 2H), 1.84 (d, *J* = 11.8 Hz, 2H), 1.39 (s, 11H), 1.15 (dd, *J* = 14.0, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.2, 156.2, 154.5, 139.8, 126.8, 124.6, 122.1, 108.4, 79.3, 71.1, 69.0, 67.6, 58.3, 31.3, 29.8, 28.2, 21.41, 21.40;

HRMS (ESI-TOF): calc'd for $C_{27}H_{40}N_2O_7$ $[M+H]^+$ 505.2908; found 505.2928.

32. Tetraisopropyl 2,2'-(decane-1,10-diylbis((4-fluorophenyl)azanediyl))dimalonate (56f)



56f

Yield: 96% (**Method E**)

Physical State: colorless oily liquid;

R_f = 0.55 (20% EtOAc/hexanes);

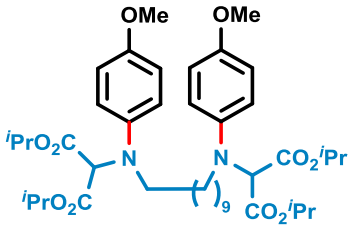
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.92 (t, *J* = 8.6 Hz, 4H), 6.79 (dd, *J* = 9.0, 4.4 Hz, 4H), 5.09 (hept, *J* = 6.2 Hz, 4H), 4.81 (s, 2H), 3.40 – 3.27 (m, 4H), 1.54 (s, 4H), 1.24 (dd, *J* = 8.6, 6.4 Hz, 36H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 157.9, 155.5, 144.43, 144.41, 117.5, 117.4, 115.5, 115.2, 69.4, 68.5, 50.0, 29.5, 29.4, 28.0, 26.9, 21.6, 21.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ –125.6 (s);

HRMS (ESI-TOF): calc'd for $C_{40}H_{58}F_2N_2O_8$ $[M+H]^+$ 733.4234; found 733.4249.

33. Tetraisopropyl 2,2'-(decane-1,10-diylbis((4-methoxyphenyl)azanediyl)) dimalonate (56g)



56g

Yield: 89% (**Method E**)

Physical State: dark brown oily liquid;

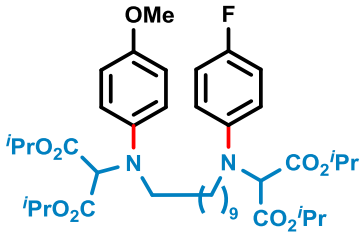
R_f = 0.30 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.93 – 6.72 (m, 8H), 5.08 (hept, *J* = 6.2 Hz, 4H), 4.79 (s, 2H), 3.75 (s, 6H), 3.37 – 3.28 (m, 4H), 1.51 (s, 4H), 1.24 (t, *J* = 6.3 Hz, 36H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.6, 153.4, 142.1, 118.6, 114.3, 69.2, 69.1, 55.5, 49.8, 29.5, 29.4, 28.2, 27.0, 21.63, 21.61;

HRMS (ESI-TOF): calc'd for $C_{42}H_{64}N_2O_{10}$ $[M+H]^+$ 757.4634; found 757.4641.

34. Diisopropyl 2-((10-((1,3-diisopropoxy-1,3-dioxopropan-2-yl)(4-fluorophenyl) amino)decyl)(4-methoxyphenyl)amino)malonate (56h)



56h

Yield: 27% (**Method E**)

Physical State: dark brown colored oily liquid;

R_f = 0.50 (20% EtOAc/hexanes);

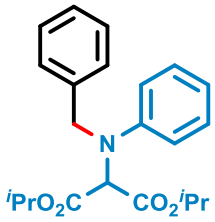
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.91 (t, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 6.79 (dd, *J* = 9.2, 3.4 Hz, 4H), 5.08 (dtt, *J* = 12.5, 6.2, 3.1 Hz, 4H), 4.80 (d, *J* = 11.3 Hz, 2H), 3.74 (s, 3H), 3.33 (q, *J* = 6.9 Hz, 4H), 1.56 – 1.48 (m, 4H), 1.30 – 1.18 (m, 36H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.6, 167.3, 157.8, 155.5, 153.4, 144.4, 144.3, 142.1, 118.7, 117.47, 117.40, 115.4, 115.2, 114.3, 69.4, 69.2, 69.1, 68.5, 55.5, 50.0, 49.8, 29.5, 29.4, 29.3, 28.2, 28.0, 26.98, 26.92, 21.6, 21.5;

^{19}F NMR (471 MHz, $CDCl_3$): δ –125.6 (s);

HRMS (ESI-TOF): calc'd for $C_{41}H_{61}FN_2O_9$ $[M+H]^+$ 745.4434; found 745.4441.

35. Diisopropyl 2-(benzyl(phenyl)amino)malonate (56i)



56i

Yield: 49% (**Method E**)

Physical State: yellow colored solid (m.p. = 76-81°C);

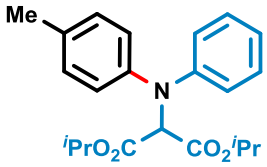
R_f = 0.43 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (dt, *J* = 26.0, 7.3 Hz, 3H), 6.83 (dd, *J* = 12.8, 8.0 Hz, 3H), 5.24 (s, 1H), 5.09 (hept, *J* = 6.2 Hz, 2H), 4.80 (s, 2H), 1.26 (d, *J* = 6.4 Hz, 6H), 1.20 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 148.3, 139.0, 128.9, 128.1, 126.55, 126.51, 118.9, 114.2, 69.7, 66.4, 54.0, 21.4, 21.3;

HRMS (ESI-TOF): calc'd for $C_{22}H_{27}NO_4$ $[M+H]^+$ 370.2013; found 370.2052.

36. Diisopropyl 2-(phenyl(*p*-tolyl)amino)malonate (56j)



56j

Yield: 59% (**Method E**)

Physical State: colorless viscous oily liquid;

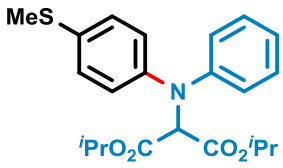
R_f = 0.23 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.0 Hz, 2H), 7.13 (s, 4H), 6.92 (dd, *J* = 12.2, 7.6 Hz, 3H), 5.35 (s, 1H), 5.04 (hept, *J* = 6.2 Hz, 2H), 2.34 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 6H), 1.15 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 146.8, 143.0, 133.5, 129.7, 128.8, 124.7, 120.9, 119.2, 69.5, 67.9, 21.37, 21.32, 20.6;

HRMS (ESI-TOF): calc'd for $C_{22}H_{27}NO_4$ $[M+H]^+$ 370.2013; found 370.2033.

37. Diisopropyl 2-((4-(methylthio)phenyl)(phenyl)amino)malonate (56k)



56k

Yield: 52% (**Method E**)

Physical State: pale yellow colored oily liquid;

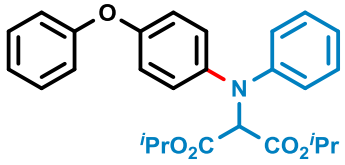
R_f = 0.46 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (td, *J* = 7.2, 1.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 5H), 5.22 (s, 1H), 4.93 (hept, *J* = 6.3 Hz, 2H), 2.35 (s, 3H), 1.08 (d, *J* = 6.3 Hz, 6H), 1.04 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.5, 146.2, 143.8, 131.8, 129.1, 123.1, 122.5, 121.6, 69.7, 67.9, 21.4, 21.3, 17.0;

HRMS (ESI-TOF): calc'd for $C_{22}H_{27}NO_4S$ $[M+H]^+$ 402.1734; found 402.1739.

38. Diisopropyl 2-((4-phenoxyphenyl)(phenyl)amino)malonate (56l)



56l

Yield: 43% (**Method E**)

Physical State: pale yellow colored viscous oily liquid;

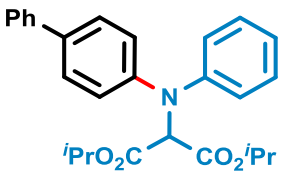
R_f = 0.37 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.39 (s, 1H), 5.10 (hept, *J* = 6.0 Hz, 2H), 1.25 (d, *J* = 6.4 Hz, 6H), 1.21 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.5, 157.2, 153.8, 147.0, 140.5, 129.5, 128.9, 127.0, 123.0, 120.8, 119.5, 118.48, 118.45, 69.6, 67.9, 21.37, 21.34;

HRMS (ESI-TOF): calc'd for $C_{27}H_{29}NO_5$ $[M+H]^+$ 448.2118; found 448.2185.

39. Diisopropyl 2-([1,1'-biphenyl]-4-yl(phenyl)amino)malonate (56m)



56m

Yield: 60% (**Method E**)

Physical State: dark brown colored oily liquid;

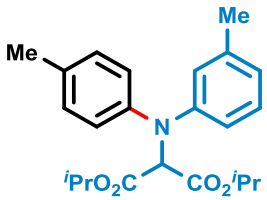
R_f = 0.40 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.34 (q, *J* = 7.6, 7.0 Hz, 3H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.04 (m, 3H), 5.43 (s, 1H), 5.08 (hept, *J* = 6.3 Hz, 2H), 1.22 (d, *J* = 6.3 Hz, 6H), 1.17 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 145.8, 145.7, 140.6, 134.8, 129.1, 128.6, 127.6, 126.6, 126.5, 123.38, 123.30, 121.2, 69.7, 67.9, 21.4, 21.3;

HRMS (ESI-TOF): calc'd for $C_{27}H_{29}NO_4$ $[M+H]^+$ 432.2169; found 432.2218.

40. Diisopropyl 2-(*m*-tolyl(*p*-tolyl)amino)malonate (56n)



56n

Yield: 55% (**Method E**)

Physical State: white solid (m.p. = 75-78 °C);

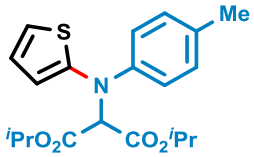
R_f = 0.45 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 – 7.01 (m, 5H), 6.83 – 6.64 (m, 3H), 5.32 (s, 1H), 5.11 – 4.96 (m, 2H), 2.33 (s, 3H), 2.27 (s, 3H), 1.17 (dd, *J* = 24.5, 6.4 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 146.9, 143.0, 138.6, 133.3, 129.6, 128.7, 124.5, 122.0, 120.1, 116.7, 116.6, 69.5, 67.9, 21.5, 21.4, 21.3, 20.7;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4$ $[M+H]^+$ 384.2169; found 384.2195.

41. Diisopropyl 2-(thiophen-2-yl(*p*-tolyl)amino)malonate (56o)



56o

Yield: 61% (**Method E**)

Physical State: yellow-colored oily liquid;

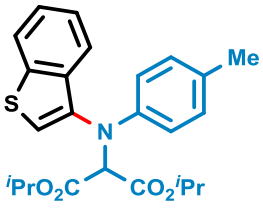
R_f = 0.46 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 1H), 5.04 (hept, *J* = 6.2 Hz, 2H), 2.19 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 6H), 1.08 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.3, 141.7, 139.4, 129.2, 127.9, 127.8, 126.7, 126.5, 114.8, 70.4, 69.3, 21.13, 21.11, 20.2;

HRMS (ESI-TOF): calc'd for $C_{20}H_{25}NO_4S$ $[M+H]^+$ 376.1577; found 376.1573.

42. Diisopropyl 2-(benzo[*b*]thiophen-3-yl(*p*-tolyl)amino)malonate (56p)



56p

Yield: 46% (**Method E**)

Physical State: orange colored waxy solid;

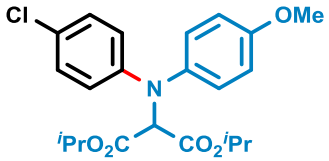
R_f = 0.42 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 6.3, 2.9 Hz, 1H), 8.15 (s, 1H), 7.81 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.30 (td, *J* = 6.5, 5.6, 3.7 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 2H), 5.48 (s, 1H), 5.05 (hept, *J* = 6.2 Hz, 2H), 2.16 (s, 3H), 1.11 (dd, *J* = 15.7, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4, 141.7, 140.5, 137.1, 129.9, 129.2, 128.6, 128.0, 125.2, 123.9, 123.5, 122.3, 115.6, 70.3, 69.8, 21.34, 21.33, 20.3;

HRMS (ESI-TOF): calc'd for $C_{24}H_{27}NO_4S$ $[M+H]^+$ 426.1734; found 426.1788.

43. Diisopropyl 2-((4-chlorophenyl)(4-methoxyphenyl)amino)malonate (56q)



56q

Yield: 36% (**Method E**)

Physical State: dark yellow colored oily liquid;

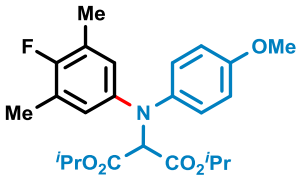
R_f = 0.43 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 9.0 Hz, 2H), 5.21 (s, 1H), 5.01 (hept, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 1.15 (dd, *J* = 11.2, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.4, 157.9, 146.4, 137.2, 129.7, 128.5, 123.9, 116.6, 114.6, 69.7, 68.0, 55.3, 21.39, 21.38;

HRMS (ESI-TOF): calc'd for $C_{22}H_{26}ClNO_5$ $[M+H]^+$ 420.1572; found 420.1576.

44. Diisopropyl 2-((4-fluoro-3,5-dimethylphenyl)(4-methoxyphenyl)amino) malonate (56r)



56r

Yield: 49% (**Method E**)

Physical State: brown colored solid (m.p. = 72-78 °C);

R_f = 0.31 (10% EtOAc/hexanes);

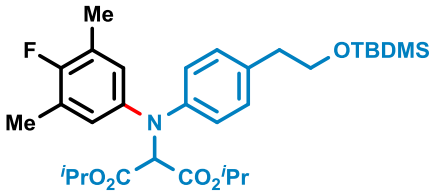
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 6.1 Hz, 2H), 5.23 (s, 1H), 5.03 (hept, *J* = 6.2 Hz, 2H), 3.78 (s, 3H), 2.16 (d, *J* = 1.6 Hz, 6H), 1.16 (dd, *J* = 15.7, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 156.3, 155.7, 154.2, 142.6, 138.8, 126.3, 124.4, 124.3, 119.2, 114.3, 69.5, 68.3, 55.3, 21.4, 21.3, 14.78, 14.76;

^{19}F NMR (471 MHz, $CDCl_3$): δ –131.74 (ddq, *J* = 6.2, 4.2, 2.2 Hz);

HRMS (ESI-TOF): calc'd for $C_{24}H_{30}FNO_5$ $[M+H]^+$ 432.2181; found 432.2178.

45. Diisopropyl 2-((4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenyl)(4-fluoro-3,5-dimethylphenyl) amino)malonate (56s)



56s

Yield: 57% (**Method E**)

Physical State: yellow colored oily liquid;

R_f = 0.48 (10% EtOAc/hexanes);

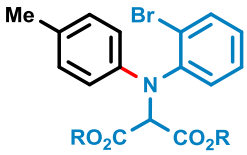
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 6.3 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.26 (s, 1H), 5.03 (hept, *J* = 6.2 Hz, 2H), 3.77 (t, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 7.1 Hz, 2H), 2.20 (s, 6H), 1.17 (dd, *J* = 21.4, 6.3 Hz, 12H), 0.89 (s, 9H), 0.01 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 157.5, 155.9, 145.2, 140.76, 140.74, 131.8, 129.6, 125.08, 125.05, 124.8, 124.7, 119.3, 69.5, 68.0, 64.5, 38.7, 25.8, 21.4, 21.3, 18.2, 14.65, 14.62, –5.4;

^{19}F NMR (471 MHz, $CDCl_3$): δ –126.5 (ddp, *J* = 6.6, 4.5, 2.2 Hz);

HRMS (ESI-TOF): calc'd for $C_{31}H_{46}FNO_5Si$ $[M+H]^+$ 560.3202; found 560.3256.

46. Diisopropyl 2-((2-bromophenyl)(*p*-tolyl)amino)malonate (56t)



56t; R = ^{i}Pr

Yield: 18% (**Method E**)

Physical State: yellow colored oily liquid;

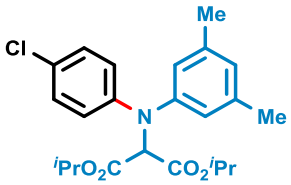
R_f = 0.40 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.34 (td, *J* = 7.7, 1.4 Hz, 1H), 7.14 (td, *J* = 7.8, 1.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 5.33 (s, 1H), 5.02 (hept, *J* = 6.3 Hz, 2H), 2.23 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 6H), 1.10 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.5, 143.8, 143.6, 133.7, 131.6, 129.3, 128.7, 128.6, 128.1, 125.6, 115.3, 69.7, 67.7, 21.4, 21.3, 20.3;

HRMS (ESI-TOF): calc'd for $C_{22}H_{26}BrNO_4$ $[M+H]^+$ 448.1118 $[M+Na]^+$ 470.0937; found 448.1045, 470.0877.

47. Diisopropyl 2-((4-chlorophenyl)(3,5-dimethylphenyl)amino)malonate (56u)



56u

Yield: 33% (**Method E**)

Physical State: dark yellow colored solid (m.p. = 55-62 °C);

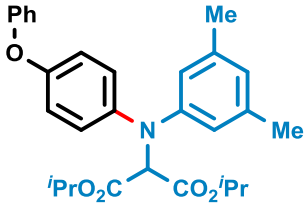
R_f = 0.48 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 3H), 5.26 (s, 1H), 5.03 (hept, *J* = 6.3 Hz, 2H), 2.25 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H), 1.14 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.5, 145.8, 145.0, 138.9, 128.8, 126.7, 125.6, 121.9, 121.2, 69.7, 68.1, 21.48, 21.42;

HRMS (ESI-TOF): calc'd for $C_{23}H_{28}ClNO_4$ $[M+H]^+$ 418.1780; found 418.1785.

48. Diisopropyl 2-((3,5-dimethylphenyl)(4-phenoxyphenyl)amino)malonate (56v)



56v

Yield: 35% (**Method E**)

Physical State: dark brown colored oily liquid;

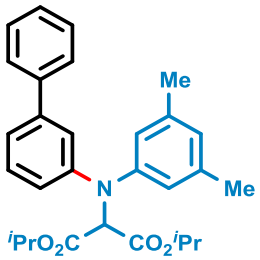
R_f = 0.42 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.61 (s, 1H), 6.53 (s, 2H), 5.33 (s, 1H), 5.06 (hept, *J* = 6.2 Hz, 2H), 2.25 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H), 1.18 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 157.4, 153.3, 147.0, 140.7, 138.5, 129.6, 126.4, 123.1, 122.9, 119.4, 118.4, 116.9, 69.5, 68.0, 21.45, 21.42;

HRMS (ESI-TOF): calc'd for $C_{29}H_{33}NO_5$ $[M+H]^+$ 476.2431; found 476.2465.

49. Diisopropyl 2-([1,1'-biphenyl]-3-yl(3,5-dimethylphenyl)amino)malonate (56w)



56w

Yield: 48% (**Method E**)

Physical State: yellow colored viscous oily liquid;

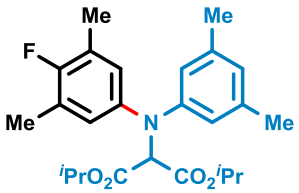
R_f = 0.40 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.83 (s, 2H), 6.76 (s, 1H), 5.45 (s, 1H), 5.10 (hept, *J* = 6.2 Hz, 2H), 2.32 (s, 6H), 1.23 (d, *J* = 6.3 Hz, 6H), 1.17 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 146.6, 146.0, 141.9, 141.0, 138.6, 129.2, 128.5, 127.1, 126.9, 124.9, 120.8, 120.5, 120.4, 120.0, 69.5, 68.1, 21.4, 21.3;

HRMS (ESI-TOF): calc'd for $C_{29}H_{33}NO_4$ $[M+H]^+$ 460.2482; found 460.2451.

50. Diisopropyl 2-((3,5-dimethylphenyl)(4-fluoro-3,5-dimethylphenyl)amino) malonate (56x)



56x

Yield: 33% (**Method E**)

Physical State: pale brown colored solid (m.p. = 65-71 °C);

R_f = 0.48 (10% EtOAc/hexanes);

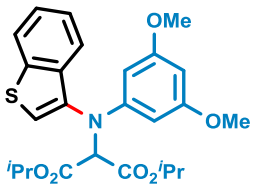
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.94 (d, *J* = 6.3 Hz, 2H), 6.56 (s, 1H), 6.43 (s, 2H), 5.28 (s, 1H), 5.06 (hept, *J* = 6.2 Hz, 2H), 2.24 (s, 12H), 1.21 (d, *J* = 6.3 Hz, 6H), 1.18 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 157.9, 156.3, 147.3, 140.1, 140.0, 138.3, 126.7, 126.6, 124.8, 124.7, 122.4, 115.8, 69.4, 68.0, 21.42, 21.40, 21.3, 14.63, 14.61;

^{19}F NMR (471 MHz, $CDCl_3$): δ –126.5 (ddp, *J* = 6.8, 4.6, 2.3 Hz);

HRMS (ESI-TOF): calc'd for $C_{25}H_{32}FNO_4$ $[M+H]^+$ 430.2388; found 430.2401.

51. Diisopropyl 2-(benzo[*b*]thiophen-3-yl(3,5-dimethoxyphenyl)amino)malonate (56y)



56y

Yield: 77% (**Method E**)

Physical State: yellow colored waxy solid;

R_f = 0.25 (30% EtOAc/hexanes);

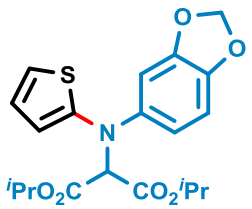
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.17 (dd, *J* = 6.7, 2.4 Hz, 1H), 7.82 (dd, *J* = 6.5, 2.4 Hz, 1H), 7.35 – 7.26 (m, 2H), 5.91 (d, *J* = 2.1 Hz, 2H), 5.87 (t, *J* = 2.1 Hz, 1H),

5.71 (s, 1H), 5.09 (hept, *J* = 6.2 Hz, 2H), 3.62 (s, 6H), 1.17 (d, *J* = 6.3 Hz, 6H), 1.12 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 161.0, 145.9, 140.2, 137.0, 129.6, 128.3, 124.8, 123.9, 123.5, 122.2, 93.8, 91.5, 70.4, 69.2, 54.8, 21.26, 21.22;

HRMS (ESI-TOF): calc'd for $C_{25}H_{29}NO_6S$ $[M+H]^+$ 472.1788; found 472.1809.

52. Diisopropyl 2-(benzo[*d*][1,3]dioxol-5-yl(thiophen-2-yl)amino)malonate (56z)



56z

Yield: 66% (**Method E**)

Physical State: yellow colored oily liquid;

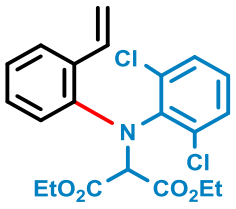
R_f = 0.29 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.30 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 5.99 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.78 (s, 2H), 5.51 (s, 1H), 5.01 (hept, *J* = 6.2 Hz, 2H), 1.16 (d, *J* = 6.3 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 147.7, 140.4, 139.48, 139.46, 128.0, 126.8, 126.6, 108.1, 106.8, 100.4, 97.8, 70.5, 69.6, 21.2, 21.1;

HRMS (ESI-TOF): calc'd for $C_{20}H_{23}NO_6S$ $[M+H]^+$ 406.1319; found 406.1320.

53. Diethyl 2-((2,6-dichlorophenyl)(2-vinylphenyl)amino)malonate (57a)



57a

Yield: 64% (**Method E**)

Physical State: beige colored viscous oily liquid;

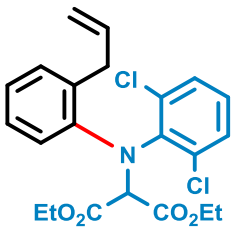
R_f = 0.48 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 5.61 (d, *J* = 17.3 Hz, 1H), 5.38 (d, *J* = 11.0 Hz, 1H), 4.51 – 3.95 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.0, 155.2, 138.7, 137.7, 135.8, 135.2, 134.4, 129.6, 129.3, 128.9, 128.5, 128.2, 127.7, 126.8, 126.6, 117.9, 62.4, 61.2, 61.0, 14.4, 13.9;

HRMS (ESI-TOF): calc'd for $C_{21}H_{21}Cl_2NO_4$ $[M+H]^+$ 422.0920; found 422.0858.

54. Diethyl 2-((2-allylphenyl)(2,6-dichlorophenyl)amino)malonate (57b)



57b

Yield: 72% (**Method E**)

Physical State: beige colored viscous oily liquid;

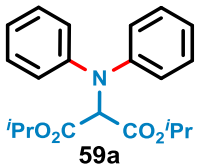
R_f = 0.19 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 5.1 Hz, 1H) 7.07 (d, *J* = 4.1 Hz, 2H), 7.04 – 7.01 (m, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.04 – 5.87 (m, 2H), 5.03 (d, *J* = 13.7 Hz, 2H), 4.27 – 4.07 (m, 4H), 3.71 (dd, *J* = 15.8, 6.2 Hz, 1H), 3.46 (dd, *J* = 15.8, 6.8 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8, 155.1, 139.5, 137.6, 136.7, 135.7, 135.2, 130.3, 129.9, 129.5, 128.9, 128.5, 128.3, 127.7, 125.6, 116.1, 62.4, 61.2, 60.8, 37.3, 14.3, 13.9;

HRMS (ESI-TOF): calc'd for $C_{22}H_{23}Cl_2NO_4$ $[M+H]^+$ 436.1077; found 436.1076.

55. Diisopropyl 2-(diphenylamino)malonate (59a)



59a

Yield: 75% (**Method C**)

Physical State: pale brown colored waxy solid;

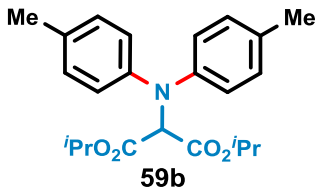
R_f = 0.42 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.8 Hz, 4H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.92 (t, *J* = 7.3 Hz, 2H), 5.25 (s, 1H), 4.93 (hept, *J* = 6.2 Hz, 2H), 1.08 (d, *J* = 6.3 Hz, 6H), 1.02 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 146.1**,** 129.0, 122.5, 122.0, 69.6, 67.9, 21.3, 21.2;

HRMS (ESI-TOF): calc'd for $C_{21}H_{25}NO_4$ $[M+H]^+$ 356.1856; found 356.1856.

56. Diisopropyl 2-(di-*p*-tolylamino)malonate (59b)



59b

Yield: 73% (**Method C**)

Physical State: off white waxy solid;

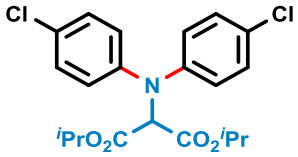
R_f = 0.46 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.2 Hz, 4H), 6.99 (d, *J* = 8.4 Hz, 4H), 5.35 (s, 1H), 5.06 (hept, *J* = 6.1 Hz, 2H), 2.33 (s, 6H), 1.22 (d, *J* = 6.4 Hz, 6H), 1.17 (d, *J* = 6.5 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 143.9, 131.7, 129.4, 121.9, 69.3, 67.9, 21.3, 21.2, 20.4;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4$ $[M+H]^+$ 384.2169; found 384.2218.

57. Diisopropyl 2-(bis(4-chlorophenyl)amino)malonate (59c)



59c

Yield: 40% (**Method C**)

Physical State: yellow colored waxy solid;

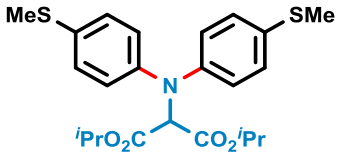
R_f = 0.50 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.9 Hz, 4H), 6.97 (d, *J* = 8.9 Hz, 4H), 5.24 (s, 1H), 5.02 (hept, *J* = 6.2 Hz, 2H), 1.18 (d, *J* = 6.4 Hz, 6H), 1.13 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 144.5, 129.2, 128.2, 123.4, 70.0, 67.9, 21.4, 21.3;

HRMS (ESI-TOF): calc'd for $C_{21}H_{23}Cl_2NO_4$ $[M+H]^+$ 424.1077; found 424.1038.

58. Diisopropyl 2-(bis(4-(methylthio)phenyl)amino)malonate (59d)



59d

Yield: 45% (**Method C**)

Physical State: brown colored oily liquid;

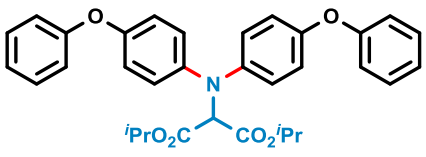
R_f = 0.37 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.3 Hz, 4H), 6.98 (d, *J* = 8.4 Hz, 4H), 5.28 (s, 1H), 5.02 (hept, *J* = 6.3 Hz, 2H), 2.43 (s, 6H), 1.16 (dd, *J* = 25.9, 6.4 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.3, 143.7, 131.6, 128.6, 122.5, 69.7, 67.7, 21.3, 21.2, 16.9;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4S_2$ $[M+H]^+$ 448.1611; found 448.1616.

59. Diisopropyl 2-(bis(4-phenoxyphenyl)amino)malonate (59e)



59e

Yield: 41% (**Method C**)

Physical State: dark purple colored viscous oily liquid;

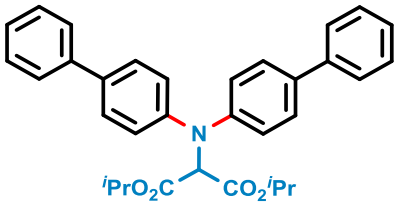
R_f = 0.35 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.9 Hz, 4H), 7.08 (dd, *J* = 16.6, 8.2 Hz, 6H), 7.01 (d, *J* = 8.0 Hz, 4H), 6.96 (d, *J* = 8.9 Hz, 4H), 5.32 (s, 1H), 5.08 (hept, *J* = 6.1 Hz, 2H), 1.21 (dd, *J* = 21.7, 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 157.6, 152.3, 142.0, 129.5, 123.4, 122.8, 119.8, 118.2, 69.7, 68.2, 21.46, 21.44;

HRMS (ESI-TOF): calc'd for $C_{33}H_{33}NO_6$ $[M+H]^+$ 540.2381; found 540.2389.

60. Diisopropyl 2-(di([1,1'-biphenyl]-4-yl)amino)malonate (59f)



59f

Yield: 60% (**Method C**)

Physical State: pale yellow colored waxy solid;

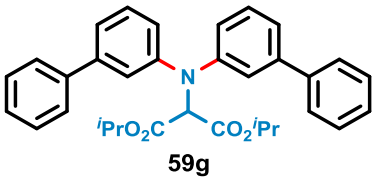
R_f = 0.38 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 23.1, 8.0 Hz, 8H), 7.51 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.53 (s, 1H), 5.16 (hept, *J* = 6.1 Hz, 2H), 1.29 (d, *J* = 6.3 Hz, 6H), 1.24 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.5, 145.3, 140.5, 135.5, 128.6, 127.7, 126.7, 126.6, 122.3, 69.8, 67.9, 21.4, 21.3;

HRMS (ESI-TOF): calc'd for $C_{33}H_{33}NO_4$ $[M+H]^+$ 508.2482 $[M+Na]^+$ 530.2302; found 508.2522, 530.2346.

61. Diisopropyl 2-(di([1,1'-biphenyl]-3-yl)amino)malonate (59g)



59g

Yield: 65% (**Method C**)

Physical State: pale yellow colored oily liquid;

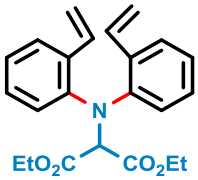
R_f = 0.45 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.7 Hz, 4H), 7.50 (dd, *J* = 14.6, 7.1 Hz, 6H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.22 (d, *J* = 7.8 Hz, 2H), 5.60 (s, 1H), 5.15 (hept, *J* = 5.9 Hz, 2H), 1.26 (d, *J* = 6.4 Hz, 6H), 1.20 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 146.5, 142.1, 140.8, 129.4, 128.5, 127.2, 126.9, 121.5, 121.1, 120.7, 69.7, 68.1, 21.38, 21.30;

HRMS (ESI-TOF): calc'd for $C_{33}H_{33}NO_4$ $[M+H]^+$ 508.2482; found 508.2525.

62. Diethyl 2-(bis(2-vinylphenyl)amino)malonate (59h)



59h

Yield: 47% (**Method C**)

Physical State: beige colored viscous oily liquid;

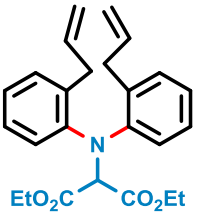
R_f = 0.38 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 20.2, 7.7 Hz, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.69 (dd, *J* = 17.1, 10.9 Hz, 2H), 6.11 (s, 1H), 5.33 (d, *J* = 17.1 Hz, 2H), 4.96 (d, *J* = 10.9 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.07 (t, *J* = 7.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.1, 137.8, 136.7, 136.0, 129.6, 128.4, 128.3, 127.0, 115.4, 70.0, 62.3, 60.7, 14.4, 13.6;

HRMS (ESI-TOF): calc'd for $C_{23}H_{25}NO_4$ $[M+H]^+$ 380.1856; found 380.1860.

63. Diethyl 2-(bis(2-allylphenyl)amino)malonate (59i)



59i

Yield: 26% (**Method C**)

Physical State: beige colored viscous oily liquid;

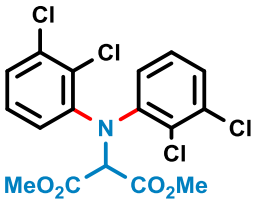
R_f = 0.41 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.08 (s, 1H), 5.65 (s, 2H), 4.99 (d, *J* = 10.1 Hz, 2H), 4.90 (d, *J* = 17.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 3.26 (dd, *J* = 15.5, 5.0 Hz, 2H), 3.16 (dd, *J* = 15.7, 5.3 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.7, 138.4, 137.5, 137.3, 131.9, 129.3, 128.0, 125.7, 115.9, 70.7, 62.2, 60.7, 37.9, 13.8;

HRMS (ESI-TOF): calc'd for $C_{25}H_{29}NO_4$ $[M+H]^+$ 408.2169; found 408.2169.

64. Dimethyl 2-(bis(2,3-dichlorophenyl)amino)malonate (59j)



59j

Yield: 54% (**Method C**)

Physical State: beige colored oily liquid;

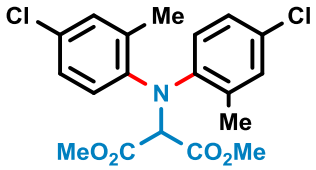
R_f = 0.24 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.47 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.1 Hz, 2H), 6.56 (s, 1H), 3.79 (s, 3H), 3.60 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.5, 136.4, 134.6, 131.4, 130.6, 130.3, 126.4, 70.2, 53.5, 52.2;

HRMS (ESI-TOF): calc'd for $C_{17}H_{13}Cl_4NO_4$ $[M+Na]^+$ 457.9491; found 457.9428.

65. Dimethyl 2-(bis(4-chloro-2-methylphenyl)amino)malonate (59k)



59k

Yield: 72% (**Method C**)

Physical State: beige colored oily liquid;

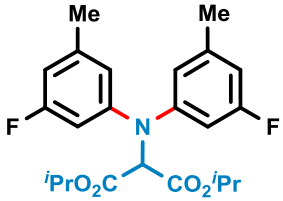
R_f = 0.23 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 2H), 7.18 – 7.12 (m, 4H), 6.24 (s, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 2.03 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.7, 138.7, 134.8, 133.7, 132.1, 130.8, 125.3, 69.4, 53.1, 52.1, 21.4;

HRMS (ESI-TOF): calc'd for $C_{19}H_{19}Cl_2NO_4$ $[M+Na]^+$ 418.0583; found 418.0588.

66. Diisopropyl 2-(bis(3-fluoro-5-methylphenyl)amino)malonate (59l)



59l

Yield: 29% (**Method C**)

Physical State: yellow colored oily liquid;

R_f = 0.22 (5% EtOAc/hexanes);

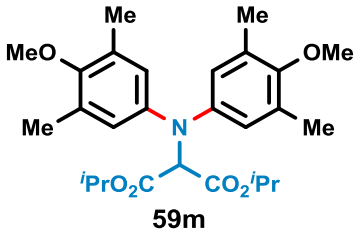
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.62 (s, 2H), 6.57 (d, *J* = 9.4 Hz, 4H), 5.23 (s, 1H), 5.04 (hept, *J* = 6.2 Hz, 2H), 2.27 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H), 1.15 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.2, 164.0, 162.4, 147.0, 146.9, 140.79, 140.73, 118.42, 118.40, 110.7, 110.6, 106.7, 106.5, 69.9, 67.9, 21.54, 21.52, 21.4, 21.3;

^{19}F NMR (471 MHz, $CDCl_3$): δ –113.0 (t, *J* = 10.1 Hz);

HRMS (ESI-TOF): calc'd for $C_{23}H_{27}F_2NO_4$ $[M+H]^+$ 420.1981; found 420.1981.

67. Diisopropyl 2-(bis(4-methoxy-3,5-dimethylphenyl)amino)malonate (59m)



59m

Yield: 67% (**Method C**)

Physical State: brown colored viscous oily liquid;

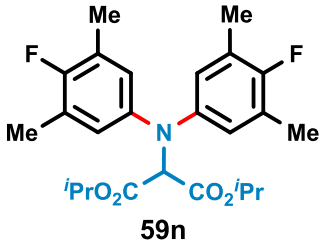
R_f = 0.36 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.66 (s, 4H), 5.21 (s, 1H), 5.02 (hept, *J* = 6.2 Hz, 2H), 3.67 (s, 6H), 2.20 (s, 12H), 1.17 (d, *J* = 6.3 Hz, 6H), 1.13 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 152.4, 141.8, 131.0, 122.2, 69.3, 68.1, 59.6, 21.4, 21.3, 16.1;

HRMS (ESI-TOF): calc'd for $C_{27}H_{37}NO_6$ $[M+H]^+$ 472.2694; found 472.2726.

68. Diisopropyl 2-(bis(4-fluoro-3,5-dimethylphenyl)amino)malonate (59n)



59n

Yield: 45% (**Method C**)

Physical State: light yellow colored solid;

R_f = 0.48 (10% EtOAc/hexanes);

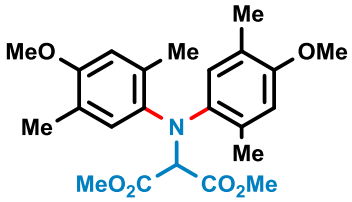
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.66 (d, *J* = 5.9 Hz, 4H), 5.21 (s, 1H), 5.04 (dt, *J* = 12.2, 6.0 Hz, 2H), 2.19 (s, 12H), 1.18 (dd, *J* = 18.1, 6.1 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 156.7, 155.1, 141.63, 141.61, 124.7, 124.6, 122.48, 122.45, 69.5, 68.3, 21.4, 21.3, 14.73, 14.71;

^{19}F NMR (471 MHz, $CDCl_3$): δ –129.3 (dtq, *J* = 6.5, 4.4, 2.2 Hz);

HRMS (ESI-TOF): calc'd for $C_{25}H_{31}F_2NO_4$ $[M+H]^+$ 448.2294; found 448.2252.

69. Dimethyl 2-(bis(4-methoxy-2,5-dimethylphenyl)amino)malonate (59o)



59o

Yield: 55% (**Method C**)

Physical State: pale pink colored puffy solid;

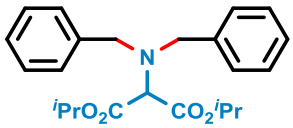
R_f = 0.23 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14 (s, 2H), 6.60 (s, 2H), 6.12 (s, 1H), 3.80 (d, *J* = 16.0 Hz, 9H), 3.62 (s, 3H), 2.18 (s, 6H), 2.06 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.0, 156.7, 135.2, 131.5, 128.6, 122.6, 113.6, 69.4, 54.9, 52.6, 51.8, 21.4, 15.8;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_6$ $[M+H]^+$ 438.1887; found 438.1886.

70. Diisopropyl 2-(dibenzylamino)malonate (59p)



59p

Yield: 53% (**Method C**)

Physical State: yellow-colored oily liquid;

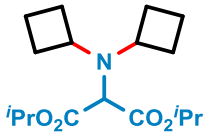
R_f = 0.69 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.2 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.28 (t, *J* = 7.3 Hz, 2H), 5.18 (hept, *J* = 6.2 Hz, 2H), 4.19 (s, 1H), 3.93 (s, 4H), 1.32 (dd, *J* = 6.3, 3.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.5, 138.9, 128.7, 128.1, 127.0, 68.7, 65.4, 55.3, 21.7, 21.6;

HRMS (ESI-TOF): calc'd for $C_{23}H_{29}NO_4$ $[M+H]^+$ 384.2169; found 384.2173.

71. Diisopropyl 2-(dicyclobutylamino)malonate (59q)



59q

Yield: 39% (**Method C**)

Physical State: colorless oily liquid;

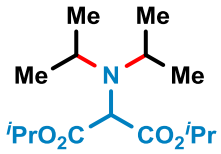
R_f = 0.51 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.05 (hept, *J* = 6.3 Hz, 2H), 4.15 (s, 1H), 3.58 (p, *J* = 8.5, 8.1 Hz, 2H), 2.05 – 1.95 (m, 8H), 1.57 (dq, *J* = 11.8, 6.9, 6.2 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.5, 68.7, 63.8, 54.8, 30.0, 21.66, 21.60, 14.9;

HRMS (ESI-TOF): calc'd for $C_{17}H_{29}NO_4$ $[M+H]^+$ 312.2169; found 312.2176.

72. Diisopropyl 2-(diisopropylamino)malonate (59r)



59r

Yield: 32% (**Method D**)

Physical State: light orange colored liquid;

R_f = 0.59 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.02 (hept, *J* = 6.3 Hz, 2H), 4.17 (s, 1H), 3.29 (hept, *J* = 6.6 Hz, 2H), 1.23 (dd, *J* = 6.3, 2.1 Hz, 12H), 1.03 (d, *J* = 6.7 Hz, 12H);

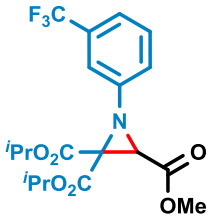
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 68.3, 62.2, 46.6, 22.3, 21.6, 21.5;

HRMS (ESI-TOF): calc'd for $C_{15}H_{29}NO_4$ $[M+H]^+$ 288.2169; found 288.2161.

Note: For this reaction to form **59r**, directly iPrMgCl·LiCl solution in THF was added on to the aminating agent **47**.

20. Characterization data of the amines formed by the addition of soft *C*-nucleophiles onto the iminomalonates in Fig. 7

1. 2,2-diisopropyl 3-methyl 1-(3-(trifluoromethyl)phenyl)aziridine-2,2,3 tricarboxylate (64a)



64a

Yield: 49% (**Method G**)

Physical State: pale brown colored viscous oily liquid;

R_f = 0.35 (20% EtOAc/hexanes);

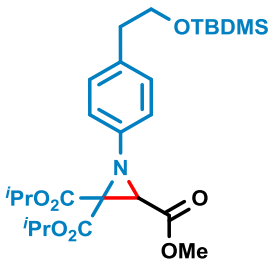
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.15 (hept, *J* = 6.2 Hz, 1H), 4.82 (hept, *J* = 6.2 Hz, 1H), 3.76 (s, 1H), 3.75 (s, 3H), 1.26 (dd, *J* = 21.5, 6.3 Hz, 6H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.95 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 163.0, 162.0, 146.6, 131.3, 131.1, 129.5, 124.4, 122.62, 122.60, 120.58, 120.55, 120.53, 120.50, 116.14, 116.11, 116.09, 116.06, 71.2, 69.9, 52.7, 52.6, 45.5, 21.29, 21.21, 20.8;

^{19}F NMR (471 MHz, $CDCl_3$): δ –62.8 (s);

HRMS (ESI-TOF): calc'd for $C_{19}H_{22}F_3NO_6$ $[M+H]^+$ 418.1472; found 418.1489.

2. 2,2-diisopropyl 3-methyl 1-(4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenyl) aziridine-2,2,3-tri-carboxylate (64b)



64b

Yield: 63% (**Method G**)

Physical State: brown colored viscous oily liquid;

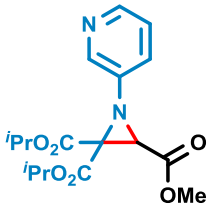
R_f = 0.41 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.15 (hept, *J* = 6.2 Hz, 1H), 4.80 (hept, *J* = 6.2 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 1H), 3.69 (t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 6.8 Hz, 2H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.81 (s, 9H), -0.09 (d, *J* = 2.1 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7, 163.5, 162.2, 144.0, 134.8, 129.4, 119.0, 70.6, 69.6, 64.1, 52.9, 52.5, 45.4, 38.6, 25.7, 21.4, 21.3, 21.2, 20.9, 18.0, –5.6;

HRMS (ESI-TOF): calc'd for $C_{26}H_{41}NO_7Si$ $[M+H]^+$ 508.2725; found 508.2768.

3. 2,2-diisopropyl 3-methyl 1-(pyridin-3-yl)aziridine-2,2,3-tricarboxylate (64c)



64c

Yield: 40% (**Method G**)

Physical State: brown colored viscous oily liquid;

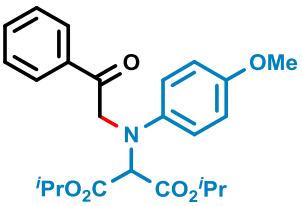
R_f = 0.27 (50% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.13 (dd, *J* = 7.9, 4.7 Hz, 1H), 5.14 (hept, *J* = 6.2 Hz, 1H), 4.83 (hept, *J* = 6.2 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 1H), 1.25 (dd, *J* = 20.1, 6.3 Hz, 6H), 1.08 (d, *J* = 6.2 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 162.9, 161.9, 145.1, 142.2, 141.5, 126.4, 123.2, 71.3, 70.0, 52.7, 52.3, 45.0, 21.4, 21.3, 21.2, 20.9;

HRMS (ESI-TOF): calc'd for $C_{17}H_{22}N_2O_6$ $[M+H]^+$ 351.1551; found 351.1593.

4. Diisopropyl 2-((4-methoxyphenyl)(2-oxo-2-phenylethyl)amino)malonate (66)



66

Yield: 66% (**Method H**)

Physical State: brown waxy solid;

R_f = 0.41 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 14.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 5.15 – 5.05 (m, 3H), 4.02 (s, 2H), 3.65 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 6H), 1.14 (d, *J* = 6.4 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.2, 168.8, 153.2, 137.9, 136.5, 133.1, 128.3, 127.8, 117.6, 114.4, 70.0, 66.9, 55.3, 40.8, 21.2;

HRMS (ESI-TOF): calc'd for $C_{24}H_{29}NO_6$ $[M+H]^+$ 428.2068; found 428.2069.

21. General experimental procedures for post-functionalization of the amines (as displayed in Figs. 6 & 7)

Method I: In a thick-walled flame dried reaction vial, the malonate protected amine (**55, 56 or 59**; 1.0 mmol, 1.0 equiv) was dissolved in anhydrous THF (10 mL, 0.1M) under argon. To this solution, NaH (60% in mineral oil; 1.0 mmol, 1.0 equiv) was added in one portion and stirred at room temperature for 10 min. Then this reaction mixture was cooled to −78 ^{o}C using a dry ice/acetone bath and N-chlorosuccinimide (NCS; 1.0 mmol, 1.0 equiv) dissolved in anhydrous THF (10 mL, 0.1M) was added dropwise over a period of 5 minutes and stirring was continued at −78 ^{o}C for 2 h. Then the reaction mixture was quenched using saturated NH_4Cl solution (3 mL) and allowed to warm to room temperature. The reaction mixture was then diluted with brine (20 mL) and extracted with ethyl acetate thrice (3 X 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method J: This procedure was adapted from the literature with slight modifications[8]. In a thick-walled uncapped reaction vial, the malonate protected amine (1.0 mmol, 1.0 equiv) was dissolved in absolute ethanol (12.8 mL, 0.078M). To this solution aqueous KOH solution (1M) (0.5 mmol, 0.5 equiv) was added at room temperature under constant stirring. Then this reaction mixture was heated to 50 ^{o}C (bath temperature) and this temperature was maintained for 6 h. Next, the reaction was quenched with saturated Na_2SO_3 solution (3 mL). Then EtOH was evaporated and the residue was extracted with ethyl acetate thrice (3 X 30 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography.

Method K: This procedure is based on the Corey-Bakshi-Shibata reduction and it was not optimized for the sole substrate (**66**). In a thick-walled flame dried reaction vial, malonate protected amine (**66**; 1.0 mmol, 1.0 equiv) made using **Method H** was dissolved in anhydrous THF (5.0 mL, 0.2M) under argon. To this solution, racemic CBS catalyst (1M solution in toluene, 10 mol%) was added first at room temperature followed by the BH_3·THF complex (1M solution in THF) (2.0 mmol, 2.0 equiv) added in one

portion and stirred overnight (14 h). Then the reaction was quenched using saturated NH_4Cl solution (3 mL). Next, the reaction mixture was diluted with brine (10 mL) and extracted with ethyl acetate thrice (3 X 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method L: In a thick walled flamed dried reaction vial, Diisopropyl 2-((2-hydroxy-2-phenylethyl)(4-methoxyphenyl)amino)malonate (**67**) (147 mg, 0.34 mmol, 1 equiv) was taken in anhydrous toluene (1.7 mL, 0.2M) under argon and to this $ZnCl_2$ (46.6 mg, 0.34 mmol, 1 equiv) was added in one portion at room temperature and this vial was capped with a screw cap. This reaction mixture was then heated at 50 ^oC overnight under constant stirring. Nextday morning when the progress was checked using TLC, the starting material got totally consumed. Then the reaction mixture was diluted with water (4 mL) and extracted with ethyl acetate thrice (3 X 4 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography.

Method M: This procedure was adapted from the literature and it was unoptimized[9]. *N*,*N*-diaryl amine (**61k**; 141 mg, 0.60 mmol), $Pd(OAc)_2$ (13.66 mg, 0.06 mmol, 10 mol%), K_2CO_3 (8.41 mg, 0.06 mmol, 10 mol%), pivalic acid (540 mg, 3.90 mmol, 6.4 equiv) were weighed open to air and transferred to a reaction vial and heated to 110 ^oC in an open vial overnight (14 h). The solution was then cooled to room temperature and diluted with DCM (10 mL). This mixture was washed with saturated solution of aqueous Na_2CO_3 twice (2 X 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography.

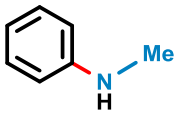
Method N: This procedure was adapted from the literature with slight modifications[10]. In a 25 mL flame dried round bottom flask, malonate protected amine **57b** (1.0 mmol, 1.0 equiv) was dissolved in anhydrous DCM (10 mL, 0.1M). To this, a solution of NaOH in MeOH (2.5M) (5.0 mmol, 5.0 equiv) was added and stirred at −78 ^oC as ozone was passed through the solution. After 45 min, the initial yellow colored reaction mixture

turned blue and a yellow precipitate has formed at the bottom. Then, ozone bubbling was stopped and oxygen flow was continued for 5 min to remove any excess ozone. The reaction mixture was diluted with water (20 mL) and extracted with DCM thrice (3 X 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Method O: In a thick-walled flame dried reaction vial, malonate protected amine (1.0 mmol, 1.0 equiv) was taken in anhydrous toluene (20 mL, 0.05M) under argon. To this solution Grubbs 2nd generation catalyst (10 or 15 mol%) was added and the reaction vial was sealed with the septum. This reaction mixture was heated to target temperature **T** for target time ***t*** under constant stirring. After confirming the completion of reaction by thin layer chromatography, the reaction was allowed to cool to room temperature. The reaction mixture was then filtered through celite pad. Toluene was evaporated and the crude product was purified by column chromatography. (The exact temperature and reaction times were presented along with the data for each substrate)

22. Characterization data of the post-functionalized amines (as displayed in Fig. 6)

1. *N*-methylaniline (60a)



60a

Yield: 53% (**Method I**)

Physical State: dark brown colored oily liquid;

R_f = 0.52 (8:1 EtOAc : hexanes);

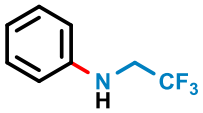
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 3.55 (s, 1H), 2.86 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.2, 129.1, 117.2, 112.3, 30.6;

HRMS (ESI-TOF): calc'd for C_7H_9N $[M+H]^+$ 108.0808; found 108.0812.

Spectral data was consistent with the data reported in the literature [11-14].

2. *N*-(2,2,2-trifluoroethyl)aniline (60b)



60b

Yield: 86% (**Method I**)

Physical State: wine red colored oily liquid;

R_f = 0.67 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14 – 7.09 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 1H), 3.63 (q, *J* = 9.0 Hz, 2H);

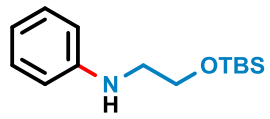
^{13}C NMR (151 MHz, $CDCl_3$): δ 146.2, 129.3, 127.8, 125.9, 124.1, 122.2, 119.0, 113.0, 46.2, 46.0, 45.8, 45.6;

^{19}F NMR (471 MHz, $CDCl_3$): δ –72.3 (t, *J* = 8.9 Hz);

HRMS (ESI-TOF): calc'd for $C_8H_8F_3N$ $[M+H]^+$ 176.0682; found 176.0680.

Spectral data was consistent with the data reported in the literature [15].

3. *N*-(2-((tert-butyldimethylsilyl)oxy)ethyl)aniline (60c)



60c

Yield: 90% (**Method I**)

Physical State: dark brownish yellow colored oily liquid;

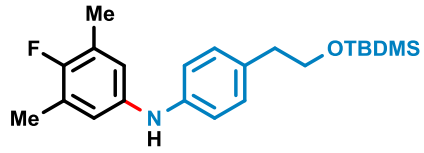
R_f = 0.73 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 2H), 4.06 (s, 1H), 3.87 (t, *J* = 5.4 Hz, 2H), 3.27 (t, *J* = 5.4 Hz, 2H), 0.97 (s, 9H), 0.13 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.3, 129.1, 117.4, 113.1, 61.5, 45.9, 25.8, 18.2;

HRMS (ESI-TOF): calc'd for $C_{14}H_{25}NOSi$ $[M+H]^+$ 252.1778; found 252.1772.

4. *N*-(4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenyl)-4-fluoro-3,5-dimethylaniline (60d)



60d

Yield: 82% (**Method I**)

Physical State: dark reddish brown viscous oily liquid;

R_f = 0.50 (10% EtOAc/hexanes);

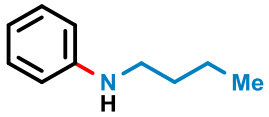
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 6.0 Hz, 2H), 5.41 (s, 1H), 3.81 (t, *J* = 7.2 Hz, 2H), 2.83 – 2.75 (m, 2H), 2.23 (s, 6H), 0.92 (s, 9H), 0.04 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.8, 154.2, 142.1, 138.5, 131.2, 129.9, 125.0, 124.9, 118.7, 117.4, 64.7, 38.8, 25.9, 18.3, 14.78, 14.75, –5.37;

^{19}F NMR (471 MHz, $CDCl_3$): δ –130.0 (s);

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}FNO_5Si$ $[M+H]^+$ 374.2310; found 374.2271.

5. *N*-butylaniline (60e)



60e

Yield: 84% (**Method I**)

Physical State: dark yellow colored oily liquid;

R_f = 0.69 (8:1 EtOAc : hexanes);

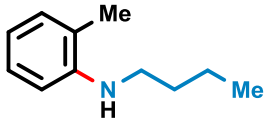
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 8.6, 7.1 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 3.58 (s, 1H), 3.16 (t, *J* = 7.2 Hz, 2H), 1.66 (p, *J* = 7.3 Hz, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.4, 129.1, 117.0, 112.6, 43.6, 31.6, 20.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{10}H_{15}N$ $[M+H]^+$ 150.1277; found 150.1282.

Spectral data was consistent with the data reported in the literature[16].

6. *N*-butyl-2-methylaniline (60f)



60f

Yield: 76% (**Method I**)

Physical State: dark yellow non-viscous liquid;

R_f = 0.65 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 1H), 3.30 (t, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.80 (p, *J* = 7.3 Hz, 2H), 1.61 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.3, 129.8, 127.0, 121.5, 116.5, 109.4, 43.5, 31.6, 20.3, 17.3, 13.8;

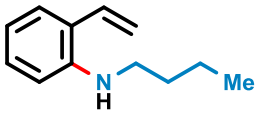
HRMS (ESI-TOF): calc'd for $C_{11}H_{17}N$ $[M+H]^+$ 164.1434; found 164.1459.

Spectral data was consistent with the data reported in the literature[17].

Note: For this substrate, the reaction did not go to completion at –78 ^oC even after stirring for 4 hours. Then it was allowed to warm to room temperature and stirred

overnight (14 hours) and some starting material was still remaining. Then an additional 1 equiv of NaH and NCS were added at room temperature and stirred at 50 ^{o}C for 3 hours and then reaction was totally finished.

7. *N*-butyl-2-vinylaniline (60g)



60g

Yield: 79% (**Method I**)

Physical State: dark yellow non-viscous liquid;

R_f = 0.60 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 1H), 6.91 – 6.80 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.72 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.42 (dd, *J* = 11.0, 1.5 Hz, 1H), 3.85 (s, 1H), 3.23 (t, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 7.3 Hz, 2H), 1.56 (h, *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H);

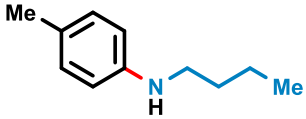
^{13}C NMR (151 MHz, $CDCl_3$): δ 145.4, 132.9, 128.8, 127.3, 123.9, 116.8, 115.8, 110.5, 43.6, 31.5, 20.3, 13.8;

HRMS (ESI-TOF): calc'd for $C_{12}H_{17}N$ $[M+H]^+$ 176.1434; found 176.1471.

Spectral data was consistent with the data reported in the literature[18].

Note: For this substrate, the reaction did not go to completion at –78 ^{o}C even after stirring for 4 hours. Then it was allowed to warm to room temperature and stirred overnight (14 hours) and the reaction was finished.

8. *N*-butyl-4-methylaniline (60h)



60h

Yield: 59% (**Method I**)

Physical State: dark yellow colored oily liquid;

R_f = 0.68 (8:1 EtOAc : hexanes);

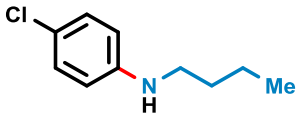
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.3 Hz, 2H), 3.37 (s, 1H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.63 (p, *J* = 7.2 Hz, 2H), 1.46 (h, *J* = 7.3 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 129.6, 126.3, 112.9, 44.0, 31.6, 20.3, 20.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{11}H_{17}N$ $[M+H]^+$ 164.1434; found 164.1441.

Spectral data was consistent with the data reported in the literature[19].

9. *N*-butyl-4-chloroaniline (60i)



60i

Yield: 49% (**Method I**)

Physical State: dark brownish yellow colored liquid;

R_f = 0.70 (8:1 EtOAc : hexanes);

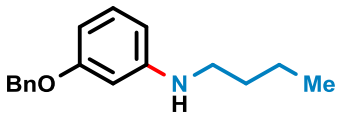
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 3.53 (s, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.0, 128.9, 121.5, 113.6, 43.7, 31.4, 20.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{10}H_{14}ClN$ $[M+H]^+$ 184.0888; found 184.0891.

Spectral data was consistent with the data reported in the literature[20].

10. 3-(benzyloxy)-*N*-butylaniline (60j)



60j

Yield: 41% (**Method I**)

Physical State: dark brown colored oily liquid;

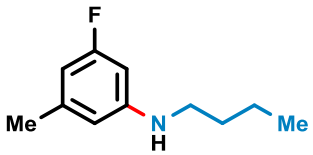
R_f = 0.53 (8:1 EtOAc : hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.42 – 6.35 (m, 1H), 6.32 – 6.25 (m, 2H), 5.07 (s, 2H), 3.65 (s, 1H), 3.13 (t, *J* = 6.7 Hz, 2H), 1.63 (p, *J* = 7.2 Hz, 2H), 1.46 (h, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.0, 149.8, 137.3, 129.8, 128.4, 127.7, 127.4, 106.2, 102.9, 99.4, 69.7, 43.6, 31.5, 20.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{17}H_{21}NO$ $[M+H]^+$ 256.1696; found 256.1709.

11. *N*-butyl-3-fluoro-5-methylaniline (60k)



60k

Yield: 92% (**Method I**)

Physical State: dark red colored oily liquid;

R_f = 0.73 (8:1 EtOAc : hexanes);

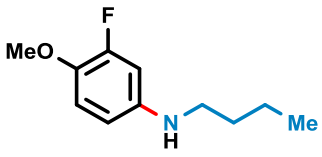
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.24 (dd, *J* = 23.5, 13.9 Hz, 2H), 6.14 (d, *J* = 11.5 Hz, 1H), 3.64 (s, 1H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.61 (p, *J* = 7.2 Hz, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.8, 163.2, 150.0, 149.9, 140.59, 140.52, 109.15, 109.14, 104.3, 104.1, 96.4, 96.2, 43.5, 31.4, 21.49, 21.48, 20.2, 13.8;

^{19}F NMR (471 MHz, $CDCl_3$): δ –113.2 (dd, *J* = 11.5, 9.6 Hz);

HRMS (ESI-TOF): calc'd for $C_{11}H_{16}FN$ $[M+H]^+$ 182.1340; found 182.1348.

12. *N*-butyl-3-fluoro-4-methoxyaniline (60l)



60l

Yield: 85% (**Method I**)

Physical State: dark yellow-brown oily liquid;

R_f = 0.46 (8:1 EtOAc : hexanes);

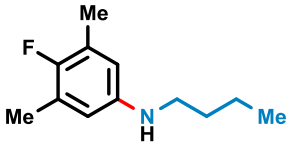
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.82 (t, *J* = 9.1 Hz, 1H), 6.39 (dd, *J* = 13.5, 2.4 Hz, 1H), 6.29 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 3H), 3.39 (s, 1H), 3.03 (t, *J* = 7.1 Hz, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.3, 152.7, 143.8, 143.7, 139.07, 139.00, 116.1, 116.0, 107.73, 107.71, 101.5, 101.3, 57.5, 44.2, 31.5, 20.1, 13.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ –133.7 (ddd, *J* = 13.5, 9.5, 1.3 Hz);

HRMS (ESI-TOF): calc'd for $C_{11}H_{16}FNO$ $[M+H]^+$ 198.1289; found 198.1299.

13. *N*-butyl-4-fluoro-3,5-dimethylaniline (60m)



60m

Yield: 60% (**Method I**)

Physical State: yellow colored oily liquid;

R_f = 0.70 (8:1 EtOAc : hexanes);

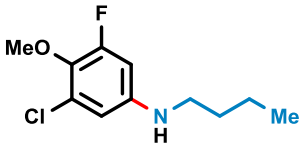
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.26 (d, *J* = 6.0 Hz, 2H), 3.22 (s, 1H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.21 (d, *J* = 1.9 Hz, 6H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 153.7, 152.2, 144.09, 144.08, 124.7, 124.5, 112.7, 112.6, 44.3, 31.7, 20.2, 14.84, 14.81, 13.8;

^{19}F NMR (471 MHz, $CDCl_3$): δ –136.7 (ddq, *J* = 6.1, 4.1, 2.2 Hz);

HRMS (ESI-TOF): calc'd for $C_{12}H_{18}FN$ $[M+H]^+$ 196.1496; found 196.1508.

14. *N*-butyl-3-chloro-5-fluoro-4-methoxyaniline (60n)



60n

Yield: 85% (**Method I**)

Physical State: brownish-yellow colored oily liquid;

R_f = 0.64 (8:1 EtOAc : hexanes);

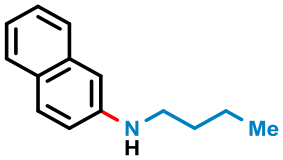
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.40 – 6.30 (m, 1H), 6.23 (dd, *J* = 12.7, 2.7 Hz, 1H), 3.82 (s, 3H), 3.61 (s, 1H), 3.01 (t, *J* = 7.1 Hz, 2H), 1.56 (p, *J* = 7.2 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.8, 156.1, 145.2, 145.1, 135.0, 134.9, 128.97, 128.93, 108.55, 108.54, 99.5, 99.4, 61.61, 61.60, 43.6, 31.2, 20.1, 13.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ –128.0 (dd, *J* = 12.6, 1.7 Hz);

HRMS (ESI-TOF): calc'd for $C_{11}H_{15}ClFNO$ $[M+H]^+$ 232.0899; found 232.0908.

15. *N*-butylnaphthalen-2-amine (60o)



60o

Yield: 59% (**Method I**)

Physical State: brown colored waxy solid;

R_f = 0.65 (8:1 EtOAc : hexanes);

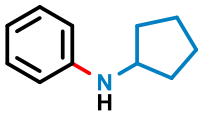
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 6.9 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 3.60 (s, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 1.54 (p, *J* = 7.3 Hz, 2H), 1.35 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.0, 135.2, 128.7, 127.5, 127.3, 126.2, 125.8, 121.7, 117.9, 104.1, 43.6, 31.4, 20.3, 13.8;

HRMS (ESI-TOF): calc'd for $C_{14}H_{17}N$ $[M+H]^+$ 200.1434; found 200.1446.

Spectral data was consistent with the data reported in the literature[21].

16. *N*-cyclopentylaniline (60p)



60p

Yield: 90% (**Method I**)

Physical State: dark brown colored oily liquid;

R_f = 0.75 (8:1 EtOAc : hexanes);

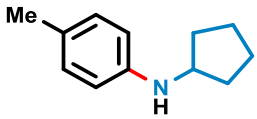
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 3.85 (p, *J* = 6.2 Hz, 1H), 3.65 (s, 1H), 2.08 (dq, *J* = 12.7, 6.7, 6.2 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.69 (tt, *J* = 11.6, 5.5 Hz, 2H), 1.53 (dq, *J* = 12.0, 6.3, 5.6 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 129.0, 116.8, 113.1, 54.5, 33.5, 24.0;

HRMS (ESI-TOF): calc'd for $C_{11}H_{15}N$ $[M+H]^+$ 162.1277; found 162.1283.

Spectral data was consistent with the data reported in the literature[22].

17. *N*-cyclopentyl-4-methylaniline (60q)



60q

Yield: 53% (**Method I**)

Physical State: dark brown colored oily liquid;

R_f = 0.58 (10% EtOAc/hexanes);

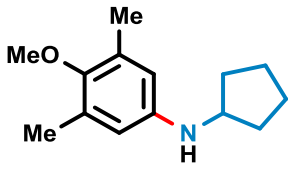
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 7.9 Hz, 2H), 3.80 (p, *J* = 6.1 Hz, 1H), 3.52 (s, 1H), 2.28 (s, 3H), 2.04 (dt, *J* = 12.4, 6.1 Hz, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.60 (m, 2H), 1.50 (dt, *J* = 11.9, 5.7 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 129.6, 126.0, 113.3, 54.9, 33.5, 24.0, 20.3;

HRMS (ESI-TOF): calc'd for $C_{12}H_{17}N$ $[M+H]^+$ 176.1434; found 176.1425.

Spectral data was consistent with the data reported in the literature[23].

18. *N*-cyclopentyl-4-methoxy-3,5-dimethylaniline (60r)



60r

Yield: 74% (**Method I**)

Physical State: pale orange colored solid (m.p. = 44-49 °C);

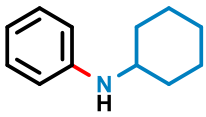
R_f = 0.41 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.29 (s, 2H), 3.74 (p, *J* = 6.2 Hz, 1H), 3.68 (s, 3H), 3.34 (s, 1H), 2.25 (s, 6H), 2.02 (dq, *J* = 12.7, 5.6 Hz, 2H), 1.75 (dq, *J* = 10.4, 6.3 Hz, 2H), 1.64 (dq, *J* = 9.0, 5.8, 4.6 Hz, 2H), 1.47 (dq, *J* = 14.0, 7.3 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.5, 144.0, 131.1, 113.1, 59.9, 55.0, 33.6, 23.9, 16.2;

HRMS (ESI-TOF): calc'd for $C_{14}H_{21}NO$ $[M+H]^+$ 220.1696; found 220.1702.

19. *N*-cyclohexylaniline (60s)



60s

Yield: 61% (**Method I**)

Physical State: pale yellow oily liquid;

R_f = 0.63 (8:1 EtOAc : hexanes);

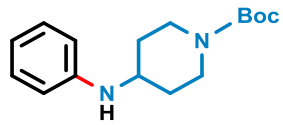
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 – 7.12 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 3.72 (s, 1H), 3.26 (tt, *J* = 10.1, 3.7 Hz, 1H), 2.07 (dd, *J* = 13.1, 4.0 Hz, 2H), 1.77 (dt, *J* = 13.4, 3.6 Hz, 2H), 1.66 (dt, *J* = 12.8, 3.7 Hz, 1H), 1.43 – 1.33 (m, 2H), 1.24 (ddd, *J* = 16.1, 9.8, 3.4 Hz, 1H), 1.21 – 1.11 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.1, 129.2, 116.9, 113.2, 51.8, 33.4, 25.9, 25.0;

HRMS (ESI-TOF): calc'd for $C_{12}H_{17}N$ $[M+H]^+$ 176.1434; found 176.1440.

Spectral data was consistent with the data reported in the literature[24].

20. *Tert*-butyl 4-(phenylamino)piperidine-1-carboxylate (60t)



60t

Yield: 88% (**Method I**)

Physical State: pale yellow colored flaky solid (m.p. = 130-138 °C);

R_f = 0.20 (8:1 EtOAc : hexanes);

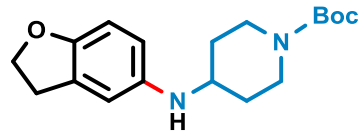
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 4.05 (s, 2H), 3.43 (tt, *J* = 10.1, 3.8 Hz, 2H), 2.93 (t, *J* = 11.0 Hz, 2H), 2.03 (d, *J* = 10.9 Hz, 2H), 1.47 (s, 9H), 1.39 – 1.28 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.7, 146.7, 129.2, 117.3, 113.2, 79.5, 50.0, 42.5, 32.3, 28.3;

HRMS (ESI-TOF): calc'd for $C_{16}H_{24}N_2O_2$ $[M+H]^+$ 277.1911; found 277.1917.

Spectral data was consistent with the data reported in the literature[25].

21. *Tert*-butyl 4-((2,3-dihydrobenzofuran-5-yl)amino)piperidine-1-carboxylate (60u)



60u

Yield: 80% (**Method I**)

Physical State: pale brown colored waxy solid;

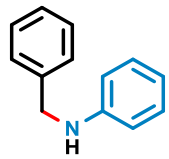
R_f = 0.28 (30% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.61 (d, *J* = 8.4 Hz, 1H), 6.54 (s, 1H), 6.39 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.47 (t, *J* = 8.6 Hz, 2H), 4.02 (s, 2H), 3.29 (dt, *J* = 10.1, 6.4 Hz, 1H), 3.12 (t, *J* = 8.5 Hz, 3H), 2.88 (s, 2H), 2.00 (d, *J* = 11.7 Hz, 2H), 1.45 (s, 9H), 1.32 – 1.21 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.6, 152.6, 140.7, 127.7, 113.6, 111.5, 109.3, 79.3, 70.7, 51.5, 32.4, 30.2, 28.3;

HRMS (ESI-TOF): calc'd for $C_{18}H_{26}N_2O_3$ $[M+H]^+$ 319.2016; found 319.2004.

22. *N*-benzylaniline (60v)



60v

Yield: 34% (**Method I**)

Physical State: yellow colored waxy solid;

R_f = 0.62 (10% EtOAc/hexanes);

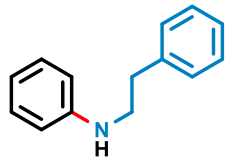
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (dt, *J* = 15.1, 7.5 Hz, 4H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 2H), 4.36 (s, 2H), 4.06 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.0, 139.3, 129.2, 128.6, 127.4, 127.1, 117.5, 112.8, 48.3;

HRMS (ESI-TOF): calc'd for $C_{13}H_{13}N$ $[M+H]^+$ 184.1121; found 184.1117.

Spectral data was consistent with the data reported in the literature[16].

23. *N*-phenethylaniline (60w)



60w

Yield: 88% (**Method I**)

Physical State: yellow-brown colored oily liquid;

R_f = 0.49 (10% EtOAc/hexanes);

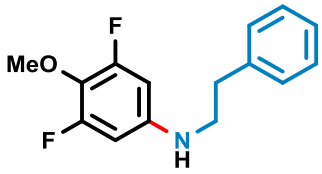
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 (dd, *J* = 11.2, 7.3 Hz, 3H), 7.21 – 7.17 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 2H), 3.67 (s, 1H), 3.41 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 7.0 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 139.2, 129.2, 128.7, 128.5, 126.3, 117.4, 117.3, 112.98, 112.91, 44.9, 35.4;

HRMS (ESI-TOF): calc'd for $C_{14}H_{15}N$ $[M+H]^+$ 198.1277; found 198.1276.

Spectral data was consistent with the data reported in the literature[26].

24. 3,5-difluoro-4-methoxy-*N*-phenethylaniline (60x)



60x

Yield: 53% (**Method I**)

Physical State: yellow colored oily liquid;

R_f = 0.35 (10% EtOAc/hexanes);

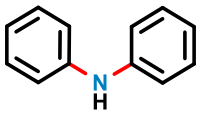
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.01 (d, *J* = 10.5 Hz, 2H), 3.76 (s, 3H), 3.59 (s, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 157.6, 156.1, 156.0, 144.1, 138.7, 128.67, 128.65, 127.3, 126.57, 126.56, 96.4, 96.2, 62.2, 45.0, 35.1;

^{19}F NMR (471 MHz, $CDCl_3$): δ –128.6 – –129.1 (m);

HRMS (ESI-TOF): calc'd for $C_{15}H_{15}F_2NO$ $[M+H]^+$ 264.1194; found 264.1199.

25. Diphenylamine (60y)



60y

Yield: 90% (**Method J**)

Physical State: off white waxy solid;

R_f = 0.55 (10% EtOAc/hexanes);

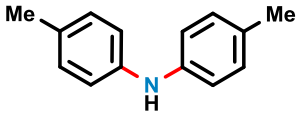
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.9 Hz, 4H), 7.10 (d, *J* = 7.7 Hz, 4H), 6.96 (t, *J* = 7.3 Hz, 2H), 5.71 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.0, 129.3, 120.9, 117.7;

HRMS (ESI-TOF): calc'd for $C_{12}H_{11}N$ $[M+H]^+$ 170.0964; found 179.0959.

Spectral data was consistent with the data reported in the literature[19].

26. Di-*p*-tolylamine (60z)



60z

Yield: 76% (**Method J**)

Physical State: off white waxy solid;

R_f = 0.73 (10% EtOAc/hexanes);

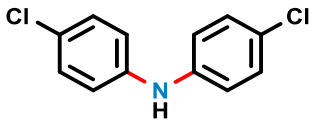
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.2 Hz, 4H), 6.99 (d, *J* = 8.3 Hz, 4H), 5.54 (s, 1H), 2.35 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.0, 130.0, 129.7, 117.8, 20.5;

HRMS (ESI-TOF): calc'd for $C_{14}H_{15}N$ $[M+H]^+$ 198.1277; found 198.1234.

Spectral data was consistent with the data reported in the literature[27].

27. Bis(4-chlorophenyl)amine (61a)



61a

Yield: 85% (**Method I**)

Physical State: off white waxy solid;

R_f = 0.47 (10% EtOAc/hexanes);

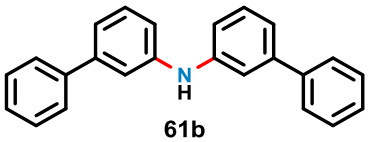
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 5.64 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.3, 129.3, 125.9, 119.0;

HRMS (ESI-TOF): calc'd for $C_{12}H_9Cl_2N$ $[M+H]^+$ 238.0185; found 238.0191.

Spectral data was consistent with the data reported in the literature[28].

28. Di([1,1'-biphenyl]-3-yl)amine (61b)



61b

Yield: 78% (**Method I**)

Physical State: pale yellow colored oily liquid;

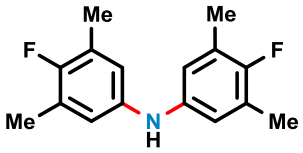
R_f = 0.37 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.2 Hz, 4H), 7.54 (t, *J* = 7.7 Hz, 4H), 7.49 – 7.41 (m, 6H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.92 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.3, 142.5, 141.0, 129.7, 128.6, 127.3, 127.0, 120.0, 116.7, 116.6;

HRMS (ESI-TOF): calc'd for $C_{24}H_{19}N$ $[M+H]^+$ 322.1590; found 322.1640.

29. Bis(4-fluoro-3,5-dimethylphenyl)amine (61c)



61c

Yield: 88% (**Method I**)

Physical State: orange colored solid;

R_f = 0.54 (10% EtOAc/hexanes);

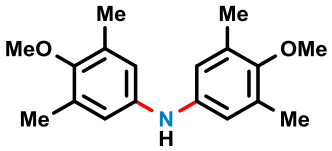
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.64 (d, *J* = 6.0 Hz, 4H), 5.23 (s, 1H), 2.23 (s, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.7, 154.1, 139.1, 125.1, 124.9, 118.4, 118.3, 14.7, 14.7;

^{19}F NMR (471 MHz, $CDCl_3$): δ −131.2 (s);

HRMS (ESI-TOF): calc'd for $C_{16}H_{17}F_2N$ $[M+H]^+$ 262.1402; found 262.1403.

30. Bis(4-methoxy-3,5-dimethylphenyl)amine (61d)



61d

Yield: 76% (**Method J**)

Physical State: off white waxy solid;

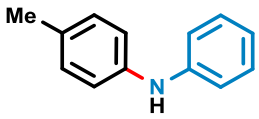
R_f = 0.46 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.69 (s, 4H), 5.37 (s, 1H), 3.72 (s, 6H), 2.27 (s, 12H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.1, 139.4, 131.4, 118.1, 59.8, 16.1;

HRMS (ESI-TOF): calc'd for $C_{18}H_{23}NO_2$ $[M+H]^+$ 286.1802; found 286.1768.

31. 4-methyl-*N*-phenylaniline (61e)



61e

Yield: 83% (**Method I**)

Physical State: grey colored waxy solid;

R_f = 0.60 (10% EtOAc/hexanes);

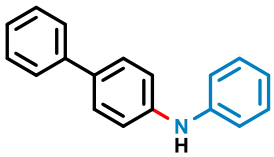
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.88 (dd, *J* = 7.5, 4.2 Hz, 4H), 6.77 (t, *J* = 7.3 Hz, 1H), 5.43 (s, 1H), 2.19 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.8, 140.2, 130.8, 129.7, 129.2, 120.2, 118.8, 116.8, 20.6;

HRMS (ESI-TOF): calc'd for $C_{13}H_{13}N$ $[M+H]^+$ 184.1121; found 184.1098.

Spectral data was consistent with the data reported in the literature[29].

32. *N*-phenyl-[1,1'-biphenyl]-4-amine (61f)



61f

Yield: 61% (**Method I**)

Physical State: off white colored solid (m.p. = 102-109 °C);

R_f = 0.71 (10% EtOAc/hexanes);

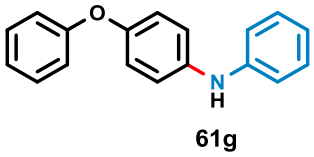
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 2H) 7.55, (d, *J* = 8.6 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.16 (dd, *J* = 10.4, 8.1 Hz, 4H), 7.00 (t, *J* = 7.3 Hz, 1H), 5.79 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 142.8, 142.5, 140.8, 133.6, 129.3, 128.7, 127.9, 126.5, 126.4, 121.1, 118.0, 117.7;

HRMS (ESI-TOF): calc'd for $C_{18}H_{15}N$ $[M+H]^+$ 246.1277; found 246.1321.

Spectral data was consistent with the data reported in the literature[30].

33. 4-phenoxy-*N*-phenylaniline (61g)



61g

Yield: 63% (**Method I**)

Physical State: off white solid (m.p. = 100-105 °C);

R_f = 0.37 (10% EtOAc/hexanes);

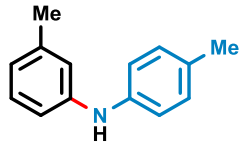
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (d, *J* = 38.2 Hz, 4H), 7.05 – 6.73 (m, 10H), 5.51 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.1, 151.1, 143.8, 138.6, 129.6, 129.3, 122.6, 120.4, 120.3, 117.9, 116.8;

HRMS (ESI-TOF): calc'd for $C_{18}H_{15}NO$ $[M+H]^+$ 262.1226; found 262.1224.

Spectral data was consistent with the data reported in the literature[31].

34. 3-methyl-*N*-(*p*-tolyl)aniline (61h)



61h

Yield: 82% (**Method I**)

Physical State: pale brown colored oily liquid;

R_f = 0.50 (10% EtOAc/hexanes);

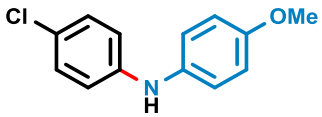
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.63 (s, 1H), 2.44 (d, *J* = 9.2 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 144.0, 140.5, 139.2, 130.8, 129.9, 129.2, 121.3, 119.0, 117.7, 114.1, 21.6, 20.8;

HRMS (ESI-TOF): calc'd for $C_{14}H_{15}N$ $[M+H]^+$ 198.1277; found 198.1310.

Spectral data was consistent with the data reported in the literature[32].

35. 4-chloro-*N*-(4-methoxyphenyl)aniline (61i)



61i

Yield: 76% (**Method I**)

Physical State: dark brown colored waxy solid;

R_f = 0.51 (10% EtOAc/hexanes);

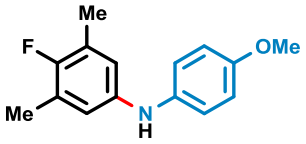
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.44 (s, 1H), 3.81 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.5, 143.8, 135.1, 129.1, 123.9, 122.5, 116.6, 114.7, 55.5;

HRMS (ESI-TOF): calc'd for $C_{13}H_{12}ClNO$ $[M+H]^+$ 234.0680; found 234.0673.

Spectral data was consistent with the data reported in the literature[33].

36. 4-fluoro-*N*-(4-methoxyphenyl)-3,5-dimethylaniline (61j)



61j

Yield: 74% (**Method I**)

Physical State: gray colored solid;

R_f = 0.33 (10% EtOAc/hexanes);

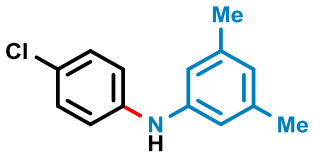
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 5.9 Hz, 2H), 5.26 (s, 1H), 3.82 (s, 3H), 2.23 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.2, 154.7, 153.6, 140.0, 136.8, 124.9, 124.8, 120.9, 116.95, 116.92, 114.6, 55.5, 14.75, 14.73;

^{19}F NMR (471 MHz, $CDCl_3$): δ –132.4 (s);

HRMS (ESI-TOF): calc'd for $C_{15}H_{16}FNO$ $[M+H]^+$ 246.1289; found 246.1288.

37. *N*-(4-chlorophenyl)-3,5-dimethylaniline (61k)



61k

Yield: 63% (**Method I**)

Physical State: off white, pale brown colored solid (m.p. = 56-62 ^oC);

R_f = 0.50 (10% EtOAc/hexanes);

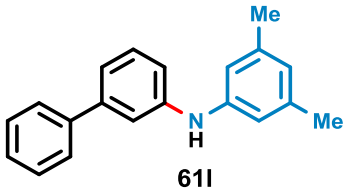
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 2H), 6.51 (s, 1H), 5.42 (s, 1H), 2.16 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 142.5, 142.0, 139.0, 129.1, 125.1, 123.3, 118.7, 115.8, 21.3;

HRMS (ESI-TOF): calc'd for $C_{14}H_{14}ClN$ $[M+H]^+$ 232.0888; found 232.0916.

Spectral data was consistent with the data reported in the literature[34].

38. *N*-(3,5-dimethylphenyl)-[1,1'-biphenyl]-3-amine (61l)



61l

Yield: 77% (**Method I**)

Physical State: Brown colored viscous oily liquid;

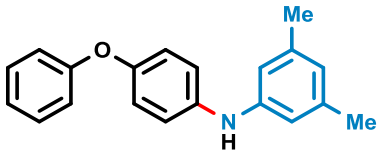
R_f = 0.49 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.28 (dt, *J* = 10.4, 7.6 Hz, 2H), 7.21 (t, *J* = 1.9 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.70 (s, 2H), 6.57 (s, 1H), 5.61 (s, 1H), 2.23 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 143.7, 142.9, 142.4, 141.1, 139.0, 129.6, 128.6, 127.2, 127.0, 123.0, 119.6, 116.57, 116.55, 115.8, 21.3;

HRMS (ESI-TOF): calc'd for $C_{20}H_{19}N$ $[M+H]^+$ 274.1590; found 274.1615.

39. 3,5-dimethyl-*N*-(4-phenoxyphenyl)aniline (61m)



61m

Yield: 82% (**Method I**)

Physical State: reddish brown colored viscous oily liquid

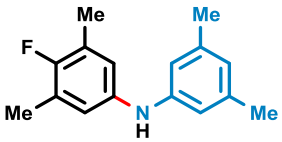
R_f = 0.44 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (ddd, *J* = 8.5, 5.8, 1.9 Hz, 2H), 7.15 (td, *J* = 14.9, 7.6 Hz, 5H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.75 (s, 2H), 6.68 (s, 1H), 5.60 (s, 1H), 2.38 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.1, 150.8, 143.7, 138.9, 129.5, 122.5, 122.3, 120.3, 120.1, 117.8, 114.6, 21.3;

HRMS (ESI-TOF): calc'd for $C_{20}H_{19}NO$ $[M+H]^+$ 290.1539; found 290.1580.

40. *N*-(3,5-dimethylphenyl)-4-fluoro-3,5-dimethylaniline (61n)



61n

Yield: 80% (**Method I**)

Physical State: dark reddish brown viscous oily liquid;

R_f = 0.51 (10% EtOAc/hexanes);

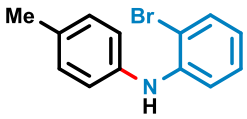
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.77 (d, *J* = 6.1 Hz, 2H), 6.64 (s, 2H), 6.60 (s, 1H), 5.39 (s, 1H), 2.32 (s, 6H), 2.28 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.0, 154.4, 144.2, 138.9, 138.09, 138.07, 125.0, 124.9, 122.1, 119.77, 119.74, 114.5, 21.3, 14.75, 14.72;

^{19}F NMR (471 MHz, $CDCl_3$): δ –130.3 (ddq, *J* = 6.4, 4.3, 2.3 Hz);

HRMS (ESI-TOF): calc'd for $C_{16}H_{18}FN$ $[M+H]^+$ 244.1496; found 244.1520.

41. 2-bromo-*N*-(*p*-tolyl)aniline (61o)



61o

Yield: 67% (**Method I**)

Physical State: pale purple colored oily liquid;

R_f = 0.71 (10% EtOAc/hexanes);

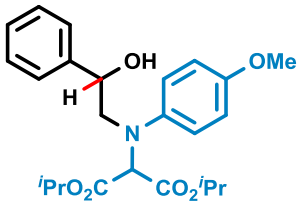
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.04 (m, 4H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.61 (ddd, *J* = 8.4, 5.8, 3.0 Hz, 1H), 5.94 (s, 1H), 2.26 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 142.1, 138.7, 132.8, 132.7, 129.9, 128.0, 121.3, 120.2, 120.1, 114.9, 111.4, 20.8;

HRMS (ESI-TOF): calc'd for $C_{13}H_{12}BrN$ $[M+H]^+$ 262.0226; found 262.0207.

23. Characterization data of the post-functionalized amines in Fig. 7

5. Diisopropyl 2-((2-hydroxy-2-phenylethyl)(4-methoxyphenyl)amino)malonate (67)



67

Yield: 53% (**Method K**)

Physical State: Brown colored viscous oily liquid;

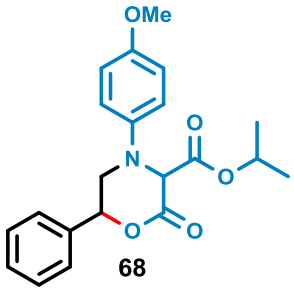
R_f = 0.26 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 4H), 7.16 (td, *J* = 5.8, 5.2, 3.3 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.07 (s, 1H), 5.01 (hept, *J* = 6.2 Hz, 1H), 4.86 (hept, *J* = 6.2 Hz, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 1H), 3.64 (s, 3H), 2.66 – 2.51 (m, 2H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.0, 168.4, 154.1, 144.1, 137.5, 128.2, 127.2, 125.4, 118.7, 114.4, 70.8, 70.1, 69.9, 68.9, 55.4, 41.7, 21.5, 21.3, 21.27, 21.24;

HRMS (ESI-TOF): calc'd for $C_{24}H_{31}NO_6$ $[M+H]^+$ 430.2224; found 430.2262.

6. Isopropyl 4-(4-methoxyphenyl)-2-oxo-6-phenylmorpholine-3-carboxylate (68)



68

Yield: 55% (**Method L**)

Physical State: Yellow colored waxy solid;

R_f = 0.31 (20% EtOAc/hexanes);

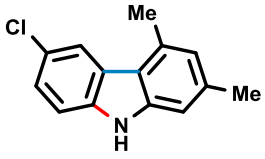
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 5H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 5.70 (dd, *J* = 10.3, 6.1 Hz, 1H), 5.04 (hept, *J* = 6.2 Hz, 1H), 4.76 (s, 1H),

3.73 (s, 3H), 3.49 (dd, *J* = 13.0, 6.1 Hz, 1H), 2.56 (dd, *J* = 13.0, 10.4 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.2, 167.8, 153.8, 137.9, 137.8, 128.9, 128.8, 125.8, 117.3, 114.7, 80.0, 71.1, 68.0, 55.5, 42.7, 21.5, 21.2.

HRMS (ESI-TOF): calc'd for $C_{21}H_{23}NO_5$ $[M+H]^+$ 370.1649; found 370.1632.

7. 6-chloro-2,4-dimethyl-9*H*-carbazole (69)



69

Yield: 14% (**Method M**)

Physical State: Brown colored waxy solid;

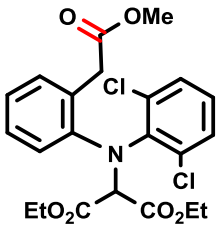
R_f = 0.26 (10% EtOAc/hexanes);

^{1}H NMR (600 MHz, DMSO-d_6): δ 11.32 (s, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.14 (s, 1H), 6.80 (s, 1H), 2.73 (s, 3H), 2.44 (s, 3H);

^{13}C NMR (151 MHz, DMSO-d_6): δ 140.8, 138.0, 135.7, 132.3, 124.1, 124.0, 122.5, 121.9, 120.7, 117.8, 111.9, 108.7, 21.5, 20.1;

HRMS (APCI-TOF): calc'd for $C_{14}H_{12}ClN$ $[M+H^+]$ 230.0731; found 230.0737.

8. Diethyl 2-((2,6-dichlorophenyl)(2-(2-methoxy-2-oxoethyl)phenyl)amino) malonate (70)



70

Yield: 50% (**Method N**)

Physical State: white solid (m.p. = 106-113 °C);

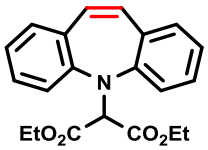
R_f = 0.24 (20% EtOAc/hexanes);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.94 (ddd, *J* = 24.3, 16.9, 7.0 Hz, 3H), 5.90 (s, 1H), 4.10 (dtd, *J* = 37.6, 12.4, 10.4, 4.7 Hz, 4H), 3.95 (d, *J* = 15.8 Hz, 1H), 3.63 (d, *J* = 14.2 Hz, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 171.1, 169.4, 154.9, 137.5, 135.5, 135.0, 133.7, 130.8, 130.7, 130.0, 129.0, 128.5, 128.3, 127.7, 126.6, 62.4, 61.2, 61.0, 51.8, 38.4, 14.2, 13.8;

HRMS (ESI-TOF): calc'd for $C_{22}H_{23}Cl_2NO_6$ $[M+H^+]$ 468.0975; found 468.0976.

9. Diethyl 2-(5*H*-dibenzo[*b*,*f*]azepin-5-yl)malonate (71)



71

Yield: 61% (**Method O**)

Physical State: colorless oily liquid;

R_f = 0.23 (20% EtOAc/hexanes);

T = 80 °C for 24 hours and 100 °C for 12 hours and 120 °C for another 12 hours;

***t* =** 48 hours;

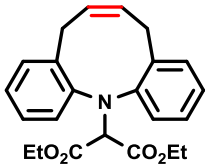
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (s, 2H), 7.40 (dd, *J* = 17.5, 7.7 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.07 (s, 2H), 6.00 (s, 1H), 4.14 (s, 4H), 1.35 – 1.07 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.9, 154.8, 136.7, 133.5, 131.2, 129.0, 128.2, 126.9, 123.0, 67.2, 61.5, 61.2, 14.4, 13.8;

HRMS (ESI-TOF): calc'd for $C_{21}H_{21}NO_4$ $[M+Na]^+$ 374.1363; found 374.1339.

Note: For the reaction to obtain this product (**71**), the conditions were unoptimized. After 24 hours of stirring at 80 °C, additional 5 mol% of the catalyst was added and the temperature increased to 100 °C and stirred for 12 hours and again increased to 120 °C and stirred for another 12 hours. Still the starting material was not totally consumed.

10. Diethyl 2-(5,8-dihydro-13*H*-dibenzo[*b*,*h*]azonin-13-yl)malonate (72)



72

Yield: 63% (**Method O**)

Physical State: colorless oily liquid;

R_f = 0.56 (20% EtOAc/hexanes);

T = 80 ^{o}C;

***t* =** 15hours

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.18 – 7.12 (m, 2H), 7.05 (d, *J* = 5.4 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.08 – 5.93 (m, 2H), 4.16 (ddt, *J* = 18.7, 11.6, 7.1 Hz, 2H), 4.04 (s, 1H), 3.90 (p, *J* = 6.8 Hz, 1H), 3.73 (dd, *J* = 27.6, 15.3 Hz, 2H), 3.00 (dd, *J* = 15.2, 9.1 Hz, 2H), 1.18 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.8, 153.4, 139.8, 139.6, 138.5, 135.9, 132.6, 132.1, 128.3, 128.2, 127.9, 126.1, 125.7, 124.9, 70.0, 63.0, 60.5, 32.5, 31.7, 14.4, 13.4;

HRMS (ESI-TOF): calc'd for $C_{23}H25NO_4$ $[M+H]^+$ 380.1856, $[M+Na]^+$ 402.1676; found 380.1790, 402.1676.

Note: For the reaction to get this product (**72**), 10 mol% of the catalyst was used.

24. Computational Details

Ground-state and transition-state geometries were optimized using Gaussian 09[35] with the M06-2X[36, 37] functional and the ultrafine integration grid. Stationary points were confirmed to be either minima or saddle-point structures by calculation and visualization of vibrational frequencies. Intrinsic reaction coordinate (IRC) calculations were used to verify key transition states. For geometries, 6-31+G(d,p) was used for all atoms expect Br where LANL2DZ was used. All optimizations were also carried out with the SMD continuum model for tetrahydrofuran (THF) or dichloromethane (DCM)[38]. M06-2X/def2-TZVP electronic energies were calculated in THF or DCM solvent using the M06-2X/6-31+G(d,p)[LANL2DZ] geometries. The def2-TZVP basis set was obtained from EMSL

(https://bse.pnl.gov/bse/portal, accessed 8/1/2016). Free energies and enthalpies reported refer to M06-2X/def2-TZVP//M06-2X/6-31+G(d,p)[LANL2DZ] where zero-point energy, thermal, and entropy corrections are used from the M06-2X/6-31+G(d,p)[LANL2DZ] geometries. 3D structures were generated using CYLview. A dinuclear phenylmagnesium bromide model where the phenyl groups bridge between two Mg centers was adopted in all reported calculations.

Proton affinities and reduction potentials

Below reports absolute proton affinities (in kcal/mol) for a variety of ester and diester aminating reagents. THF values are nearly identical to DCM values. As expected, the highly electrophilic diester imine with an *N*-OMs group has the smallest proton affinity of 106 kcal/mol (reaction **a**). Change of the *N*-OMs group to *N*-Ph increases the proton affinity by 22 kcal/mol (c.f. reaction **d**). Similarly, the *N*-PMP type diester imines have proton affinities greater than 129 kcal/mol. Comparison of the *N*-OMs diester (reaction **a**) to the *N*-OMs monoester shows the proton affinities increases to 119 kcal/mol. These proton affinities show the importance of the *N*-OMs group and diester group on controlling the electrophilicity of the imine.

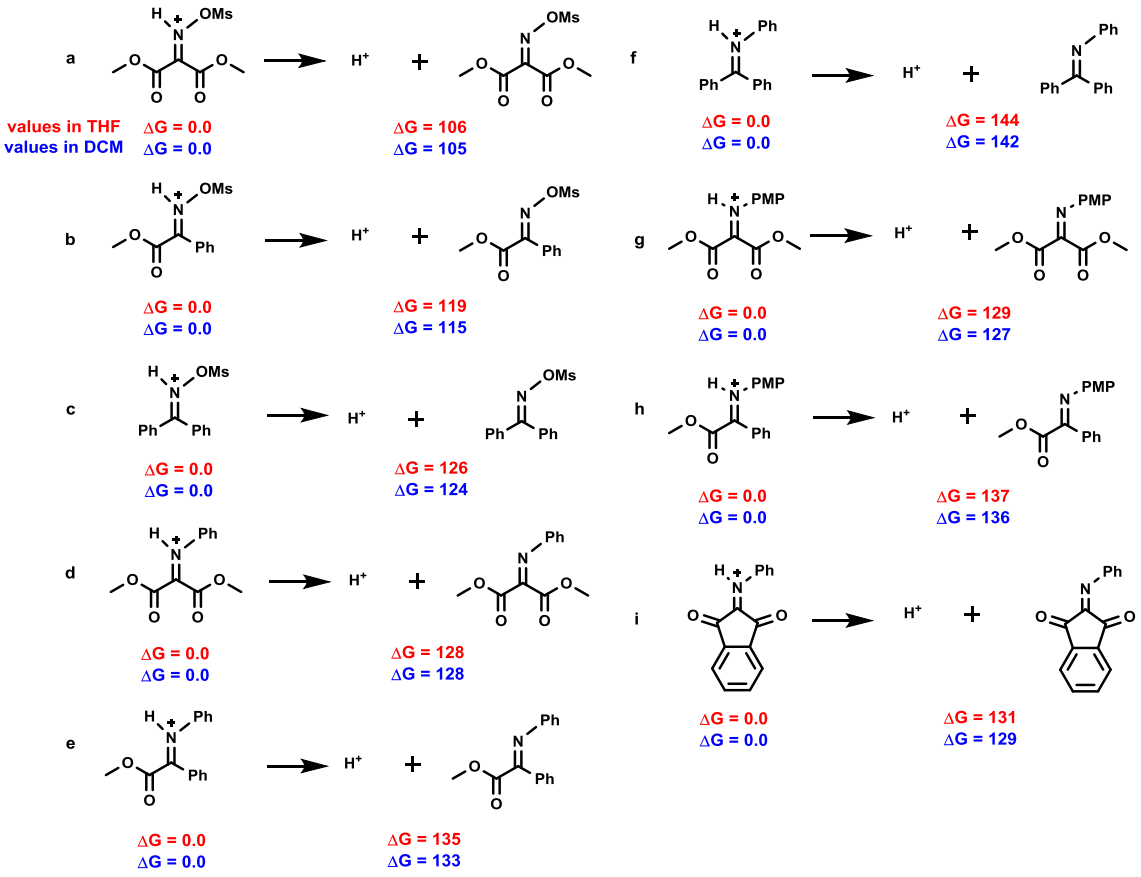


Table S10. Proton affinities (kcal/mol) for ester and diester aminating agents in THF (red) and DCM (blue)

The absolute reduction potential of *N*-PMP substituted dimethyl iminomalonate is compared to *N*-PMP substituted α-keto ester (reactions **j** and **k** shown below). The dimethyl iminomalonate has a 0.3 eV greater reduction potential compared to the α-oxime ester, which provides another measure of the electrophilic impact of the diester group.

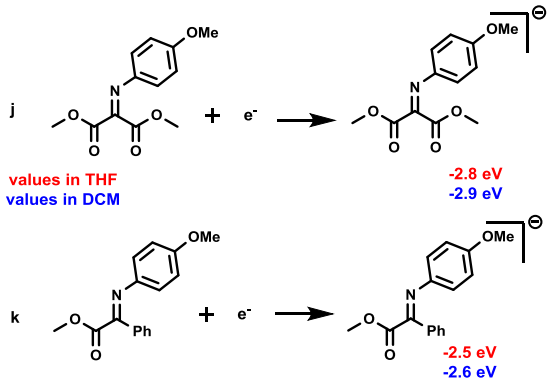


Table S11. Comparison of reduction potentials

Alkyl versus aryl Grignard reagents

Our calculations suggest a larger energy difference between transitions states for alkyl-type versus aryl-type Grignard additions to α-iminoesters. Below shows that the free energy barriers for the ethyl Grignard is less than 10 kcal/mol while for the phenyl Grignard the free energy barrier is greater than 20 kcal/mol.

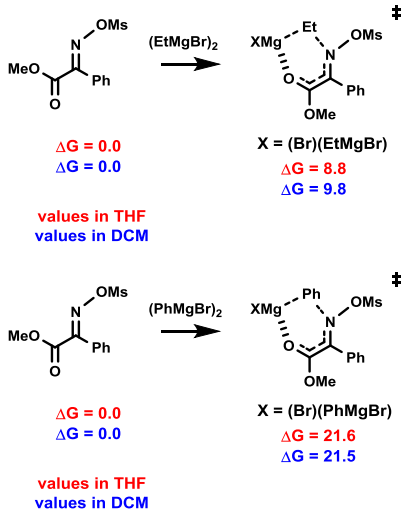


Table S12. Comparison of free energies of alkyl and aryl Grignard reagents

Further reaction pathway details

Our initial calculations focused on THF solvent since the Grignard reagents are prepared in this solvent. THF free energies are reported in red color below (kcal/mol). We also examined the energies in DCM solvent, including re-optimization of structures. DCM free energies are reported in blue color below. THF and DCM energies are nearly identical.

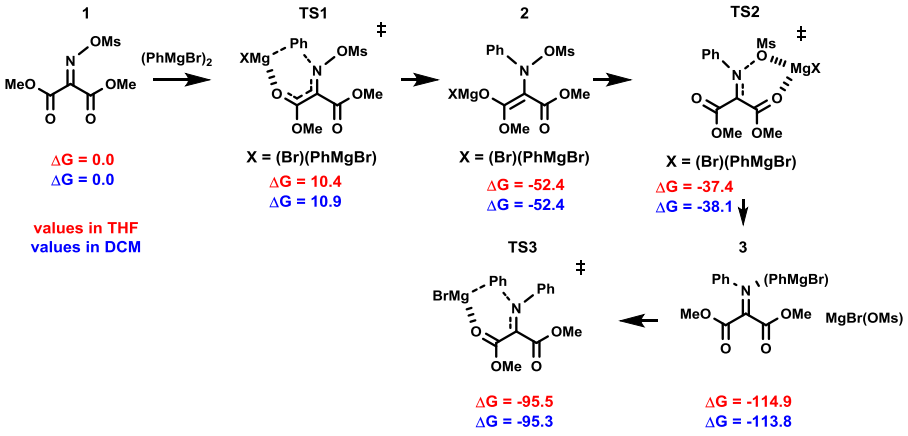


Table S13. Comparison of free energies in THF (red) and DCM (blue)

Experimentally, a mixture of *N*-attack and *C*-attack products are observed. Our calculations replicate the small the energy difference between these transition states. In THF solvent the *N*-attack transition state is slightly favored, but in DCM the *C*-attack transition state is slightly favored. We also ruled out the possibility of reaction at ester carbonyl. The C-attack transition state has a free energy barrier that is > 20 kcal/mol.

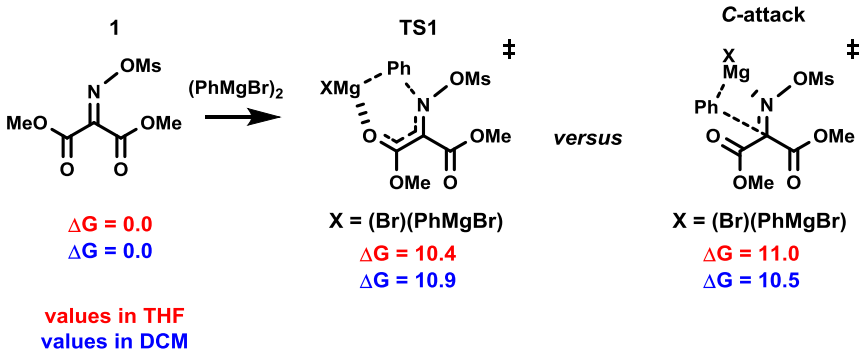


Table S14. Comparison of free energies of *N*-attack and *C*-attack

Xyz coordinates and thermochemistry in THF solvent (Hartree and Å)

1

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.859533
Enthalpy = -2102.46657
Free Energy = -2102.572128
M06-2X/def2-TZVP
Electronic Energy = -7225.566095

C	-0.15828600	2.63508300	-1.01480200
O	0.85795700	1.99439000	-1.25985700
C	-0.97915400	2.31533200	0.22355700
C	-2.16012000	3.16061500	0.65899300
O	-2.27414900	4.30878600	0.31389200
O	-2.97441200	2.50132100	1.45778700
O	-0.62379000	3.58955400	-1.75231600
C	0.07966000	3.84544500	-2.99077200
H	0.10725200	2.93220700	-3.58807000
H	-0.49746100	4.62156600	-3.48714900
H	1.09131600	4.18851000	-2.77070400
C	-4.16303000	3.21320300	1.85062400
H	-4.73394400	2.51097200	2.45415400
H	-3.89464000	4.09580200	2.43407300
H	-4.72708800	3.50820200	0.96321300
N	-0.48125800	1.29107900	0.79545200
O	-1.07966900	0.81110600	1.92339700
S	-0.24726900	-0.57789000	2.36106300

O	-0.75851200	-1.68368400	1.55664700
O	1.16306100	-0.24179800	2.21310800
C	-0.77154700	-0.69275600	4.02840500
H	-1.85748000	-0.80406400	4.03267800
H	-0.28448800	-1.58555100	4.43067000
H	-0.43896800	0.20871900	4.54586800
C	-1.79284500	-0.63589500	-1.29203800
C	-1.60994000	0.22055500	-2.39953600
C	-2.95239700	-0.38224800	-0.52802800
C	-2.48137600	1.27172900	-2.70047700
H	-0.74782800	0.08340800	-3.05304700
C	-3.84255400	0.65779800	-0.81234200
H	-3.17224000	-1.00576200	0.34033200
C	-3.59744400	1.50741400	-1.89218000
H	-2.29183900	1.91327200	-3.55900100
H	-4.71515700	0.81897200	-0.18273200
H	-4.27160100	2.33136000	-2.11217400
Mg	-0.39934900	-2.08234400	-0.57766000
Br	-0.76178100	-4.53956600	-0.52426000
Mg	1.62941800	0.62389600	0.12349400
C	1.81068600	-1.35396800	-0.71371200
C	1.75636600	-1.64808800	-2.09959800
C	2.46065600	-2.32802300	0.08286700
C	2.30795600	-2.80932400	-2.64971700
H	1.27312600	-0.94550400	-2.77858300
C	3.02898700	-3.48613600	-0.45175000
H	2.53252500	-2.17706000	1.15970800
C	2.95030100	-3.72877800	-1.82207900
H	2.23546700	-2.99455200	-3.71784700
H	3.51903600	-4.20398300	0.20020600
H	3.37688400	-4.63522600	-2.24174700
Br	3.35485200	2.12420400	1.08849500

$(PhMgBr)_2$

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -889.66743563

Enthalpy = -889.465265

Free Energy = -889.536643

M06-2X/def2-TZVP

Electronic Energy = -6011.99159

Mg	1.80327900	-0.01194500	-0.35822200
C	3.89456000	-0.00080700	-0.35622300
C	4.63984300	-0.01064700	-1.55189100
C	4.63888900	0.01881900	0.83990900
C	6.03770000	-0.00082900	-1.55979400
H	4.12831900	-0.02653900	-2.51320300

C	6.03673700	0.02821300	0.84869600
H	4.12657500	0.02778500	1.80088700
C	6.74133900	0.01852100	-0.35532600
H	6.57680400	-0.00861400	-2.50383100
H	6.57507500	0.04340400	1.79308300
H	7.82785800	0.02596900	-0.35497800
Br	0.00726600	-1.90029800	-0.43860400
Br	-0.00744500	1.86290200	-0.29172900
Mg	-1.80345500	-0.02545000	-0.37211200
C	-3.89473700	-0.03658700	-0.37411100
C	-4.63906300	-0.05625500	-1.57024400
C	-4.64002200	-0.02669800	0.82155500
C	-6.03691100	-0.06564300	-1.57903400
H	-4.12674600	-0.06526100	-2.53122100
C	-6.03787900	-0.03651000	0.82945600
H	-4.12849900	-0.01077100	1.78286800
C	-6.74151600	-0.05590200	-0.37501300
H	-6.57524800	-0.08086800	-2.52342100
H	-6.57698500	-0.02868700	1.77349100
H	-7.82803400	-0.06334500	-0.37536200

TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.836453

Enthalpy = -2102.445424

Free Energy = -2102.550607

M06-2X/def2-TZVP

Electronic Energy = -7225.547959

C	-3.24417200	-0.63627600	4.03339700
C	-3.36430300	-1.70424900	3.14523000
H	-2.46776000	1.35521500	4.32887900
C	-2.55548600	0.51464400	3.64614200
C	-2.79258200	-1.62486500	1.86935400
C	-2.08386500	-0.47880300	1.48464200
C	-1.99508400	0.58360400	2.36808900
H	-2.89631900	-2.48090400	1.20338100
H	-1.49405600	1.51292400	2.07715900
Mg	-0.57540400	-1.15693200	-0.10760300
Mg	2.38779400	-0.55066900	-0.13793000
H	-3.89918800	-2.60313500	3.44087000
H	-3.69312300	-0.69523800	5.02043900
C	4.38529100	0.08699700	-0.04326400
C	5.12352000	0.39351800	-1.20477800
C	5.07000700	0.25434000	1.17814500
C	6.44940800	0.83633000	-1.15935700
H	4.66038700	0.28352800	-2.18565300

C	6.39502500	0.69587900	1.24431000
H	4.56354200	0.03057800	2.11764000
C	7.09010100	0.99038800	0.07039200
H	6.98201600	1.05926200	-2.08079900
H	6.88601400	0.80752700	2.20815500
H	8.12060000	1.33230100	0.11365000
Br	1.21251100	-2.38236800	1.34020400
Br	1.05194500	-1.30947600	-2.24464900
C	-2.19196900	2.95027000	-0.27121300
O	-3.37032400	2.86928000	-0.00685600
C	-1.29317400	1.76540300	-0.33287800
C	0.09697600	1.72656100	0.09458400
O	0.66686200	0.61045100	0.22974500
O	0.68240900	2.85148200	0.38009600
O	-1.55395900	4.07861600	-0.56017100
C	-2.35126000	5.27269700	-0.50589100
H	-2.76988100	5.40067800	0.49423800
H	-1.66967000	6.08784600	-0.74081400
H	-3.15516400	5.22247000	-1.24281700
C	2.04728600	2.79866500	0.85290800
H	2.29895700	3.82739400	1.10014400
H	2.11083900	2.16385100	1.73927200
H	2.69897200	2.42854100	0.05876500
N	-1.71584100	0.53922100	-0.58537200
O	-2.98048700	0.44473800	-1.10775600
S	-3.20275700	-1.06104100	-1.79859300
O	-3.18291600	-0.90779200	-3.23034600
O	-2.20973400	-1.95203600	-1.17265700
C	-4.81629700	-1.40542200	-1.19050000
H	-5.48839400	-0.64126600	-1.58607800
H	-5.08567600	-2.39307100	-1.57395900
H	-4.78300300	-1.39193700	-0.10000100

2

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.94382

Enthalpy = -2102.549795

Free Energy = -2102.652029

M06-2X/def2-TZVP

Electronic Energy = -7225.653969

C	-2.39769000	1.16796300	-1.55315800
O	-1.38289400	1.90164100	-1.61497300
C	-2.57980800	0.11130200	-0.63821600
C	-3.86687100	-0.42042500	-0.29171100
O	-4.96908400	0.08573100	-0.60740900
O	-3.82298300	-1.49337500	0.47661500

O	-3.40799200	1.39704800	-2.43956000
C	-3.14326600	2.39129600	-3.46605900
H	-2.23081800	2.12832200	-3.99913200
H	-4.00682500	2.34627300	-4.12729500
H	-3.04933800	3.38396000	-3.01798100
C	-5.07887300	-2.01631800	0.94365900
H	-4.81850400	-2.86978600	1.56663200
H	-5.60722000	-1.26216000	1.52938200
H	-5.69263400	-2.33291100	0.09910000
N	-1.41222300	-0.37164200	-0.01453700
O	-1.40151300	-0.06343300	1.39908600
S	-0.12685000	0.88753000	1.73279000
O	1.10298500	0.28722600	1.27473800
O	-0.42584800	2.24954400	1.24167900
C	-0.27474800	0.89739600	3.48666700
H	-0.11717600	-0.12145000	3.84354800
H	0.50706300	1.56453400	3.85707900
H	-1.26488900	1.27185500	3.75051400
C	-1.02130200	-1.73064400	-0.22920000
C	-1.09071000	-2.21806500	-1.53934600
C	-0.53602100	-2.54427800	0.79470800
C	-0.68341200	-3.51979600	-1.81329000
H	-1.45645800	-1.57961600	-2.33725500
C	-0.13105700	-3.84719700	0.50298000
H	-0.47895500	-2.17958900	1.81248000
C	-0.20254900	-4.34491200	-0.79554000
H	-0.74077300	-3.88699700	-2.83344700
H	0.24088600	-4.47416800	1.30782200
H	0.11381200	-5.35957700	-1.01434100
Mg	-1.31219100	3.31754200	-0.21609000
Br	0.01641300	5.22799700	-0.95168600
Mg	-5.11759400	1.96084800	-1.25828500
C	-4.03475300	3.44873200	-0.12701400
C	-4.09252400	4.80910200	-0.52136300
C	-3.35884700	3.21688300	1.09816200
C	-3.54960600	5.84874000	0.23643300
H	-4.59111600	5.07330500	-1.45342100
C	-2.78543200	4.25087200	1.86607200
H	-3.28566500	2.19781200	1.48463100
C	-2.89080000	5.57274900	1.43611900
H	-3.62130500	6.87374200	-0.11606200
H	-2.26928800	4.01975200	2.79445000
H	-2.44806000	6.37463800	2.01839300
Br	-6.93237300	2.42353900	-2.84704100

TS2

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.918001
Enthalpy = -2102.525638
Free Energy = -2102.626524
M06-2X/def2-TZVP
Electronic Energy = -7225.629292

C	0.97513500	1.14684100	-1.74425700
O	1.34728800	0.72575300	-2.81152700
C	1.62616500	0.91406700	-0.46002200
C	1.27329300	1.54834300	0.77726000
O	0.33014700	2.35923900	0.94861000
O	2.01839300	1.18534800	1.80873400
O	-0.15377700	1.96293200	-1.69697800
C	-0.66003100	2.37117600	-2.99305700
H	-1.01261300	1.50047100	-3.54617200
H	-1.47667800	3.06053400	-2.78392900
H	0.13367800	2.87263200	-3.54589000
C	1.68618800	1.75558700	3.08533600
H	2.39155400	1.31362200	3.78659800
H	1.80540800	2.83999200	3.05786100
H	0.66042500	1.50056700	3.36029100
N	2.56655600	-0.07250600	-0.51344300
O	1.98595000	-1.38386900	0.33924000
S	1.26705600	-2.35483400	-0.64848600
O	0.04871100	-1.66187400	-1.17691700
O	2.13996700	-2.88516100	-1.67315500
C	0.73326100	-3.62539200	0.45975000
H	0.11646200	-3.18074000	1.24363900
H	0.16022800	-4.33983100	-0.13655900
H	1.62463600	-4.09751100	0.87648400
Mg	-1.36217800	2.04356000	-0.01649500
Br	-2.93601200	3.90057700	-0.35024100
Mg	-1.83654800	-1.33669600	-0.73809000
C	-2.09040100	0.15837200	0.83669500
C	-3.47535400	0.09812100	1.12577500
C	-1.24455600	-0.53370800	1.74340400
C	-3.98013500	-0.57535200	2.23998800
H	-4.18270300	0.60004400	0.46740700
C	-1.73583300	-1.21659200	2.85856200
H	-0.16401100	-0.53676300	1.58255300
C	-3.10864900	-1.23579800	3.10501600
H	-5.04947200	-0.59177400	2.42863100
H	-1.05249800	-1.72719900	3.53156900
H	-3.49833000	-1.76804300	3.96777300
Br	-3.05064000	-3.46200800	-0.67111600
C	3.89361600	0.06488800	-0.03018600

C	4.46130800	1.34553100	-0.00420500
C	4.68636600	-1.05180000	0.25603700
C	5.80866800	1.49952000	0.31100000
H	3.85517500	2.21122600	-0.24896000
C	6.02816000	-0.87955800	0.58557200
H	4.25793000	-2.04557000	0.22420100
C	6.59951400	0.39239300	0.61456600
H	6.23659000	2.49740900	0.32151200
H	6.63133300	-1.75339100	0.81262300
H	7.64790400	0.51814100	0.86529600

3

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2103.034509

Enthalpy = -2102.63971

Free Energy = -2102.746515

M06-2X/def2-TZVP

Electronic Energy = -7225.749857

C	-0.35951600	-1.57376300	-1.04103800
O	-0.00960800	-2.65808700	-1.50700700
C	-1.81437700	-1.31967400	-0.76689100
C	-2.72790700	-2.40075000	-1.31816900
O	-2.70980000	-2.73535300	-2.49327200
O	-3.50620400	-2.92882300	-0.42094900
O	0.43972200	-0.61129500	-0.71523400
C	1.84080300	-0.80384000	-1.01966800
H	1.96231400	-0.90794900	-2.10043800
H	2.33609800	0.09604900	-0.66284800
H	2.21456100	-1.68856000	-0.50195800
C	-4.47318900	-3.90119300	-0.89148400
H	-4.99788000	-4.23380200	0.00047100
H	-5.15608400	-3.41523800	-1.59087300
H	-3.95760700	-4.73227200	-1.37625600
N	-2.17109900	-0.28735000	-0.12725400
O	-0.79748200	-0.36960700	-3.43536000
S	-0.34873200	-1.16407800	-4.58187900
O	0.86948100	-1.99233200	-4.26595700
O	-1.42836500	-2.05078200	-5.14706100
C	0.12261000	-0.09456900	-5.90349800
H	0.92444900	0.54967900	-5.53978300
H	0.46211400	-0.70906400	-6.73800800
H	-0.75300400	0.49436400	-6.18081900
Mg	0.86494200	-3.60149100	-3.07715300
Br	3.15944800	-4.25854200	-2.45727900
Mg	-2.25992100	-3.60302200	-4.24242400
C	-0.65335200	-5.04501100	-3.66245700

C	-1.35943500	-5.74387900	-2.65221100
C	-0.55859100	-5.70952100	-4.90970700
C	-1.91347700	-7.00930700	-2.85699500
H	-1.47117600	-5.28983700	-1.66605600
C	-1.10672900	-6.97568000	-5.13233100
H	-0.03783400	-5.22415100	-5.73555500
C	-1.78602200	-7.62501000	-4.10259000
H	-2.44356200	-7.51263100	-2.05290900
H	-1.01069000	-7.45028000	-6.10472400
H	-2.22188500	-8.60555200	-4.27139400
Br	-4.37506200	-4.33453000	-5.24998500
C	-3.52661000	0.04031400	0.07541200
C	-4.47122600	-0.02598500	-0.95730300
C	-3.88911500	0.51141700	1.34153100
C	-5.78979600	0.33921800	-0.70082500
H	-4.16844600	-0.31005300	-1.96250000
C	-5.21653500	0.84271500	1.59392000
H	-3.13048200	0.59075400	2.11397300
C	-6.16817700	0.75756800	0.57563300
H	-6.52014300	0.30330700	-1.50306100
H	-5.50578600	1.18369200	2.58291900
H	-7.19895500	1.03550800	0.77141700

OMs anion

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -663.7396229

Enthalpy = -663.682761

Free Energy = -663.716914

M06-2X/def2-TZVP

Electronic Energy = -663.929577

O	0.55132800	1.33254000	-0.52522600
S	0.15830900	0.00013500	-0.00063300
O	0.54586700	-1.12071700	-0.89433800
O	0.55900400	-0.21387300	1.41353800
C	-1.63649600	0.00168200	0.00603500
H	-1.99162700	0.15840000	-1.01442200
H	-1.98512800	-0.96169000	0.38273300
H	-1.98680400	0.80743900	0.65381600

C_6H_5 anion

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -231.5909347

Enthalpy = -231.498287

Free Energy = -231.531018

M06-2X/def2-TZVP

Electronic Energy = -231.6650036

C	0.00000100	-1.36495300	0.00000000
C	1.19904500	-0.64903000	-0.00000100
C	1.17735900	0.75318700	0.00000200
C	-0.00000100	1.54363000	0.00000000
C	-1.17736000	0.75318600	-0.00000200
C	-1.19904500	-0.64903200	0.00000100
H	0.00000100	-2.45244700	0.00000000
H	2.14836600	-1.18387700	-0.00000100
H	2.15252000	1.24913800	-0.00000200
H	-2.15252200	1.24913600	0.00000200
H	-2.14836400	-1.18387900	0.00000100

TS3

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1670.854604

Enthalpy = -1670.425739

Free Energy = -1670.530162

M06-2X/def2-TZVP

Electronic Energy = -6793.453525

C	3.64517400	-2.81934100	-2.78294400
C	3.72590000	-3.19687000	-1.44091700
H	2.80334700	-1.42702100	-4.19988300
C	2.85160800	-1.73415600	-3.15890200
C	3.00640700	-2.49071200	-0.47200800
C	2.18676900	-1.41975300	-0.85087200
C	2.14262700	-1.03015600	-2.18152700
H	3.09411000	-2.79023500	0.57172000
H	1.56863600	-0.14864500	-2.48492400
Mg	0.41359300	-1.18052600	0.46969100
Mg	-2.50382200	-0.54899200	0.29304100
H	4.35184800	-4.03536800	-1.14745600
H	4.21408500	-3.36025200	-3.53352000
C	-4.42129200	0.27469800	0.07850000
C	-4.98964800	1.11484100	1.05725800
C	-5.20970200	0.05015100	-1.06903600
C	-6.25340500	1.69528900	0.90816800
H	-4.43932400	1.32981100	1.97345300
C	-6.47515500	0.62072300	-1.23593200
H	-4.83573600	-0.59412600	-1.86532300
C	-7.00116700	1.44945800	-0.24378400
H	-6.65452000	2.33671800	1.68920900
H	-7.05070400	0.41813600	-2.13601500
H	-7.98414900	1.89615800	-0.36586600
Br	-1.45288000	-2.80530800	-0.49597500
Br	-1.10363000	-0.65198500	2.54567900
C	2.20547500	2.44632100	-1.09292400

O	3.31163000	2.19599200	-1.51833600
C	1.30219100	1.42056800	-0.48926500
C	-0.08938100	1.29466000	-0.88372000
O	-0.75218500	0.28698200	-0.50350700
O	-0.60031800	2.19863400	-1.66773300
O	1.66491900	3.66191500	-1.07648900
C	2.46281000	4.70367000	-1.66086200
H	2.67068000	4.47637900	-2.70847700
H	1.86650900	5.61026200	-1.57760000
H	3.40061800	4.81070500	-1.11210600
C	-1.98111000	2.04508700	-2.06532700
H	-2.17014700	2.86571500	-2.75350700
H	-2.12013200	1.08456900	-2.56636300
H	-2.62741100	2.12722500	-1.18918700
N	1.70066600	0.48243100	0.35228300
C	2.89459800	0.61439000	1.14001900
C	2.67669000	0.87936500	2.49549400
C	4.19049200	0.46028700	0.64565500
C	3.76440800	1.02108300	3.35519300
H	1.65899100	0.98465400	2.86091800
C	5.26928400	0.58612200	1.51843100
H	4.34197900	0.23800100	-0.40359500
C	5.06236100	0.87138500	2.86885300
H	3.59181300	1.23875900	4.40449900
H	6.27767900	0.45993100	1.13677900
H	5.90978300	0.97020000	3.54006400

4

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1902.636148

Enthalpy = -1902.108443

Free Energy = -1902.226455

M06-2X/def2-TZVP

Electronic Energy = -7025.305301

C	-0.41444500	-1.18691400	1.90355800
O	-0.15332600	-1.44972500	3.12920800
C	-1.34370600	-0.24491800	1.45019700
C	-2.05738800	0.58102600	2.36992400
O	-1.93364200	0.59442100	3.61252100
O	-2.91810300	1.41995900	1.79063100
O	0.25258800	-1.83615100	0.95092600
C	1.34458000	-2.67756400	1.34347300
H	0.97728700	-3.60308900	1.79304700
H	1.87584500	-2.90609600	0.42022200
H	2.00673200	-2.15485400	2.03727200
C	-3.67104900	2.26520700	2.66932400

H	-4.29083200	2.87901300	2.01706600
H	-4.29759300	1.66408600	3.33187900
H	-3.00608400	2.89381200	3.26511400
N	-1.54765000	-0.07558300	0.05733500
C	-2.68686300	-0.67524800	-0.52681000
C	-3.13108500	-1.92618100	-0.07624700
C	-3.42431900	-0.01355300	-1.52028100
C	-4.27957900	-2.50304600	-0.61498900
H	-2.57450700	-2.44815800	0.69631300
C	-4.56350400	-0.60264300	-2.06125400
H	-3.10792000	0.96832800	-1.85838000
C	-5.00130700	-1.85088800	-1.61437500
H	-4.60347800	-3.47463000	-0.25267400
H	-5.12185800	-0.07159800	-2.82704800
H	-5.89367700	-2.30401200	-2.03461400
Mg	-0.32372000	-3.06268200	4.43548000
Mg	-0.87393100	-0.50253400	4.91503700
C	1.12019900	-2.03041700	5.68557700
C	1.26214500	-2.36684500	7.05112700
C	2.14309900	-1.20925100	5.16535100
C	2.33025300	-1.93008300	7.83580400
H	0.51282200	-2.99925900	7.52870500
C	3.21931500	-0.75050800	5.93341300
H	2.10577500	-0.90892300	4.11696000
C	3.31447100	-1.11180600	7.27562400
H	2.39636000	-2.21895700	8.88222400
H	3.97863300	-0.11254000	5.48688500
H	4.14594200	-0.76094300	7.88142800
Br	-0.47293500	-5.35806300	3.51217400
Br	-0.63134400	1.22363400	6.71590400
C	-0.64050300	0.70472100	-0.68172500
C	-0.43133900	0.47670400	-2.05307100
C	0.12166100	1.69846400	-0.04654500
C	0.49265900	1.23716800	-2.76321300
H	-0.98416300	-0.30765600	-2.55950500
C	1.04961100	2.44803000	-0.76643900
H	-0.01043300	1.88277900	1.01464600
C	1.24055400	2.23182600	-2.13054300
H	0.63762300	1.03653200	-3.82109600
H	1.62321200	3.21239900	-0.24974900
H	1.96303100	2.81921000	-2.68814100
C	-3.91276400	-3.22989000	6.74685500
C	-4.87908000	-3.31115300	5.74368200
C	-4.57937800	-2.85634600	4.45814500
C	-3.31463500	-2.32770300	4.19103400
C	-2.30189100	-2.22683900	5.17095600

C	-2.65321600	-2.69821600	6.45381500
H	-4.14181200	-3.57795100	7.75101400
H	-5.86005900	-3.72493400	5.96207400
H	-5.32768400	-2.91483800	3.67136600
H	-3.11472000	-1.97845500	3.17534600
H	-1.92211100	-2.64450800	7.26133800

S_N2 TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.7976

Enthalpy = -2102.407439

Free Energy = -2102.515195

M06-2X/def2-TZVP

Electronic Energy = -7225.512673

C	2.50182600	4.49899800	1.69513800
C	3.40543200	3.56112300	1.19778800
H	0.42057300	5.01128200	1.94015100
C	1.12895700	4.28377700	1.55218900
C	2.92644600	2.40437300	0.57432200
C	1.55747300	2.18600600	0.38920600
C	0.66435600	3.13706000	0.90393300
H	3.64825500	1.66010600	0.23492800
H	-0.41036400	3.00779600	0.78570700
Mg	1.12029900	0.87362300	-1.38311700
Mg	-2.05205400	0.24605300	-0.54950800
H	4.47464800	3.71850500	1.31076900
H	2.86325800	5.39057100	2.19937600
C	-4.11197800	0.09727600	-0.15440100
C	-5.08120300	0.74096300	-0.95106600
C	-4.61750600	-0.66381100	0.91997000
C	-6.45330300	0.63964300	-0.70063800
H	-4.76745700	1.34621600	-1.80182500
C	-5.98524700	-0.77860700	1.18768300
H	-3.92842400	-1.19380600	1.57869500
C	-6.91063000	-0.12374300	0.37410500
H	-7.16434400	1.15381100	-1.34298400
H	-6.32927400	-1.37847800	2.02702600
H	-7.97529300	-0.20827800	0.57454200
Br	-1.08950700	2.18019500	-2.03947900
Br	-0.40469600	-1.38118300	-1.67073600
C	1.32151800	-1.95377100	2.04717000
O	2.30123900	-2.25797100	2.66705600
C	1.17028800	-0.59168700	1.37153300
C	0.03389900	0.27366700	1.87447700
O	-0.96687900	0.48906700	1.20586600
O	0.21827500	0.64038000	3.10100400

O	0.20640000	-2.63044700	1.88940300
C	0.17926100	-3.95457000	2.47330400
H	0.35091000	-3.88500900	3.54845400
H	-0.81513700	-4.33896100	2.26050600
H	0.94333000	-4.57366600	2.00133200
C	-0.82896200	1.43986000	3.71853000
H	-0.47271400	1.63395300	4.72663600
H	-0.94633700	2.36761500	3.15740300
H	-1.75719700	0.86781700	3.72917900
N	1.88931300	-0.18709600	0.41269100
O	2.72275600	-1.68129500	-0.14843600
S	3.38227600	-1.33093500	-1.51244900
O	3.34821800	-2.47857100	-2.39816700
O	2.76115000	-0.07901400	-2.06273500
C	5.05302700	-0.91404700	-1.11673600
H	5.53013000	-1.80873300	-0.71396500
H	5.54147200	-0.59264100	-2.03827300
H	5.04181400	-0.11217600	-0.37633600

C-attack TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.837825

Enthalpy = -2102.445925

Free Energy = -2102.550176

M06-2X/def2-TZVP

Electronic Energy = -7225.548752

C	2.94305100	2.57766400	-2.68401200
C	3.48860900	2.64393600	-1.40413200
H	1.35603000	1.76828000	-3.90206400
C	1.78369700	1.83057700	-2.90542000
C	2.86462600	1.97504500	-0.34672300
C	1.70243800	1.20639600	-0.54281500
C	1.17475900	1.16064800	-1.84498100
H	3.33070900	2.05362300	0.63524700
H	0.27203300	0.58934100	-2.05261400
Mg	2.07316700	-0.69578000	0.56660000
Mg	-1.97815000	-0.33679000	-0.05774200
H	4.39642500	3.21277400	-1.22429800
H	3.41834300	3.10232500	-3.50759700
Br	0.12252800	-2.00989500	-0.55593300
C	1.34468500	1.50356700	2.14347500
O	2.16591700	0.59971500	2.27729400
C	0.17133900	1.28685500	1.22879400
C	-0.51437200	2.23981200	0.29295100
O	-1.44364800	1.81355500	-0.38840800
O	-0.06837500	3.46004700	0.29555500

O	1.35848500	2.63591000	2.77197100
C	2.46860800	2.86310400	3.68170700
H	3.40697200	2.80576100	3.12886800
H	2.30856400	3.86312800	4.07616200
H	2.44205400	2.11654800	4.47587200
C	-0.62483000	4.34723500	-0.70337600
H	-0.08356200	5.28270000	-0.58508900
H	-0.45806300	3.92143800	-1.69474500
H	-1.69056500	4.48803500	-0.51910400
N	-0.68135100	0.33127300	1.50867500
O	-0.22285300	-0.62685100	2.42962000
S	-1.50159200	-1.60122600	2.84839200
O	-2.38851100	-1.63227400	1.67940400
O	-0.89415500	-2.80962000	3.33867300
C	-2.26544800	-0.66867200	4.13659500
H	-2.52901300	0.31087900	3.73226100
H	-3.16124800	-1.21831500	4.43623000
H	-1.55553500	-0.59307300	4.96149700
Br	4.17846300	-1.92848500	0.65001500
C	-3.65751500	-0.53887000	-1.31478600
C	-4.25263600	-1.79144300	-1.57324200
C	-4.26773200	0.56246900	-1.95015700
C	-5.37069400	-1.94292500	-2.39920500
H	-3.83454300	-2.69081700	-1.11952600
C	-5.38792700	0.43450600	-2.77840700
H	-3.86007400	1.56262800	-1.80106400
C	-5.94489700	-0.82442400	-3.00561400
H	-5.79376100	-2.93011500	-2.57038000
H	-5.82535700	1.31364600	-3.24627200
H	-6.81453400	-0.93331000	-3.64813500

Ester Addition TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.82468

Enthalpy = -2102.433503

Free Energy = -2102.537022

M06-2X/def2-TZVP

Electronic Energy = -7225.534458

C	-0.36525500	1.23327900	-0.45551900
O	0.50421300	0.31288500	-0.47847300
C	-1.59399500	1.17665900	-1.33291000
C	-2.09421800	2.47399300	-1.94134900
O	-1.36723300	3.19439400	-2.57742800
O	-3.37772000	2.65815900	-1.70524500
O	-0.09089700	2.45699800	-0.09984500
C	1.18257000	2.70513000	0.53370100

H	1.97654100	2.62232000	-0.21184000
H	1.11860000	3.72215000	0.91402500
H	1.34175400	2.00205500	1.35404900
C	-3.95526900	3.84271200	-2.29066700
H	-4.99835400	3.83632400	-1.98247300
H	-3.44588700	4.73026400	-1.91170800
H	-3.87301000	3.79641400	-3.37804500
N	-2.24964600	0.14255300	-1.69037200
O	-1.67546500	-1.01299600	-1.15172300
S	-2.72634800	-2.26917700	-0.80060800
O	-2.08295300	-2.65618900	0.46682200
O	-4.09022800	-1.81696600	-0.82365800
C	-2.38777900	-3.42872900	-2.08073500
H	-1.31482400	-3.62822300	-2.07239100
H	-2.96637600	-4.32679300	-1.84764700
H	-2.71737100	-2.97875300	-3.01978000
C	-1.74596800	0.64086000	1.43988000
C	-3.13784700	0.70297500	1.24557600
C	-1.26540100	1.26948700	2.60994300
C	-4.00313600	1.31202100	2.15871600
H	-3.59523100	0.28216100	0.35106800
C	-2.11142300	1.89418600	3.52740500
H	-0.20227100	1.26204700	2.83737800
C	-3.48900400	1.91518600	3.30478800
H	-5.07249500	1.32435800	1.96588900
H	-1.69562800	2.35863400	4.41770200
H	-4.15269200	2.40107200	4.01440100
Mg	-0.53512100	-1.13367400	0.77423600
Br	1.53732700	-0.95264400	2.38076300
Mg	2.33246200	-0.56312600	-0.12085500
C	4.13245500	0.44862100	-0.50881200
C	4.74423500	0.49687600	-1.77811600
C	4.79216600	1.16132800	0.51387600
C	5.92619500	1.20458500	-2.01830100
H	4.29268300	-0.03280900	-2.61668600
C	5.97420300	1.87552800	0.29383000
H	4.38100400	1.16639900	1.52427900
C	6.54619200	1.89887900	-0.97878900
H	6.36349300	1.21375700	-3.01389300
H	6.44951300	2.40983200	1.11299600
H	7.46521600	2.45035500	-1.15783800
Br	1.11970900	-2.78943400	-0.75151800

tBu-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2338.636561

Enthalpy = -2338.069629
Free Energy = -2338.190674
M06-2X/def2-TZVP
Electronic Energy = -7461.416665

C	-2.65807400	-2.02882600	4.06606300
C	-2.57532000	-3.07585400	3.14915400
H	-2.38610800	0.08833300	4.38169000
C	-2.31135000	-0.73409800	3.67559100
C	-2.14091700	-2.83187600	1.84029800
C	-1.77402000	-1.53655600	1.45459200
C	-1.88535800	-0.50093000	2.36564100
H	-2.07731000	-3.67378600	1.15187800
H	-1.66113100	0.52910600	2.07099900
Mg	-0.16771800	-1.83229900	-0.19654300
Mg	2.55885400	-0.60303500	-0.29505100
H	-2.84384400	-4.08589100	3.44774000
H	-3.00024100	-2.21807000	5.07919000
C	4.46847000	0.27229600	-0.19027700
C	5.11531400	0.79902700	-1.32671300
C	5.16270000	0.41371700	1.02800100
C	6.36172900	1.42937000	-1.25963500
H	4.63843800	0.72366500	-2.30463200
C	6.41017300	1.04016100	1.11654900
H	4.72587500	0.02505000	1.94883800
C	7.01340800	1.55455900	-0.03182000
H	6.82382800	1.82262000	-2.16205600
H	6.91083600	1.12669000	2.07806300
H	7.98167400	2.04405600	0.02862000
Br	1.84813900	-2.64234600	1.20946200
Br	1.36897500	-1.59009100	-2.38130600
C	-2.73854200	1.74441800	-0.24389000
O	-3.81488100	1.39627600	0.19107200
C	-1.57427200	0.81338500	-0.32479900
C	-0.21855900	1.12587200	0.09785300
O	0.64014600	0.19768700	0.14698400
O	-0.01884800	2.34974200	0.48443200
O	-2.43031400	2.93470200	-0.73834400
C	-3.37538500	4.05866700	-0.67353800
C	1.25942800	2.88928800	1.00791900
N	-1.69857700	-0.48252000	-0.56129500
O	-2.91882900	-0.86710900	-1.07561100
S	-2.79600900	-2.36840600	-1.78439700
O	-2.86285500	-2.20625200	-3.21417300
O	-1.59565300	-3.00030800	-1.20551100
C	-4.25692100	-3.09918100	-1.13189700
H	-5.10654200	-2.52095200	-1.50114800

H	-4.28886700	-4.12362600	-1.51113500
H	-4.19398600	-3.07356500	-0.04275300
C	-3.67887300	4.37891600	0.78536500
H	-4.25538200	5.30774400	0.83300000
H	-4.26074800	3.58724200	1.26090900
H	-2.74739200	4.52432400	1.34226900
C	-4.62969200	3.73874100	-1.47921600
H	-5.22712100	4.65050600	-1.57617700
H	-4.35843100	3.40090800	-2.48442300
H	-5.23764200	2.97253400	-0.99673600
C	-2.59352000	5.19086200	-1.32511400
H	-3.19857400	6.10169300	-1.32945900
H	-1.66949700	5.38806700	-0.77382200
H	-2.33798800	4.93680400	-2.35806600
C	1.81383300	2.00597200	2.11970100
H	2.29993300	1.10054200	1.75733600
H	2.56560700	2.58219100	2.66685200
H	1.02078500	1.72559000	2.82023500
C	2.19725700	3.07154000	-0.17581400
H	3.17696400	3.40229200	0.18198000
H	2.34439100	2.14313100	-0.73198700
H	1.79864000	3.82425000	-0.86199700
C	0.83145200	4.23455200	1.57654300
H	0.32755200	4.83084800	0.81145700
H	0.15692500	4.09915500	2.42709300
H	1.71738000	4.77807100	1.91575600

tBu-*C*-attack TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2338.644527

Enthalpy = -2338.077225

Free Energy = -2338.198058

M06-2X/def2-TZVP

Electronic Energy = -7461.42411

C	1.54233800	2.20879000	-3.88976800
C	2.55612600	1.99262000	-2.95780400
H	-0.52868700	1.85305200	-4.37938300
C	0.26866300	1.68508500	-3.66067500
C	2.29328900	1.24276500	-1.80715000
C	1.02485300	0.68626000	-1.55871800
C	0.01729300	0.94704000	-2.50364900
H	3.12046200	1.07991500	-1.11671600
H	-0.98940700	0.56156400	-2.35256300
Mg	1.36963900	-1.45798900	-1.10880700
Mg	-2.31068900	-0.33400200	0.37173100
H	3.55099500	2.39516700	-3.12746300

H	1.74151000	2.78512800	-4.78867200
Br	-1.12653400	-2.18921000	-1.27005400
C	1.97230100	0.24413500	1.04276400
O	2.49182200	-0.75483600	0.54518300
C	0.51082500	0.49704100	0.76273200
C	-0.21620300	1.77206500	0.43872500
O	-1.41385500	1.68580500	0.16487900
O	0.50386300	2.84216600	0.54594700
O	2.50775800	1.08139700	1.86411100
C	3.91953700	0.93641600	2.35313500
C	-0.02907600	4.19594100	0.22679400
N	-0.36579600	-0.33671900	1.25817400
O	0.15506000	-1.56086100	1.71220300
S	-1.05386100	-2.37525700	2.50376100
O	-2.31390900	-1.93729500	1.89050400
O	-0.65917900	-3.75817400	2.45656200
C	-0.93680200	-1.70756000	4.13165200
H	-1.05206800	-0.62412500	4.05892900
H	-1.74932300	-2.14831500	4.71426200
H	0.03581200	-1.98874000	4.53739000
Br	2.90739200	-2.91884400	-2.32734800
C	-4.33737400	0.09858400	-0.00810100
C	-5.36070000	-0.86566200	0.10458300
C	-4.75753100	1.37957200	-0.42270800
C	-6.70201900	-0.58242800	-0.17126900
H	-5.11193800	-1.88104800	0.41477100
C	-6.09338400	1.68522600	-0.70409400
H	-4.02127400	2.17614700	-0.53509200
C	-7.07351300	0.70013500	-0.57795200
H	-7.45620300	-1.35982900	-0.07225900
H	-6.36995800	2.68796400	-1.02207500
H	-8.11354300	0.92821800	-0.79562200
C	-0.42950900	4.23053900	-1.23883700
H	-1.27863600	3.57539000	-1.44518500
H	-0.71520500	5.25568500	-1.49314200
H	0.41391500	3.93963500	-1.87251800
C	1.17345400	5.08551400	0.49434300
H	0.91015900	6.12332300	0.27386300
H	1.47957100	5.01790200	1.54236500
H	2.01478200	4.79613400	-0.14242100
C	-1.17771600	4.51846200	1.17160600
H	-2.06544600	3.92198800	0.95527700
H	-0.87579600	4.35625900	2.21090900
H	-1.43379900	5.57527800	1.05275200
C	4.86466800	1.06236500	1.16889500
H	5.88885400	1.08487400	1.55239200

H	4.77797900	0.21795500	0.48200300
H	4.68355300	1.99695300	0.62929500
C	4.04866100	-0.38845500	3.08888300
H	3.26813600	-0.48258800	3.85036800
H	4.00129000	-1.24204700	2.41140900
H	5.01837200	-0.40333900	3.59447500
C	4.05247100	2.11608100	3.30031500
H	5.06025800	2.11993900	3.72345000
H	3.89326400	3.05904200	2.76994500
H	3.33085700	2.04066800	4.11856400

α-Et-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1801.248743

Enthalpy = -1800.875158

Free Energy = -1800.970522

M06-2X/def2-TZVP

Electronic Energy = -6923.8488219

Mg	0.66116900	-0.96490400	0.53546400
Mg	2.64833000	1.12657900	-0.42362600
Br	2.96306000	-0.52623100	1.65376400
Br	1.84763700	-0.94202500	-1.88197700
C	-1.65235700	0.88248300	-0.08184000
C	-0.48197700	1.71776400	-0.04439700
O	0.66174000	1.20291100	0.14264300
O	-0.64861900	3.01234900	-0.18048900
C	0.53016100	3.83998400	-0.14676600
H	0.16403900	4.86201500	-0.21651100
H	1.06900000	3.69195600	0.79159100
H	1.17111400	3.61244600	-1.00276600
N	-1.26418200	-0.38662400	0.01655200
O	-2.29898500	-1.31507900	-0.00324000
S	-1.66346500	-2.79527000	-0.37968100
O	-0.29934400	-2.82319800	0.17654900
C	-3.04135100	1.38354100	-0.05385900
C	-3.98825100	0.89265800	-0.96314200
C	-3.42251800	2.36094100	0.87524800
C	-5.29683700	1.36792700	-0.93725300
H	-3.69562500	0.14797600	-1.69735300
C	-4.73128000	2.83607800	0.89527300
H	-2.69526000	2.73960900	1.58771700
C	-5.67081000	2.34010900	-0.00906200
H	-6.02286000	0.98307700	-1.64666200
H	-5.01851200	3.59015500	1.62139600
H	-6.69113900	2.71062500	0.00875400
C	-0.76175400	-0.56442500	2.33974400

H	-1.82914800	-0.35602400	2.28918700
C	-0.43386100	-1.73498700	3.24323700
H	-0.97359000	-2.63796100	2.93610800
H	0.63596100	-1.97452700	3.26311300
H	-0.19823200	0.35650600	2.53926500
C	3.98309600	2.68737100	-0.87740100
H	3.80379500	3.52379100	-0.18464900
H	3.76744000	3.08394200	-1.88072000
C	5.45872100	2.26258100	-0.79884800
H	5.71702900	1.88829500	0.19949800
H	5.68148100	1.45052000	-1.50182700
H	-0.72852800	-1.53183200	4.28522400
H	6.16241000	3.07789400	-1.02316900
O	-2.63260200	-3.74767000	0.09403200
C	-1.57878700	-2.73557800	-2.14020800
H	-1.08028500	-3.65240400	-2.46517800
H	-2.60060000	-2.68347000	-2.51925000
H	-0.99290000	-1.85621200	-2.41966800

α-Ph-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2106.014245

Enthalpy = -2105.584729

Free Energy = -2105.688282

M06-2X/def2-TZVP

Electronic Energy = -7228.7112993

C	-2.64033000	-1.33726900	4.18990600
C	-2.78420700	-2.34012600	3.23229600
H	-1.97358300	0.67915600	4.57371600
C	-2.08210100	-0.10807700	3.83269400
C	-2.36825600	-2.11943600	1.91274900
C	-1.79735200	-0.89229600	1.56440100
C	-1.67678700	0.10570500	2.51339800
H	-2.47655300	-2.92784700	1.19190500
H	-1.27070400	1.08275800	2.23906000
Mg	-0.22866900	-1.36929900	-0.13248400
Mg	2.56413100	-0.28606000	-0.18706200
H	-3.21470100	-3.29941500	3.50743100
H	-2.96779400	-1.50899300	5.21090700
C	4.47319200	0.58345300	-0.04229000
C	5.23027400	0.92709000	-1.18093400
C	5.06801000	0.88694000	1.19996800
C	6.48818700	1.53274300	-1.09526800
H	4.83672900	0.71779100	-2.17596800
C	6.32385700	1.49253700	1.30683400
H	4.54447900	0.64314000	2.12507900

C	7.03948600	1.81916800	0.15397100
H	7.03769300	1.77898100	-2.00073200
H	6.74504200	1.70674500	2.28629800
H	8.01631600	2.28924200	0.22864800
Br	1.72711800	-2.36344500	1.23671500
Br	1.33175900	-1.19612100	-2.30620800
C	-1.42754000	1.39969700	-0.21438500
C	-0.04250400	1.56312600	0.11273600
O	0.71182700	0.54706500	0.25178100
O	0.40335500	2.78541700	0.28991000
C	1.79208400	2.95167600	0.63156400
H	1.91185200	4.01374100	0.83537500
H	2.03847800	2.36482500	1.51935600
H	2.42255000	2.66095300	-0.21235700
N	-1.66799200	0.09579300	-0.40022800
O	-2.94712000	-0.20116400	-0.85207600
S	-2.89056500	-1.62415800	-1.70233500
O	-2.83477300	-1.32994200	-3.11226400
O	-1.78499900	-2.40456600	-1.10955100
C	-4.44579300	-2.29387300	-1.22777500
H	-5.21791600	-1.59316200	-1.55187500
H	-4.54393100	-3.24638600	-1.75397200
H	-4.45178500	-2.43015000	-0.14566200
C	-2.43075500	2.48697900	-0.21245400
C	-3.29056400	2.64682500	-1.30903800
C	-2.51929400	3.38645400	0.85903600
C	-4.22675500	3.67753600	-1.32537400
H	-3.21398600	1.97307200	-2.15648100
C	-3.45201300	4.42058400	0.83593400
H	-1.85881700	3.27800200	1.71406300
C	-4.31060800	4.56630600	-0.25343300
H	-4.88408200	3.79181400	-2.18180800
H	-3.50952100	5.11025300	1.67240300
H	-5.03870800	5.37167200	-0.26922200

H^+

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -0.190089936

Enthalpy = -0.187729

Free Energy = -0.20009

M06-2X/def2-TZVP

Electronic Energy = -0.1900899

H	0.00000000	0.00000000	0.00000000

a

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1213.129368
Enthalpy = -1212.940984
Free Energy = -1213.004591
M06-2X/def2-TZVP
Electronic Energy = -1213.52473

C	-1.18652800	1.43472000	0.39145800
O	-1.27479500	1.86517000	1.51382700
C	-0.94995400	-0.03329400	0.10602400
C	-2.17459000	-0.89873600	0.01248000
O	-3.27798300	-0.40650300	0.06850700
O	-1.90087000	-2.18091900	-0.13196400
O	-1.27826200	2.12867000	-0.72702900
C	-1.51501800	3.54193200	-0.56816400
H	-0.69180800	3.99564000	-0.01387200
H	-1.56559500	3.94211100	-1.57831200
H	-2.45828700	3.70141800	-0.04285200
C	-3.04322600	-3.05224100	-0.23307700
H	-2.63296900	-4.05187000	-0.35936400
H	-3.63767700	-2.99305500	0.68041300
H	-3.65069800	-2.77456400	-1.09625800
N	0.19978200	-0.55880200	-0.01769900
O	1.19388300	0.40162600	0.10305100
S	2.70316200	-0.26837900	-0.16298100
O	2.65640000	-0.99327000	-1.41386800
O	3.57043800	0.87703700	0.00345200
C	2.84219300	-1.38476800	1.20047300
H	3.82395700	-1.85594600	1.11435800
H	2.76670000	-0.80793300	2.12282000
H	2.04956800	-2.13029200	1.12167500

a^{+}
M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -1213.510993
Enthalpy = -1213.309354
Free Energy = -1213.37227
M06-2X/def2-TZVP
Electronic Energy = -1213.907387

C	-1.01148800	1.47214600	0.24961100
O	-0.64190200	1.83657100	1.33275600
C	-0.96469700	-0.00816700	-0.09451500
C	-2.21297600	-0.84870000	0.10463500
O	-3.20902200	-0.33583300	0.53592800
O	-2.00034000	-2.09520600	-0.23385600
O	-1.49583000	2.16153100	-0.74421600
C	-1.62649400	3.59337500	-0.52585600
H	-0.63842600	4.02311000	-0.35748200

H	-2.06890600	3.97734700	-1.44098300
H	-2.27972100	3.76769200	0.32958400
C	-3.11372100	-3.01367500	-0.05869700
H	-2.73302700	-3.98095500	-0.37527800
H	-3.40381100	-3.02860600	0.99225400
H	-3.94370700	-2.69277300	-0.68891100
N	0.13269000	-0.54503900	-0.45774300
O	1.20933700	0.23565000	-0.69695000
S	2.70722400	-0.44266400	-0.07251200
O	2.46907400	-1.86673800	-0.11760400
O	3.67249100	0.21967800	-0.90040100
C	2.67729000	0.18336500	1.57574000
H	3.60393100	-0.16498400	2.04252500
H	2.65223400	1.27278200	1.52414200
H	1.81138100	-0.23710100	2.09079100
H	0.23769500	-1.55390500	-0.66301200

b

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1216.308438

Enthalpy = -1216.081848

Free Energy = -1216.146089

M06-2X/def2-TZVP

Electronic Energy = -1216.688528

C	-1.47677100	-1.85424700	0.08561100
O	-1.14580400	-2.90749500	0.57185300
C	-0.60499500	-0.61280200	0.05913000
O	-2.64066200	-1.62476600	-0.51322800
C	-3.54168300	-2.74240000	-0.57066400
H	-3.80056700	-3.06732600	0.43905500
H	-4.42412200	-2.37833400	-1.09317700
H	-3.08313400	-3.56716200	-1.11957000
N	0.63966700	-0.90067900	0.04829900
O	1.43498100	0.24187000	0.05295100
S	3.03826900	-0.19857900	0.02210800
O	3.34241300	-0.91395600	1.24608000
O	3.31095400	-0.82401800	-1.25806200
C	3.66742600	1.45060400	0.07293100
H	3.33580400	1.92264200	0.99811100
H	4.75584400	1.35955800	0.05536000
H	3.31227700	1.98733600	-0.80752000
C	-1.22187300	0.73542100	0.04829000
C	-2.22142900	1.03109400	0.98171100
C	-0.83068900	1.70059500	-0.88652400
C	-2.81102800	2.29258700	0.99393100
H	-2.53155200	0.27830700	1.70180200

C	-1.43725500	2.95413300	-0.88182100
H	-0.06713900	1.46662900	-1.62107600
C	-2.42120800	3.25393600	0.06092800
H	-3.57840400	2.52171400	1.72650600
H	-1.13957500	3.69758200	-1.61458200
H	-2.88742500	4.23445700	0.06538700

b^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1216.71261

Enthalpy = -1216.472358

Free Energy = -1216.53588

M06-2X/def2-TZVP

Electronic Energy = -1217.093064

C	-1.74830500	-1.65337000	-0.09689500
O	-1.41768700	-2.79474900	0.11111500
C	-0.69071500	-0.56714800	-0.34262400
O	-2.96344900	-1.18300600	-0.19883600
C	-4.02892100	-2.14794400	-0.01721200
H	-3.94996700	-2.59432400	0.97485700
H	-4.94836300	-1.57674000	-0.11713100
H	-3.95888100	-2.91512600	-0.78972700
N	0.43477700	-1.11486900	-0.68507500
O	1.55242400	-0.40147800	-0.96786200
S	2.64985600	-0.39936000	0.38351000
O	2.23766500	0.68720200	1.23791100
O	2.63919300	-1.76151500	0.86546500
C	4.08035200	-0.00569400	-0.56588700
H	3.89773300	0.93642200	-1.08620400
H	4.89482700	0.10570600	0.15517000
H	4.27500200	-0.83003700	-1.25268100
C	-0.93161100	0.85015400	-0.20923100
C	-1.82080100	1.27971500	0.79642400
C	-0.28262400	1.79080700	-1.03543500
C	-2.02863200	2.63742100	0.99131600
H	-2.31295200	0.55992800	1.44087800
C	-0.53700600	3.14099400	-0.85586900
H	0.37872500	1.46641800	-1.82953300
C	-1.39542900	3.56485100	0.16297700
H	-2.69034200	2.97160600	1.78276100
H	-0.06265200	3.86795400	-1.50610700
H	-1.57526600	4.62569100	0.30754900
H	0.52799600	-2.13400000	-0.76819000

c

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1219.492606
Enthalpy = -1219.227612
Free Energy = -1219.292025
M06-2X/def2-TZVP
Electronic Energy = -1219.858484

C	0.52159100	-0.10918300	-0.04147800
N	-0.52961800	-0.84264500	-0.08602800
O	-1.70797500	-0.07460300	0.02075500
S	-3.00682000	-1.08835200	0.00334100
O	-3.09923300	-1.70498700	-1.30844500
O	-2.95398800	-1.93869800	1.17957200
C	-4.23108800	0.17190900	0.19252900
H	-4.16433900	0.85681200	-0.65332100
H	-5.19450100	-0.34238300	0.19576600
H	-4.06569600	0.68393400	1.14090500
C	0.52760500	1.37774500	0.02920400
C	-0.16153500	2.14294200	-0.91829000
C	1.26267500	2.01278500	1.03575100
C	-0.11442400	3.53358900	-0.85538800
H	-0.72079300	1.64958000	-1.70726900
C	1.28913000	3.40421100	1.10779000
H	1.80820000	1.41678000	1.76243700
C	0.60440000	4.16551500	0.16047600
H	-0.64010500	4.12367100	-1.59977500
H	1.85106200	3.89239300	1.89790200
H	0.63461100	5.24976400	0.21018400
C	1.81271900	-0.84856800	-0.06164200
C	1.89405800	-2.14880900	0.45501400
C	2.95419900	-0.25027200	-0.60873000
C	3.10035300	-2.84143700	0.41497200
H	1.01314600	-2.60484300	0.89563700
C	4.15852700	-0.95029600	-0.65174100
H	2.89932400	0.75700000	-1.01108700
C	4.23445100	-2.24506500	-0.13979400
H	3.15717600	-3.84562800	0.82356700
H	5.03686000	-0.48234900	-1.08538300
H	5.17509900	-2.78667700	-0.16792200

c^{+}
M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -1219.909165
Enthalpy = -1219.630209
Free Energy = -1219.693027
M06-2X/def2-TZVP
Electronic Energy = -1220.275041

C	-0.57868700	-0.09437900	-0.16549700

N	0.42239300	-0.92045600	-0.33252000
O	1.65155300	-0.49082700	-0.75110500
S	2.89859600	-1.12604800	0.23210200
O	2.99863300	-0.28106700	1.40077800
O	2.58003100	-2.53097000	0.37774100
C	4.19897000	-0.82608300	-0.91664100
H	4.22700000	0.24442900	-1.12846300
H	5.11747000	-1.14421700	-0.41594500
H	4.01484500	-1.42071500	-1.81194300
C	-0.39649800	1.35588600	-0.13520400
C	0.69641400	1.94862100	0.51964000
C	-1.36857700	2.15723500	-0.75796500
C	0.80747200	3.33235100	0.54744100
H	1.42601000	1.33740700	1.03906300
C	-1.22812600	3.54019000	-0.75032200
H	-2.21148300	1.69705200	-1.26365200
C	-0.14518700	4.12669700	-0.09511900
H	1.63687500	3.79299300	1.07358000
H	-1.96748100	4.15877900	-1.24771500
H	-0.04537300	5.20750700	-0.07776600
H	0.30218900	-1.93638700	-0.33620100
C	-1.90008300	-0.71363800	-0.03358300
C	-2.22165500	-1.87696600	-0.75323200
C	-2.84085400	-0.13444600	0.83357200
C	-3.47555300	-2.45454800	-0.60084000
H	-1.51532400	-2.29890800	-1.46284900
C	-4.08584500	-0.73107100	0.99064900
H	-2.58561200	0.75839200	1.39528600
C	-4.40362200	-1.88599000	0.27382100
H	-3.73321500	-3.34035000	-1.17150600
H	-4.80905300	-0.29465300	1.67123700
H	-5.38187300	-2.34161200	0.39124400

d

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -781.1548653

Enthalpy = -780.928745

Free Energy = -780.990001

M06-2X/def2-TZVP

Electronic Energy = -781.4360533

C	2.26073500	-0.97828300	0.11744100
O	2.56756700	-2.12548800	0.32106400
C	0.84005900	-0.45287400	0.13617400
C	0.68155600	1.05569700	0.24009100
O	0.97803300	1.67920600	1.23128500
O	0.18884600	1.56984300	-0.87652300

O	3.10661300	0.00166000	-0.18840100
C	4.49163900	-0.37000500	-0.27614900
H	4.62534700	-1.13438700	-1.04399500
H	5.02354300	0.54011100	-0.54595100
H	4.83862000	-0.74553400	0.68852700
C	-0.04374400	2.98969100	-0.85965300
H	-0.45234200	3.23007700	-1.83895800
H	-0.75905400	3.23910000	-0.07325900
H	0.89558200	3.52083200	-0.69417900
N	-0.10336700	-1.29474800	0.05693300
C	-1.45670300	-0.88695500	0.07903400
C	-1.96443500	-0.02868900	1.06154700
C	-2.30691200	-1.43283300	-0.88863000
C	-3.31707700	0.30763900	1.04589300
H	-1.31579700	0.34161200	1.85016000
C	-3.64928600	-1.06739700	-0.91139300
H	-1.89918700	-2.12386900	-1.62011500
C	-4.15859700	-0.19735800	0.05507800
H	-3.71220100	0.96382500	1.81532800
H	-4.30288900	-1.47452400	-1.67668000
H	-5.20993400	0.07241000	0.04457700

d^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -781.5727389

Enthalpy = -781.33285

Free Energy = -781.393152

M06-2X/def2-TZVP

Electronic Energy = -781.8554557

C	2.21827500	-1.02042400	0.04343500
O	2.30357300	-2.22124200	-0.01680500
C	0.86166500	-0.33804600	0.10816600
C	0.77589700	1.17415400	0.19438800
O	1.13783500	1.76633100	1.17570300
O	0.30485400	1.66497600	-0.92744700
O	3.18059200	-0.13557000	0.03777500
C	4.52961600	-0.65969100	-0.03927500
H	4.64924200	-1.21565300	-0.97011400
H	5.17598000	0.21393100	-0.01943300
H	4.71584900	-1.30400800	0.82112300
C	0.17354300	3.10719500	-0.98106500
H	-0.23038600	3.31926800	-1.96767500
H	-0.51235300	3.43713100	-0.19915500
H	1.15310700	3.56940200	-0.85265600
N	-0.15653200	-1.11301100	0.06640700
C	-1.54344400	-0.78665700	0.11280300

C	-2.00485400	0.28901400	0.87407900
C	-2.40200000	-1.60356500	-0.62439700
C	-3.36529700	0.57268600	0.85324400
H	-1.33783300	0.86153900	1.51095300
C	-3.75766300	-1.29730700	-0.63912000
H	-2.01029500	-2.44452100	-1.18847000
C	-4.23661500	-0.20929800	0.09216500
H	-3.74614200	1.39663000	1.44683200
H	-4.43871500	-1.91068300	-1.21878000
H	-5.29689500	0.02128400	0.08294700
H	0.06460000	-2.11756900	-0.03077600

e

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -784.3386567

Enthalpy = -784.074217

Free Energy = -784.135249

M06-2X/def2-TZVP

Electronic Energy = -784.6057855

C	0.01640200	1.30430500	0.19534900
O	0.19786000	1.98055500	1.18135300
C	0.53076900	-0.12320800	0.04792500
O	-0.64426500	1.69630200	-0.88647400
C	-1.25356500	2.99619000	-0.81021800
H	-0.49478900	3.76130200	-0.63496000
H	-1.73619800	3.14899400	-1.77358700
H	-1.99242800	3.01125800	-0.00566600
N	-0.25720000	-1.12149300	-0.05021400
C	2.00167600	-0.30528200	0.03118100
C	2.85962200	0.79101400	-0.11706000
C	2.54203200	-1.59457400	0.13895000
C	4.23965200	0.60018200	-0.16371300
H	2.46112300	1.79823100	-0.19898600
C	3.91869600	-1.78035600	0.09745400
H	1.87248700	-2.44013500	0.25840000
C	4.77110900	-0.68342100	-0.05530200
H	4.89690100	1.45563000	-0.28295400
H	4.33038500	-2.78086000	0.18649200
H	5.84627200	-0.83131000	-0.08683400
C	-1.65770700	-0.96726300	0.03570300
C	-2.44634900	-1.53663500	-0.97118300
C	-2.26933700	-0.33383800	1.12502600
C	-3.83191600	-1.42072700	-0.91619700
H	-1.95966300	-2.05039700	-1.79487400
C	-3.65980100	-0.24062300	1.18090500
H	-1.65990800	0.05739100	1.93490800

C	-4.44484700	-0.77199100	0.15862900
H	-4.43687800	-1.84787600	-1.71041600
H	-4.12764800	0.24564700	2.03180900
H	-5.52661600	-0.69491300	0.20445000

e^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -784.7685961
Enthalpy = -784.489708
Free Energy = -784.549452
M06-2X/def2-TZVP
Electronic Energy = -785.036812

C	0.03198000	1.27308200	0.40270700
O	-0.45226500	1.54716100	1.47010200
C	0.48047000	-0.14839000	0.08577200
O	0.29590300	2.09438800	-0.59026300
C	-0.07552400	3.47654300	-0.37775100
H	0.49182500	3.88323200	0.46095300
H	0.18096000	3.98792000	-1.30243200
H	-1.14675200	3.54178000	-0.17896500
N	-0.43186900	-1.06677000	0.00038700
C	1.90036100	-0.43422400	-0.00439100
C	2.81299400	0.49818100	0.52094800
C	2.36805400	-1.62189900	-0.59828100
C	4.17447700	0.22847500	0.48093200
H	2.46578400	1.42010200	0.97935800
C	3.73058800	-1.87445600	-0.64389000
H	1.68140300	-2.32860600	-1.05601900
C	4.63206100	-0.95492300	-0.09944400
H	4.87739900	0.94120100	0.89805500
H	4.09450800	-2.78197700	-1.11326500
H	5.69739900	-1.15951000	-0.13812300
H	-0.12107600	-2.04085400	-0.02182100
C	-1.85023200	-0.87955100	-0.05557600
C	-2.64772300	-1.75568500	0.67832700
C	-2.39593200	0.12617900	-0.85194900
C	-4.02868600	-1.59082200	0.64077800
H	-2.19153600	-2.53967900	1.27556500
C	-3.77948700	0.28026500	-0.87429800
H	-1.76155500	0.75219300	-1.47328700
C	-4.59344700	-0.57110100	-0.12717100
H	-4.66301700	-2.25878500	1.21371600
H	-4.21985900	1.05597200	-1.49179200
H	-5.67121700	-0.44803800	-0.15363900

f

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -787.5170198
Enthalpy = -787.214344
Free Energy = -787.275482
M06-2X/def2-TZVP
Electronic Energy = -787.7693246

C	0.54899000	-0.35694100	-0.06495400
N	-0.20181300	-1.39532300	-0.09206900
C	0.04599900	1.05399100	-0.07372000
C	-0.84826600	1.47719300	-1.06302200
C	0.46496400	1.95690100	0.90934600
C	-1.32209900	2.78741800	-1.06464000
H	-1.17045600	0.77992200	-1.83150100
C	-0.02604500	3.26142200	0.91812300
H	1.16693900	1.63380200	1.67387300
C	-0.91791100	3.67924500	-0.07030300
H	-2.00976300	3.11052000	-1.84015800
H	0.29230100	3.95216100	1.69298800
H	-1.29389600	4.69787100	-0.06799300
C	2.02640900	-0.56925300	-0.04317400
C	2.54578800	-1.77590800	0.44603400
C	2.90745400	0.41056300	-0.51776100
C	3.91892700	-1.99862300	0.45706000
H	1.86099700	-2.53020600	0.82036400
C	4.28288800	0.18099600	-0.51643500
H	2.52052600	1.34933700	-0.90263100
C	4.79156800	-1.02096500	-0.02657500
H	4.31069700	-2.93355500	0.84610400
H	4.95568100	0.94305600	-0.89760800
H	5.86323100	-1.19609100	-0.01898000
C	-1.60617200	-1.31803500	0.01448900
C	-2.23063500	-0.71949600	1.11742700
C	-2.38760600	-1.94777800	-0.96150700
C	-3.61975200	-0.72913300	1.22157200
H	-1.62310800	-0.25442400	1.88873600
C	-3.77702100	-1.93546300	-0.86011400
H	-1.89424800	-2.43307900	-1.79889600
C	-4.40016000	-1.32717700	0.23091900
H	-4.09346400	-0.26484300	2.08167200
H	-4.37412000	-2.41274600	-1.63167100
H	-5.48254100	-1.32820500	0.31359100

f^+
M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -787.9606211
Enthalpy = -787.643553

Free Energy = -787.704261

M06-2X/def2-TZVP

Electronic Energy = -788.2133491

C	0.56006800	-0.28027700	-0.10394100
N	-0.29533000	-1.26730500	-0.19840000
C	0.11480300	1.11989100	-0.07615900
C	-0.88599500	1.56156800	-0.95539100
C	0.72647500	2.01889400	0.80827500
C	-1.26993300	2.89629200	-0.94299400
H	-1.34163900	0.86904200	-1.65685100
C	0.31194200	3.34718300	0.83588500
H	1.50517700	1.67382500	1.48168500
C	-0.68093400	3.78558100	-0.04021300
H	-2.02923300	3.24444300	-1.63530500
H	0.76968300	4.04023000	1.53392700
H	-0.99330700	4.82509100	-0.02598900
C	1.98972300	-0.60785600	-0.05301400
C	2.42634700	-1.79166000	0.56654100
C	2.92444100	0.26653400	-0.63123200
C	3.78133200	-2.09699900	0.59786100
H	1.71462800	-2.44850100	1.05968600
C	4.27641000	-0.05655000	-0.61015900
H	2.58952000	1.17741500	-1.11734400
C	4.70501100	-1.23369800	0.00504500
H	4.11866800	-3.00097300	1.09391300
H	4.99598200	0.61118500	-1.07203600
H	5.76284500	-1.47634500	0.02939200
C	-1.71972100	-1.24195300	-0.02795900
C	-2.28836800	-0.56922600	1.05254500
C	-2.49579500	-1.95251300	-0.93998600
C	-3.67212000	-0.59060600	1.19878300
H	-1.66022400	-0.04491900	1.76610300
C	-3.87978700	-1.96691100	-0.77956200
H	-2.02172000	-2.47529100	-1.76558400
C	-4.46795700	-1.28292300	0.28393700
H	-4.12815800	-0.07213200	2.03580000
H	-4.49546500	-2.51180300	-1.48761500
H	-5.54611400	-1.29595400	0.40680900
H	0.09102300	-2.19281000	-0.38736900

g

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -856.3600203

Enthalpy = -856.128297

Free Energy = -856.190531

M06-2X/def2-TZVP

Electronic Energy = -856.6724508

C	-0.96644800	1.38859100	0.19285600
O	-1.18581500	2.04671300	1.18159000
C	-1.27942200	-0.09559200	0.09062000
C	-2.75784200	-0.38032300	0.01712100
O	-3.55939100	0.50900000	-0.17288000
O	-3.05851400	-1.66088600	0.15307200
O	-0.43016100	1.84299800	-0.93077900
C	-0.04769000	3.22923800	-0.92681500
H	0.72568700	3.39905700	-0.17409000
H	0.34122300	3.42700300	-1.92360500
H	-0.91487000	3.85865600	-0.71963700
C	-4.45419400	-1.98231900	0.04165500
H	-4.51794900	-3.05931100	0.18442800
H	-5.02383500	-1.46023800	0.81307900
H	-4.82648100	-1.70448400	-0.94641900
N	-0.43695800	-1.04175200	0.01854600
C	0.95558200	-0.82701000	0.06745500
C	1.57577500	0.09176900	0.92364500
C	1.74743500	-1.64682300	-0.74824000
C	2.96120100	0.21520200	0.93282100
H	0.98899900	0.68169700	1.62115900
C	3.12665300	-1.50402400	-0.76695700
H	1.26128300	-2.38375700	-1.38018000
C	3.73672000	-0.56980700	0.07596300
H	3.43906900	0.91438300	1.61448900
H	3.74428100	-2.12005700	-1.41254800
O	5.09045400	-0.48257900	0.03510400
H	5.40211500	0.18393600	0.66391600

g^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -856.7783108

Enthalpy = -856.532411

Free Energy = -856.5943

M06-2X/def2-TZVP

Electronic Energy = -857.0922783

C	-2.75063500	-0.45843900	0.02695000
O	-3.63230500	0.34809100	-0.11762100
C	-1.31077200	-0.01390000	0.11009500
C	-1.08791200	1.47999500	0.22666900
O	-1.37608000	2.07963800	1.22848700
O	-0.58693100	1.95765700	-0.88919000
O	-2.86209700	-1.76883900	0.09983500
C	-4.20417600	-2.30118400	-0.02241300
H	-4.62947800	-1.99535000	-0.97879600

H	-4.08863100	-3.38082600	0.02630900
H	-4.81374900	-1.93510300	0.80467200
C	-0.32585900	3.38212500	-0.90700100
H	0.09663900	3.58221400	-1.88846100
H	-1.26109900	3.92568900	-0.76647200
H	0.38516700	3.63188600	-0.11765800
N	-0.36486200	-0.88283600	0.04546600
C	1.03891100	-0.72493200	0.08446600
C	1.65959600	0.37352800	0.69118300
C	1.79352000	-1.74811400	-0.50552000
C	3.03920600	0.46347800	0.66917900
H	1.09653200	1.12850300	1.22924500
C	3.17025100	-1.65110700	-0.53573400
H	1.29363700	-2.60299700	-0.95253600
C	3.79763400	-0.54005000	0.04569400
H	3.53243300	1.30096600	1.15344200
H	3.77474300	-2.42365900	-0.99739700
O	5.13781900	-0.49893000	-0.00796300
H	5.48047900	0.29815200	0.42529300
H	-0.67447000	-1.85895800	-0.06569000

h

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -859.5424924

Enthalpy = -859.272704

Free Energy = -859.336326

M06-2X/def2-TZVP

Electronic Energy = -856.6724508

C	-0.42955000	1.35106300	0.18444000
O	-0.63569400	2.02225100	1.16958500
C	-0.87750300	-0.09874400	0.04395000
O	0.20026900	1.77356500	-0.90464600
C	0.75673000	3.09688200	-0.83210000
H	1.50539200	3.13986000	-0.03747900
H	1.21947800	3.27264000	-1.80128800
H	-0.03015100	3.82960300	-0.64315900
N	-0.05243200	-1.06636700	-0.06425400
C	1.34364900	-0.87246500	0.01182800
C	1.95707100	-0.13164800	1.02851800
C	2.14647700	-1.52285600	-0.93463300
C	3.34444300	-0.00751100	1.07266600
H	1.35747700	0.32432000	1.81106300
C	3.52712100	-1.38354200	-0.90816600
H	1.67104800	-2.12594000	-1.70240600
C	4.12984300	-0.62169900	0.09708500
H	3.81321900	0.55940600	1.87343000

H	4.15076800	-1.87066300	-1.65099200
O	5.48784100	-0.52973100	0.08520100
H	5.79027200	0.01030200	0.82878500
C	-2.33993800	-0.34230100	0.04060900
C	-3.24428400	0.71316800	-0.12901700
C	-2.82635100	-1.64960200	0.18365700
C	-4.61528600	0.46372100	-0.16411100
H	-2.88897200	1.73415700	-0.23790600
C	-4.19427200	-1.89382700	0.15372700
H	-2.12167700	-2.46309500	0.32207300
C	-5.09262900	-0.83783900	-0.02169900
H	-5.30840500	1.28777800	-0.30067800
H	-4.56301100	-2.90825000	0.27042900
H	-6.16087400	-1.03102000	-0.04375000

h^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -859.974468

Enthalpy = -859.690192

Free Energy = -859.753167

M06-2X/def2-TZVP

Electronic Energy = -860.2738715

C	-0.46556600	1.38594400	0.21086000
O	-0.74436800	2.02320700	1.19403700
C	-0.92105700	-0.05663800	0.03237600
O	0.21324400	1.79693600	-0.83886700
C	0.75528800	3.13404000	-0.75357500
H	1.44742200	3.19118700	0.08890900
H	1.27719700	3.29263800	-1.69427100
H	-0.05401400	3.85553300	-0.63119700
N	-0.02155300	-0.98019000	-0.12325800
C	1.39657600	-0.84772600	-0.02034200
C	1.97650400	-0.08714200	0.99415000
C	2.18190800	-1.52441500	-0.95566200
C	3.35908200	0.03471200	1.04566400
H	1.36903400	0.38025200	1.76360900
C	3.56054800	-1.40453500	-0.90158100
H	1.71274600	-2.12372100	-1.73027500
C	4.15109900	-0.61621100	0.09400400
H	3.82209700	0.61758800	1.83699000
H	4.19205500	-1.91198300	-1.62277300
O	5.49861600	-0.53442400	0.09481400
H	5.80746100	0.02614800	0.82207200
C	-2.34414400	-0.34149000	0.04430600
C	-3.24471200	0.69496600	-0.25927700
C	-2.82541400	-1.63252000	0.32872500

C	-4.60719400	0.43108200	-0.31224300
H	-2.88503900	1.69716900	-0.47278700
C	-4.18895100	-1.88171400	0.28448900
H	-2.14980400	-2.43060300	0.62282500
C	-5.07840300	-0.85407800	-0.04232500
H	-5.30042600	1.22768000	-0.55892900
H	-4.56248000	-2.87315800	0.51706300
H	-6.14447300	-1.05591600	-0.07438700
H	-0.35421300	-1.92290200	-0.34132400

i

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -781.9226814
Enthalpy = -781.705427
Free Energy = -781.761285
M06-2X/def2-TZVP
Electronic Energy = -782.1880985

C	1.97349400	-0.70917800	-0.13146500
C	2.43040200	0.59919700	0.07187900
C	3.79074500	0.88504300	0.14581100
C	4.68344200	-0.17621300	0.01339600
C	4.22557600	-1.48802300	-0.19100100
C	2.86383900	-1.77096800	-0.26914200
H	4.13833300	1.90178200	0.29936100
H	5.75142200	0.01021400	0.06668600
H	4.94826900	-2.29194000	-0.28942000
H	2.50457500	-2.78304600	-0.42774200
C	1.28114600	1.53303600	0.16555500
C	0.48880000	-0.75220800	-0.17585700
C	0.02484500	0.68437600	0.05484400
N	-1.12447800	1.21985900	0.07698300
C	-2.33175700	0.49311000	0.06076200
C	-2.57769800	-0.57648600	0.93028700
C	-3.34648900	0.96101300	-0.78272400
C	-3.82389300	-1.19449500	0.92276100
H	-1.80136400	-0.90483600	1.61401000
C	-4.57750100	0.31140500	-0.81008000
H	-3.14990500	1.81989700	-1.41737600
C	-4.82120800	-0.76432100	0.04476200
H	-4.01606900	-2.01830100	1.60334300
H	-5.35371000	0.65993700	-1.48427900
H	-5.78855500	-1.25684700	0.03806000
O	1.31581400	2.73388200	0.30805200
O	-0.19882800	-1.71983300	-0.41308400

i^+

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -782.3447851
Enthalpy = -782.113927
Free Energy = -782.169294
M06-2X/def2-TZVP
Electronic Energy = -782.611715

C	-2.45088600	0.64251400	0.06857200
C	-2.11233800	-0.71542800	-0.07787900
C	-3.09409600	-1.69265000	-0.20428500
C	-4.42301600	-1.27583700	-0.17074600
C	-4.76019900	0.08030800	-0.02335600
C	-3.77778500	1.06023800	0.09730000
H	-2.83095500	-2.73897600	-0.32003800
H	-5.21624600	-2.01095200	-0.26021400
H	-5.80678700	0.36577100	-0.00436100
H	-4.03240500	2.10931300	0.20672800
C	-0.64744000	-0.91997400	-0.09304300
C	-1.23290300	1.45748000	0.15392000
C	-0.07292700	0.47821600	0.08593000
N	1.11783500	0.95416200	0.08396000
C	2.40312800	0.35852700	0.05891700
C	3.43331800	1.15614100	-0.45431600
C	2.63834600	-0.92382900	0.56231200
C	4.71723800	0.63255100	-0.51489900
H	3.22080100	2.16033400	-0.81067000
C	3.93289600	-1.42400600	0.50496300
H	1.84188200	-1.50375200	1.00935700
C	4.96544800	-0.65728100	-0.04059600
H	5.52331400	1.23160300	-0.92398200
H	4.13769500	-2.41404800	0.89742800
H	5.97172700	-1.06145200	-0.08117000
H	1.13745900	1.98749300	0.10320200
O	-1.07472500	2.65170800	0.25040300
O	-0.03578100	-1.94499600	-0.26549700

Xyz coordinates and thermochemistry in DCM solvent (Hartree and Å)

1

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.863765
Enthalpy = -2102.470988
Free Energy = -2102.576991
M06-2X/def2-TZVP
Electronic Energy = -7225.570052

C	-0.16069200	2.63123700	-1.01492100
O	0.85703400	1.99088600	-1.25572300
C	-0.98240900	2.31421200	0.22267300

C	-2.16562600	3.15845300	0.65425000
O	-2.28509700	4.30444500	0.30157900
O	-2.97711800	2.50002500	1.45490400
O	-0.62659000	3.58183600	-1.75659000
C	0.08805400	3.84618300	-2.98737900
H	0.12077700	2.93665400	-3.58994400
H	-0.48429600	4.62623800	-3.48304400
H	1.09762600	4.18667500	-2.75436200
C	-4.16878500	3.20680200	1.84921100
H	-4.73573100	2.50014400	2.45142000
H	-3.90252800	4.08870400	2.43451500
H	-4.73383900	3.50064300	0.96194400
N	-0.48422000	1.29255500	0.79877100
O	-1.08153400	0.82009800	1.92955000
S	-0.24895100	-0.56514700	2.37507300
O	-0.75691500	-1.67173600	1.56981900
O	1.16167500	-0.22926300	2.22466100
C	-0.78037200	-0.67228800	4.04070400
H	-1.86918900	-0.75606900	4.03693700
H	-0.31562100	-1.57599300	4.44472300
H	-0.43166400	0.22319300	4.55855600
C	-1.80030000	-0.64622800	-1.28539900
C	-1.61088900	0.20856600	-2.39322100
C	-2.96047500	-0.38622100	-0.52404500
C	-2.47687400	1.26343800	-2.69774200
H	-0.74674900	0.06835400	-3.04326700
C	-3.84652300	0.65628100	-0.81305900
H	-3.18283300	-1.00583100	0.34661800
C	-3.59532800	1.50336500	-1.89384000
H	-2.27855700	1.90625600	-3.55337200
H	-4.71951800	0.82303700	-0.18537300
H	-4.26532200	2.33008200	-2.11628200
Mg	-0.40271900	-2.08578700	-0.55970900
Br	-0.76745500	-4.54494000	-0.49065700
Mg	1.62539700	0.61648200	0.12659100
C	1.80772400	-1.36281700	-0.71359600
C	1.75859000	-1.64090800	-2.10307300
C	2.45827100	-2.34334800	0.07438900
C	2.31672000	-2.79345000	-2.66493900
H	1.27470600	-0.93160300	-2.77446900
C	3.03235200	-3.49355600	-0.47171500
H	2.52475000	-2.20409400	1.15333800
C	2.95961700	-3.72017300	-1.84533500
H	2.24967100	-2.96609500	-3.73557600
H	3.52286500	-4.21741800	0.17326700
H	3.39204000	-4.61958400	-2.27424700

Br	3.39074300	2.09000300	1.06389500

$(PhMgBr)_2$

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -889.6841435

Enthalpy = -889.481631

Free Energy = -889.550929

M06-2X/def2-TZVP

Electronic Energy = -6012.004722

Mg	1.81200500	0.04983700	-0.17222800
Br	0.06546400	-1.78725000	-0.87624700
Mg	-1.36714100	0.34118700	-0.34523300
C	-3.46851100	0.36448300	-0.36341700
C	-4.22486400	-0.77340700	-0.71004500
C	-4.21039100	1.52689400	-0.06693400
C	-5.62251400	-0.75990800	-0.76234100
H	-3.72000300	-1.70850000	-0.95274200
C	-5.60748900	1.55925600	-0.11314900
H	-3.69197700	2.44511400	0.20880200
C	-6.31958200	0.41105600	-0.46284800
H	-6.16641500	-1.66066800	-1.03638100
H	-6.13997000	2.47766700	0.12229300
H	-7.40533600	0.42901500	-0.50191500
Br	3.99538300	-0.87251300	0.43020000
C	0.45164800	1.71947300	-0.16913700
C	-0.00008400	2.25944700	-1.40184800
C	0.07876100	2.44162200	0.99120100
C	-0.75086100	3.43941900	-1.47534300
H	0.24507000	1.75422400	-2.33733900
C	-0.66420500	3.62275700	0.93031500
H	0.37945500	2.07412400	1.97037200
C	-1.07988700	4.12250800	-0.30570600
H	-1.07552800	3.81952700	-2.43952000
H	-0.92437100	4.14931000	1.84422000
H	-1.66540700	5.03578600	-0.35440000

TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.841188

Enthalpy = -2102.450158

Free Energy = -2102.554225

M06-2X/def2-TZVP

Electronic Energy = -7225.552801

C	-3.49347500	-0.53317900	4.01059800
C	-3.62356600	-1.60514500	3.12848000
H	-2.61413500	1.41118300	4.33336000

C	-2.70633600	0.56511000	3.65788300
C	-2.95965400	-1.58539600	1.89567700
C	-2.14656200	-0.49830800	1.54979600
C	-2.05437200	0.57591400	2.42203700
H	-3.08143900	-2.43659000	1.22731900
H	-1.48056300	1.47032600	2.15609800
Mg	-0.60950300	-1.19095000	0.03214800
Mg	2.36119000	-0.48930800	-0.02577100
H	-4.24272800	-2.45839700	3.39300200
H	-4.01529500	-0.54462400	4.96297600
C	4.36081800	0.14704700	0.04731800
C	5.10428200	0.42413300	-1.11841700
C	5.04248500	0.33923200	1.26702900
C	6.43218500	0.86188700	-1.07859300
H	4.64401300	0.29325000	-2.09807300
C	6.36949600	0.77613000	1.32771500
H	4.53194400	0.13932500	2.20968300
C	7.06962000	1.04125900	0.14967000
H	6.96906600	1.06132700	-2.00294500
H	6.85781000	0.90741800	2.29043400
H	8.10154300	1.37932200	0.18871700
Br	1.23023900	-2.31980000	1.48963700
Br	1.05352800	-1.37187900	-2.11720400
C	-2.29632000	2.88481300	-0.32291000
O	-3.47685600	2.77828600	-0.08027100
C	-1.36952100	1.71864900	-0.34871200
C	0.02231200	1.72109500	0.09253900
O	0.60183700	0.61984500	0.28463300
O	0.59122100	2.86498700	0.32174500
O	-1.67795900	4.02170500	-0.61665300
C	-2.50202000	5.19981800	-0.59461600
H	-2.94086100	5.33161700	0.39621800
H	-1.83293300	6.02513100	-0.82969500
H	-3.29129600	5.12048900	-1.34484300
C	1.94601500	2.85370000	0.82826800
H	2.17668500	3.89623300	1.03382100
H	1.99377100	2.25985600	1.74355700
H	2.62017600	2.45588100	0.06665400
N	-1.75840500	0.48011300	-0.57089900
O	-3.02530000	0.32093200	-1.07861100
S	-3.13006600	-1.17391500	-1.81102200
O	-2.17188400	-2.04634400	-1.11229800
C	-2.54877400	-0.83380100	-3.43910000
H	-2.50711400	-1.79085300	-3.96531800
H	-3.26096100	-0.15093300	-3.90566300
H	-1.55361000	-0.39050200	-3.35489800

O	-4.53055100	-1.49734600	-1.77946800

2

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.947961
Enthalpy = -2102.554244
Free Energy = -2102.656923
M06-2X/def2-TZVP
Electronic Energy = -7225.657763

C	-2.41170700	1.16559800	-1.57165300
O	-1.39783700	1.90056100	-1.64264500
C	-2.58366700	0.10480800	-0.66060500
C	-3.86691500	-0.44220500	-0.32240400
O	-4.97146100	0.05793200	-0.63848400
O	-3.81737200	-1.52175700	0.43601000
O	-3.43659000	1.40634500	-2.43777400
C	-3.17971800	2.39902700	-3.46714200
H	-2.28465600	2.12119800	-4.02194700
H	-4.05950100	2.37052800	-4.10743600
H	-3.05727300	3.38813600	-3.01832500
C	-5.07073200	-2.05527200	0.89908500
H	-4.80509300	-2.91399200	1.51251600
H	-5.60074300	-1.30852400	1.49291800
H	-5.68353400	-2.36469400	0.05120600
N	-1.41461700	-0.36625100	-0.02913300
O	-1.41953400	-0.04717400	1.38341200
S	-0.13751400	0.88925600	1.72661100
O	1.09097900	0.25176500	1.31482800
O	-0.39208800	2.24138400	1.18896600
C	-0.32682800	0.94630500	3.47501900
H	-0.17835700	-0.06323500	3.86129100
H	0.44592500	1.62407100	3.84538800
H	-1.32391400	1.32655500	3.70219000
C	-1.01908300	-1.72697900	-0.22937800
C	-1.06484000	-2.21851900	-1.53898900
C	-0.55300700	-2.53692900	0.80647200
C	-0.65271300	-3.52128300	-1.80131200
H	-1.41680700	-1.58186100	-2.34453200
C	-0.14327100	-3.84119000	0.52635200
H	-0.51356100	-2.16896400	1.82401700
C	-0.19095300	-4.34314600	-0.77181200
H	-0.69116800	-3.89193000	-2.82108900
H	0.21341500	-4.46557800	1.34005100
H	0.12919400	-5.35861000	-0.98128400
Mg	-1.32452000	3.31059600	-0.23991000
Br	0.02073500	5.19757000	-1.01461000

Mg	-5.12131400	1.96091000	-1.20732900
C	-4.01785400	3.44916500	-0.09114300
C	-4.06972300	4.80856600	-0.49137000
C	-3.33421700	3.21899400	1.13033000
C	-3.51377400	5.84815000	0.25729100
H	-4.57338100	5.07189200	-1.42092800
C	-2.74387300	4.25196400	1.88647000
H	-3.26267700	2.20046800	1.51785700
C	-2.84437300	5.57276900	1.45151000
H	-3.58214300	6.87208700	-0.09895100
H	-2.21724800	4.02027200	2.80885300
H	-2.38961300	6.37414000	2.02518700
Br	-6.96816600	2.43861300	-2.76332100

TS2

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.924036

Enthalpy = -2102.531883

Free Energy = -2102.633016

M06-2X/def2-TZVP

Electronic Energy = -7225.634964

C	0.92590800	1.16293300	-1.76379300
O	1.28483400	0.72401300	-2.82971600
C	1.59006900	0.94439200	-0.48374200
C	1.22821700	1.57338800	0.75494600
O	0.27963700	2.37669500	0.92358400
O	1.97060400	1.20981100	1.78806100
O	-0.19952200	1.98466000	-1.71822500
C	-0.69645400	2.40945300	-3.01250200
H	-1.04881800	1.54756300	-3.57890600
H	-1.51185600	3.09909800	-2.79908400
H	0.10278900	2.91635500	-3.55263800
C	1.63157800	1.77319500	3.06613600
H	2.33517800	1.32904400	3.76776600
H	1.74822600	2.85806500	3.04333600
H	0.60522500	1.51328900	3.33418900
N	2.55309600	-0.02164000	-0.53571300
O	2.00125700	-1.34435600	0.31435200
S	1.33706700	-2.34978900	-0.67625800
O	0.10093600	-1.71332800	-1.22868600
O	2.24806600	-2.84568700	-1.68690800
C	0.84189400	-3.63430700	0.43282800
H	0.19871300	-3.20655700	1.20538800
H	0.30414400	-4.37415400	-0.16525200
H	1.74638800	-4.06728400	0.86370500
Mg	-1.40915800	2.01303800	-0.04115800

Br	-3.04611800	3.82920200	-0.32358200
Mg	-1.76570700	-1.35178900	-0.71751800
C	-2.06489600	0.13461400	0.85822400
C	-3.44600700	0.03872500	1.15670800
C	-1.19733900	-0.55410900	1.74679200
C	-3.92787700	-0.66170800	2.26415000
H	-4.16890900	0.53523100	0.51110600
C	-1.66618800	-1.26735100	2.85359000
H	-0.11815200	-0.53096000	1.57990600
C	-3.03596100	-1.31894100	3.11112500
H	-4.99521400	-0.70314700	2.46061000
H	-0.96699400	-1.77677800	3.51103800
H	-3.40765200	-1.87472600	3.96695600
Br	-2.97611300	-3.48741900	-0.65831800
C	3.87297500	0.14320500	-0.03496700
C	4.41453000	1.43418700	0.01382500
C	4.68241800	-0.96066500	0.25589500
C	5.75154600	1.61125000	0.36143100
H	3.79628600	2.29083200	-0.23279700
C	6.01292300	-0.76595500	0.61727200
H	4.27525600	-1.96263300	0.20559100
C	6.55725900	0.51694100	0.67317400
H	6.15903900	2.61715100	0.39295800
H	6.62757800	-1.63044000	0.84931100
H	7.59639300	0.66082300	0.95128000

3

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2103.038903
Enthalpy = -2102.643971
Free Energy = -2102.749631
M06-2X/def2-TZVP
Electronic Energy = -7225.75384

C	-0.29540000	-1.77377700	-0.85591500
O	0.65218200	-0.98406200	-0.72866400
C	-1.70471700	-1.26333400	-0.78957000
C	-2.82321900	-2.25033100	-1.07231600
O	-2.97983800	-2.73509300	-2.16611500
O	-3.53947800	-2.48204500	0.00694600
O	-0.20194200	-3.04496200	-1.01169100
C	1.11815300	-3.64470700	-0.95651900
H	1.53638400	-3.47689600	0.03861300
H	0.95465000	-4.70488600	-1.13142800
H	1.74388900	-3.20976600	-1.73602900
C	-4.67191000	-3.35995900	-0.16338200
H	-5.12765100	-3.43528700	0.82120500

H	-5.36873000	-2.92151800	-0.88070700
H	-4.33453500	-4.33792600	-0.51048500
N	-1.83071100	-0.04646900	-0.44602700
O	-0.45223700	-2.00684000	1.85179300
S	0.44212200	-0.94095200	2.31704300
O	1.87513100	-1.18388400	1.90742500
O	0.01644700	0.42523100	1.85101200
C	0.44179800	-0.88217900	4.07991700
H	0.77623900	-1.85495200	4.44380300
H	1.12143500	-0.08921300	4.39456100
H	-0.57957400	-0.67577300	4.40340600
Mg	2.57796800	-0.61430500	0.13280700
Br	4.42518200	-2.00090700	-0.70738200
Mg	0.09537100	1.11578000	-0.04627300
C	2.33845100	1.50939500	-0.22130300
C	2.67791100	1.95482700	-1.51956400
C	2.71677600	2.36281800	0.83930200
C	3.33381500	3.16483500	-1.75100300
H	2.42093700	1.33952400	-2.38300100
C	3.37925000	3.57350100	0.62952800
H	2.48038800	2.07952700	1.86565600
C	3.68516200	3.97584900	-0.67095700
H	3.57266200	3.47501400	-2.76465000
H	3.65306700	4.20277500	1.47208100
H	4.19736100	4.91865900	-0.84265200
Br	-0.89172200	3.37747100	-0.39967100
C	-3.12355800	0.52535500	-0.27731500
C	-4.09431900	0.43255300	-1.27638200
C	-3.37550300	1.19560100	0.92090300
C	-5.34510100	1.00627600	-1.05750600
H	-3.86241100	-0.04418800	-2.22481500
C	-4.63826000	1.73621800	1.13821700
H	-2.59341900	1.26961800	1.67037700
C	-5.62165300	1.64631500	0.15049700
H	-6.10026000	0.95481600	-1.83535600
H	-4.84972200	2.24335200	2.07413800
H	-6.59903000	2.08788700	0.31777300

OMs anion

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -663.7433089

Enthalpy = -663.686466

Free Energy = -663.720625

M06-2X/def2-TZVP

Electronic Energy = -663.9331943

O	0.55525700	1.35778100	-0.45034500

S	0.15494600	0.00004000	-0.00021800
O	0.55038300	-1.06908000	-0.95262100
O	0.55747300	-0.29069300	1.39988800
C	-1.63707500	0.00174800	0.00299200
H	-1.98850200	0.21416000	-1.00829500
H	-1.98618200	-0.98089400	0.32528600
H	-1.98690600	0.77154500	0.69317500

C_6H_5 anion

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -231.5956457
Enthalpy = -231.502977
Free Energy = -231.535702
M06-2X/def2-TZVP
Electronic Energy = -231.669802

TS3

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -1670.861154
Enthalpy = -1670.432313
Free Energy = -1670.535777
M06-2X/def2-TZVP
Electronic Energy = -6793.459861

C	3.60761900	-2.81903900	-2.81241400
C	3.67106900	-3.22876600	-1.47880000
H	2.81088700	-1.37241800	-4.20089900
C	2.84596400	-1.70396300	-3.16690500
C	2.96667300	-2.52479900	-0.49689100
C	2.17933400	-1.42237300	-0.85463100
C	2.15234800	-1.00249400	-2.17634200
H	3.03892100	-2.85191400	0.53959700
H	1.60326900	-0.09874300	-2.46141500
Mg	0.41493300	-1.17369100	0.48000500
Mg	-2.49962500	-0.50784200	0.27765000
H	4.27131500	-4.09138800	-1.20189400
H	4.16484700	-3.35870200	-3.57260900
C	-4.43236200	0.28755600	0.07497100
C	-5.00356100	1.12861000	1.05169200
C	-5.22698700	0.04603800	-1.06508600
C	-6.27484500	1.69428900	0.90769500
H	-4.44914700	1.35635900	1.96234700
C	-6.50008600	0.60140900	-1.22703200
H	-4.85104600	-0.59899800	-1.85980700
C	-7.02818600	1.43179700	-0.23716700
H	-6.67733500	2.33728600	1.68677200
H	-7.07952400	0.38632800	-2.12172600

H	-8.01677000	1.86700500	-0.35558600
Br	-1.46461800	-2.78354500	-0.49474200
Br	-1.11740000	-0.63089600	2.54607100
C	2.24660600	2.42636600	-1.08858900
O	3.37187000	2.16117400	-1.45243500
C	1.32572600	1.42154400	-0.48014400
C	-0.06599800	1.30101700	-0.88304700
O	-0.73321200	0.29824000	-0.49995600
O	-0.57009400	2.19986400	-1.67543500
O	1.70426000	3.63926500	-1.15227900
C	2.52711900	4.65810200	-1.74314700
H	2.76874300	4.39477100	-2.77506900
H	1.93199300	5.56875200	-1.71064800
H	3.44597600	4.77982800	-1.16627900
C	-1.94674200	2.04201800	-2.08711400
H	-2.12899900	2.85960500	-2.78049900
H	-2.07721900	1.07845100	-2.58428900
H	-2.60279000	2.12485500	-1.21829800
N	1.71233700	0.48233800	0.36456200
C	2.90094600	0.60337200	1.16291000
C	2.67246600	0.91077400	2.50790700
C	4.19835000	0.39637600	0.69272000
C	3.75141700	1.03948700	3.38073400
H	1.65330100	1.05565000	2.85523400
C	5.26784200	0.50862800	1.57920800
H	4.35884800	0.14622400	-0.34884100
C	5.05094600	0.83467300	2.91883500
H	3.57044300	1.28911700	4.42150800
H	6.27712100	0.34098800	1.21615000
H	5.89117300	0.92233800	3.60059100

4

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1902.64924

Enthalpy = -1902.121648

Free Energy = -1902.241446

M06-2X/def2-TZVP

Electronic Energy = -7025.320058

C	-1.13852400	0.14972300	-1.18507600
O	0.10089300	0.15067300	-1.35236500
C	-1.83418200	-0.21658800	-0.00697700
C	-1.15773500	-0.64976700	1.15969300
O	0.07796700	-0.78183000	1.31172700
O	-1.96825000	-0.95202000	2.18402800
O	-1.93058400	0.52565200	-2.19881500

C	-1.26960200	0.93837900	-3.40020000
H	-0.66844300	0.12407400	-3.81097400
H	-2.06839600	1.20478700	-4.09131900
H	-0.63009700	1.80346000	-3.20961800
C	-1.33257800	-1.37777500	3.39441400
H	-2.14552300	-1.57437700	4.09218000
H	-0.74882000	-2.28546300	3.22631600
H	-0.67969600	-0.59283200	3.78334300
N	-3.25266200	-0.14363000	0.00130800
C	-4.00260200	-1.31760300	-0.19762200
C	-3.45883600	-2.39336000	-0.91781700
C	-5.28334900	-1.46692900	0.36261300
C	-4.18220600	-3.57267500	-1.08404000
H	-2.46581900	-2.30524700	-1.34623600
C	-6.00031200	-2.64624200	0.18291200
H	-5.71040800	-0.66051500	0.95022600
C	-5.46007800	-3.71000200	-0.54288500
H	-3.73857400	-4.38771200	-1.64905200
H	-6.98653100	-2.73725900	0.62954100
H	-6.02113400	-4.62949400	-0.67633500
Mg	2.01765400	0.45500800	-1.27097500
Mg	1.99029100	-0.42101800	1.26373200
C	2.11134700	1.73832900	0.57826200
C	3.31264100	2.42191600	0.86935500
C	0.92474200	2.46482600	0.82224000
C	3.33783300	3.72680400	1.36712100
H	4.26722500	1.92012700	0.70584700
C	0.92532400	3.77084600	1.32099900
H	-0.03909900	1.99765900	0.61266600
C	2.13806600	4.40373500	1.59564100
H	4.28571700	4.21533800	1.57801200
H	-0.01332600	4.29224100	1.49338700
H	2.14957200	5.41866200	1.98406300
Br	2.97836800	1.27652500	-3.40597300
Br	3.06138800	-0.94075000	3.44769200
C	-3.85901500	1.12205300	0.15188700
C	-5.02298400	1.46140600	-0.55606500
C	-3.26599000	2.09032100	0.97558400
C	-5.58402000	2.72860700	-0.42473800
H	-5.47826700	0.73263900	-1.21944400
C	-3.82906100	3.35958700	1.09276800
H	-2.36153100	1.84496800	1.52393100
C	-4.99366800	3.68894500	0.39938600
H	-6.48171500	2.97082600	-0.98667600
H	-3.35316800	4.09219500	1.73864300
H	-5.43096200	4.67792200	0.49347600

C	4.54593900	-3.08418900	-1.13323500
C	3.64438500	-4.09285500	-1.47968800
C	2.27309900	-3.86379000	-1.36400700
C	1.81452700	-2.62485300	-0.90596800
C	2.68715200	-1.57629600	-0.54130800
C	4.06561100	-1.85625200	-0.67241400
H	5.61533600	-3.25713500	-1.22290500
H	4.00962600	-5.05195800	-1.83720400
H	1.56688300	-4.64603100	-1.63093200
H	0.73767200	-2.46895800	-0.82750600
H	4.79558500	-1.09010500	-0.40746000

S_N2 TS

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.801248
Enthalpy = -2102.41131
Free Energy = -2102.517365
M06-2X/def2-TZVP
Electronic Energy = -7225.516234

C-attack TS

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -2102.841896
Enthalpy = -2102.450442
Free Energy = -2102.55583
M06-2X/def2-TZVP
Electronic Energy = -7225.552574

C	2.27526700	4.00776800	-1.61924500
C	3.17112100	3.31909500	-0.80488700
H	0.29326700	4.01802600	-2.47411500
C	0.99539800	3.49038300	-1.83478400
C	2.77948400	2.12213700	-0.19687100
C	1.50125100	1.57248000	-0.40587300
C	0.61840300	2.29202300	-1.22997100
H	3.51546900	1.61701000	0.42828900
H	-0.38631800	1.91821700	-1.41804900
Mg	1.88232200	-0.59688500	-0.81659400
Mg	-2.07100200	-0.14636900	0.22722100
H	4.17214500	3.70749800	-0.64043600
H	2.57044400	4.94243100	-2.08694900
Br	-0.47610700	-1.05138200	-1.82332000
C	1.99318400	0.17951800	1.86774800
O	2.66513800	-0.58711300	1.18061000
C	0.58295900	0.48063600	1.44441100
C	-0.19581100	1.76085100	1.53673800
O	-1.33558600	1.77829900	1.07746500

O	0.40632600	2.75630000	2.11395600
O	2.37938800	0.73957100	2.96926600
C	3.74379100	0.47311400	3.39168400
H	4.43117400	0.77537400	2.60051300
H	3.88282000	1.07650100	4.28490700
H	3.85125700	-0.58934100	3.61154600
C	-0.28925900	4.02551800	2.08931000
H	0.38491200	4.72700800	2.57459800
H	-0.47301600	4.31311300	1.05220400
H	-1.22810900	3.94019100	2.63751900
N	-0.28564700	-0.49854200	1.35968300
O	0.27282800	-1.78832800	1.31349200
S	-0.95686300	-2.89776500	1.42350400
O	-2.14127800	-2.25598400	0.84014700
O	-0.41550500	-4.09749600	0.84134100
C	-1.17133400	-3.04192900	3.16760000
H	-1.40039900	-2.04929000	3.56118100
H	-2.00925500	-3.72534300	3.32583400
H	-0.24762000	-3.44481000	3.58545700
Br	3.72123600	-1.49048100	-2.15695200
C	-4.02510800	0.36633000	-0.37480500
C	-4.85578700	-0.53999100	-1.06708700
C	-4.58460800	1.63961300	-0.13997100
C	-6.14642800	-0.21103700	-1.49367300
H	-4.49024700	-1.54326000	-1.29004200
C	-5.87312600	1.99042900	-0.55760600
H	-4.00002400	2.39530500	0.38559300
C	-6.66100900	1.06130200	-1.23826700
H	-6.74929100	-0.94345900	-2.02564100
H	-6.26145000	2.98594900	-0.35443500
H	-7.66259600	1.32575400	-1.56673400

Ester Addition TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2102.828153

Enthalpy = -2102.4371

Free Energy = -2102.540141

M06-2X/def2-TZVP

Electronic Energy = -7225.537643

C	-0.36992200	1.23359500	-0.44649100
O	0.49807700	0.31126000	-0.46002700
C	-1.59286800	1.17309700	-1.33068400
C	-2.10713500	2.46722500	-1.93349000
O	-1.37845500	3.22708100	-2.52070400
O	-3.40605800	2.60365400	-1.75537900
O	-0.09461600	2.45764700	-0.09203700

C	1.17749300	2.70832600	0.54290100
H	1.97262800	2.61992800	-0.20061000
H	1.11315100	3.72772900	0.91642500
H	1.33430400	2.01015100	1.36784200
C	-3.99309200	3.78174200	-2.34457900
H	-5.05283700	3.72580400	-2.10626100
H	-3.54526200	4.67559200	-1.90682800
H	-3.83760300	3.77102400	-3.42472200
N	-2.23791700	0.13436500	-1.69506100
O	-1.66065000	-1.01817700	-1.15542000
S	-2.71032400	-2.27800100	-0.81776000
O	-2.08008500	-2.66438300	0.45594500
O	-4.07502000	-1.82790700	-0.85331900
C	-2.35788200	-3.43639500	-2.09455600
H	-1.28455300	-3.63264600	-2.07560900
H	-2.93648800	-4.33560400	-1.86580400
H	-2.68030700	-2.98653500	-3.03614500
C	-1.76720100	0.64596400	1.43141400
C	-3.15890000	0.69120900	1.22862500
C	-1.30148600	1.27661800	2.60622600
C	-4.03722500	1.28535300	2.13943900
H	-3.60558200	0.26914400	0.32911000
C	-2.16093100	1.88555100	3.52227800
H	-0.23905900	1.28446900	2.83712000
C	-3.53749800	1.88887300	3.29205500
H	-5.10548400	1.28544400	1.94018100
H	-1.75616300	2.35166600	4.41676600
H	-4.21162600	2.36227200	4.00024700
Mg	-0.53780700	-1.13529600	0.79453900
Br	1.55038700	-0.90477700	2.39885400
Mg	2.33286000	-0.54262300	-0.11139400
C	4.14378900	0.44615500	-0.51902000
C	4.75424000	0.47298100	-1.78981000
C	4.80611300	1.17548700	0.49066000
C	5.93648200	1.17607700	-2.04351200
H	4.30071900	-0.06958100	-2.61905300
C	5.98871200	1.88487100	0.25736500
H	4.39554400	1.19921700	1.50104900
C	6.55897400	1.88687500	-1.01643800
H	6.37198300	1.16920300	-3.03994200
H	6.46523400	2.43280200	1.06681100
H	7.47773100	2.43527500	-1.20612800
Br	1.13527400	-2.78744900	-0.71455100

tBu-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2338.642939
Enthalpy = -2338.076387
Free Energy = -2338.195987
M06-2X/def2-TZVP
Electronic Energy = -7461.423189

C	-2.72287300	-1.99500300	4.16872300
C	-2.64829100	-3.05765100	3.26890800
H	-2.37226600	0.11333900	4.47009900
C	-2.29859100	-0.72251100	3.77970900
C	-2.13872700	-2.85384100	1.98029900
C	-1.68465200	-1.58561600	1.60024000
C	-1.80114900	-0.52875500	2.48881900
H	-2.09220200	-3.70209300	1.29930500
H	-1.52549500	0.48789000	2.19126300
Mg	-0.06818500	-1.84571200	0.00575200
Mg	2.57363100	-0.41027700	-0.21690700
H	-2.98743600	-4.04720400	3.56395400
H	-3.12502900	-2.15236300	5.16523600
C	4.47431400	0.48549000	-0.25206300
C	5.06819400	0.91726600	-1.45590500
C	5.21864100	0.73379300	0.91901600
C	6.31211500	1.55510200	-1.49682600
H	4.55119200	0.75633000	-2.40266300
C	6.46425800	1.37013200	0.89979800
H	4.82544000	0.42208000	1.88744600
C	7.01438000	1.78713300	-0.31315100
H	6.73247100	1.87140000	-2.44859900
H	7.00473100	1.54008900	1.82800400
H	7.98113400	2.28269800	-0.33629900
Br	2.03748000	-2.40684100	1.41174600
Br	1.44904800	-1.62253700	-2.23210300
C	-2.85592800	1.56957400	-0.19202000
O	-3.88834400	1.15267400	0.28480200
C	-1.62912800	0.72044300	-0.28164500
C	-0.28839800	1.13815700	0.11431500
O	0.62299200	0.26660300	0.19508100
O	-0.16163600	2.38729700	0.43683100
O	-2.64999000	2.76449600	-0.72428700
C	-3.68243100	3.81292900	-0.67483900
C	1.07974600	3.02417100	0.94737200
N	-1.66471300	-0.58260200	-0.47845000
O	-2.86523200	-1.08745600	-0.94088800
S	-2.58118700	-2.53997100	-1.69677200
O	-1.39151200	-3.11945100	-1.04954000
C	2.00907300	3.22284400	-0.23985400
H	2.96111800	3.63335100	0.10958600

H	2.22214500	2.28426000	-0.75740000
H	1.56450700	3.91984200	-0.95587900
C	1.68332700	2.21474100	2.08938100
H	2.35991600	2.87079000	2.64449200
H	0.90320800	1.87044800	2.77559400
H	2.26690100	1.35566600	1.75769500
C	0.56306700	4.35687400	1.46942900
H	0.01728400	4.88937700	0.68627300
H	-0.09675800	4.20631000	2.32895800
H	1.41191700	4.97039100	1.78289200
C	-4.00078200	4.14124900	0.77888500
H	-4.63442700	5.03269300	0.80967500
H	-4.52873000	3.32427800	1.27398400
H	-3.07885000	4.35795800	1.32818200
C	-2.99768800	4.98751800	-1.35955900
H	-3.67745000	5.84347600	-1.38619700
H	-2.09263800	5.27656900	-0.81740000
H	-2.72472300	4.72677100	-2.38641700
C	-4.91056000	3.37196500	-1.46275300
H	-4.62125700	3.05826100	-2.47074900
H	-5.43760200	2.55420200	-0.96963900
H	-5.59329500	4.22234400	-1.55290100
C	-2.17996900	-2.04050400	-3.33806900
H	-1.86941800	-2.93984200	-3.87614200
H	-3.07824500	-1.60212500	-3.77588800
H	-1.36241300	-1.31811300	-3.27747800
O	-3.83293800	-3.24469400	-1.62379600

tBu-*C*-attack TS

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2338.650186

Enthalpy = -2338.083019

Free Energy = -2338.202607

M06-2X/def2-TZVP

Electronic Energy = -7461.42953

C	1.55705000	2.18554800	-3.89500100
C	2.57507600	1.94592900	-2.97332000
H	-0.52684000	1.87795300	-4.36284500
C	0.27399900	1.69083700	-3.65271200
C	2.30705200	1.20072000	-1.82039700
C	1.02909600	0.67262700	-1.55910600
C	0.01791000	0.95830800	-2.49311400
H	3.13754500	1.01627200	-1.13968400
H	-0.99577900	0.59623400	-2.33103200
Mg	1.33573700	-1.47596100	-1.09430500
Mg	-2.32137200	-0.29048700	0.39273200

H	3.57716900	2.32563800	-3.15296400
H	1.76004200	2.75770800	-4.79574900
Br	-1.17602700	-2.15567200	-1.28770300
C	1.97924900	0.22190200	1.04357800
O	2.47997700	-0.78897000	0.55024500
C	0.51897200	0.49109000	0.77422700
C	-0.18916500	1.77862600	0.45730000
O	-1.39013100	1.71440300	0.19280500
O	0.55244100	2.83446600	0.55535200
O	2.53509200	1.06274100	1.84718700
C	3.95078100	0.90677000	2.32207800
C	0.04716100	4.19980700	0.23933500
N	-0.36688700	-0.33671600	1.26081600
O	0.13897000	-1.57246500	1.69783700
S	-1.07613300	-2.37718000	2.48950700
O	-2.33179000	-1.93156800	1.87351400
O	-0.68947000	-3.76282800	2.43852700
C	-0.95844400	-1.71481200	4.11930700
H	-1.08371200	-0.63224000	4.05182100
H	-1.76633900	-2.16520100	4.70115200
H	0.01760100	-1.99042400	4.52056400
Br	2.86471800	-2.95873000	-2.30334600
C	-4.34639500	0.14763200	0.00587600
C	-5.37723500	-0.80374900	0.15603300
C	-4.75864300	1.41847300	-0.44685900
C	-6.71822200	-0.51802000	-0.12003700
H	-5.13432900	-1.81054900	0.49763300
C	-6.09385200	1.72638200	-0.72966800
H	-4.01653700	2.20492700	-0.58891700
C	-7.08150500	0.75407700	-0.56570900
H	-7.47832700	-1.28518900	0.00899400
H	-6.36432700	2.72077400	-1.07763400
H	-8.12101400	0.98414100	-0.78372300
C	-0.38129700	4.23923500	-1.21814100
H	-1.24954100	3.60375500	-1.40532200
H	-0.64703700	5.27035700	-1.46980300
H	0.44284200	3.92618800	-1.86638300
C	1.27774300	5.05900400	0.47784100
H	1.03778300	6.10186200	0.25461000
H	1.60179800	4.99015700	1.52032300
H	2.09799100	4.74147100	-0.17297400
C	-1.07394100	4.55273700	1.20571500
H	-1.97713000	3.97145900	1.01262300
H	-0.75229500	4.39287800	2.23934200
H	-1.31227000	5.61321400	1.08276500
C	4.88436200	0.98869100	1.12494700

H	5.91245500	1.00926500	1.49788900
H	4.77913200	0.12739600	0.46206500
H	4.70722500	1.91052400	0.56266100
C	4.06339600	-0.40249900	3.08750900
H	3.29699000	-0.45612500	3.86693100
H	3.97781500	-1.27023400	2.43173300
H	5.04388300	-0.43055800	3.57127400
C	4.11310800	2.10716000	3.23831200
H	5.12394000	2.10260400	3.65414100
H	3.96716200	3.03855400	2.68405300
H	3.39564800	2.06542100	4.06255300

α-Et-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1801.252076

Enthalpy = -1800.878633

Free Energy = -1800.973569

M06-2X/def2-TZVP

Electronic Energy = -6923.851938

Mg	0.66623900	-0.95103400	0.53733600
Mg	2.62763400	1.17592000	-0.41073900
Br	2.95705600	-0.48578400	1.66878700
Br	1.85838200	-0.91090200	-1.87455300
C	-1.66619400	0.87518100	-0.07829100
C	-0.50351300	1.72158600	-0.04145100
O	0.64435100	1.21808900	0.15053400
O	-0.68254400	3.01342200	-0.18289200
C	0.48571000	3.85494500	-0.15066400
H	0.10682200	4.87202700	-0.22407000
H	1.02561900	3.71505600	0.78821300
H	1.12916000	3.63117100	-1.00577600
N	-1.26570900	-0.38994300	0.02110700
O	-2.29114200	-1.32872300	0.00113200
S	-1.64202000	-2.79930100	-0.38703000
O	-0.27682000	-2.81687400	0.16639300
C	-3.05920800	1.36437800	-0.05489300
C	-4.00450100	0.84978400	-0.95315100
C	-3.44590300	2.35560900	0.85760800
C	-5.31695600	1.31489400	-0.93199300
H	-3.70755100	0.09422600	-1.67438000
C	-4.75861900	2.82021100	0.87273500
H	-2.71870800	2.75330800	1.55973600
C	-5.69666800	2.30038100	-0.02005600
H	-6.04152300	0.91162900	-1.63262900
H	-5.05016900	3.58504100	1.58580400
H	-6.72000700	2.66267700	-0.00603200

C	-0.76284800	-0.57491500	2.34289000
H	-1.83059500	-0.36843100	2.29276000
C	-0.43371400	-1.75607200	3.23235100
H	-0.96713300	-2.65752000	2.90959200
H	0.63723800	-1.99043500	3.25348400
H	-0.20141000	0.34474800	2.55344900
C	4.05603900	2.63864200	-0.90973200
H	3.93627200	3.51306900	-0.25241400
H	3.86579400	3.00685800	-1.92889300
C	5.49937200	2.11553100	-0.81261600
H	5.73577200	1.77488800	0.20298200
H	5.66101400	1.25523500	-1.47401200
H	-0.73472900	-1.56929200	4.27559000
H	6.25800400	2.86649000	-1.07907300
O	-2.60028500	-3.76362100	0.08625100
C	-1.56460500	-2.73076000	-2.14715800
H	-1.04774200	-3.63544100	-2.47737800
H	-2.58938800	-2.69959800	-2.52035900
H	-1.00004500	-1.83661100	-2.42402400

α-Ph-TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -2106.014245

Enthalpy = -2105.584729

Free Energy = -2105.688285

M06-2X/def2-TZVP

Electronic Energy = -7228.716757

C	-2.64033000	-1.33726900	4.18990600
C	-2.78420700	-2.34012600	3.23229600
H	-1.97358300	0.67915600	4.57371600
C	-2.08210100	-0.10807700	3.83269400
C	-2.36825600	-2.11943600	1.91274900
C	-1.79735200	-0.89229600	1.56440100
C	-1.67678700	0.10570500	2.51339800
H	-2.47655300	-2.92784700	1.19190500
H	-1.27070400	1.08275800	2.23906000
Mg	-0.22866900	-1.36929900	-0.13248400
Mg	2.56413100	-0.28606000	-0.18706200
H	-3.21470100	-3.29941500	3.50743100
H	-2.96779400	-1.50899300	5.21090700
C	4.47319200	0.58345300	-0.04229000
C	5.23027400	0.92709000	-1.18093400
C	5.06801000	0.88694000	1.19996800
C	6.48818700	1.53274300	-1.09526800
H	4.83672900	0.71779100	-2.17596800
C	6.32385700	1.49253700	1.30683400

H	4.54447900	0.64314000	2.12507900
C	7.03948600	1.81916800	0.15397100
H	7.03769300	1.77898100	-2.00073200
H	6.74504200	1.70674500	2.28629800
H	8.01631600	2.28924200	0.22864800
Br	1.72711800	-2.36344500	1.23671500
Br	1.33175900	-1.19612100	-2.30620800
C	-1.42754000	1.39969700	-0.21438500
C	-0.04250400	1.56312600	0.11273600
O	0.71182700	0.54706500	0.25178100
O	0.40335500	2.78541700	0.28991000
C	1.79208400	2.95167600	0.63156400
H	1.91185200	4.01374100	0.83537500
H	2.03847800	2.36482500	1.51935600
H	2.42255000	2.66095300	-0.21235700
N	-1.66799200	0.09579300	-0.40022800
O	-2.94712000	-0.20116400	-0.85207600
S	-2.89056500	-1.62415800	-1.70233500
O	-2.83477300	-1.32994200	-3.11226400
O	-1.78499900	-2.40456600	-1.10955100
C	-4.44579300	-2.29387300	-1.22777500
H	-5.21791600	-1.59316200	-1.55187500
H	-4.54393100	-3.24638600	-1.75397200
H	-4.45178500	-2.43015000	-0.14566200
C	-2.43075500	2.48697900	-0.21245400
C	-3.29056400	2.64682500	-1.30903800
C	-2.51929400	3.38645400	0.85903600
C	-4.22675500	3.67753600	-1.32537400
H	-3.21398600	1.97307200	-2.15648100
C	-3.45201300	4.42058400	0.83593400
H	-1.85881700	3.27800200	1.71406300
C	-4.31060800	4.56630600	-0.25343300
H	-4.88408200	3.79181400	-2.18180800
H	-3.50952100	5.11025300	1.67240300
H	-5.03870800	5.37167200	-0.26922200

H^+

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -0.195249401
Enthalpy = -0.192889
Free Energy = -0.205249
M06-2X/def2-TZVP
Electronic Energy = -0.195249401

H	0.00000000	0.00000000	0.00000000

a

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -1213.126794
Enthalpy = -1212.938546
Free Energy = -1213.002441
M06-2X/def2-TZVP
Electronic Energy = -1213.521941

C	-1.17020000	1.44577600	0.38788600
O	-1.27956300	1.87281000	1.51030300
C	-0.95823300	-0.02594900	0.10225800
C	-2.19541900	-0.87270700	0.01008200
O	-3.29111700	-0.36376900	0.07605600
O	-1.94190700	-2.15674600	-0.14497500
O	-1.21093800	2.14737000	-0.72796700
C	-1.39583200	3.56910000	-0.56872100
H	-0.57807500	3.98283100	0.02355100
H	-1.38565300	3.97534000	-1.57741800
H	-2.35339800	3.76401100	-0.08278500
C	-3.09716900	-3.01250400	-0.23857200
H	-2.70089700	-4.01939400	-0.35056500
H	-3.69305000	-2.93070000	0.67198800
H	-3.69603200	-2.73544300	-1.10787700
N	0.18401100	-0.56784200	-0.02025700
O	1.18962900	0.38050700	0.10296900
S	2.69202800	-0.30293700	-0.15824600
O	2.63781700	-1.03629200	-1.40438300
O	3.56570600	0.83997700	-0.00462100
C	2.83087000	-1.40838000	1.21338900
H	3.81219000	-1.88104800	1.12933500
H	2.75600700	-0.82307500	2.13068300
H	2.03726100	-2.15350500	1.13980900

a^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -1213.512044
Enthalpy = -1213.310541
Free Energy = -1213.374758
M06-2X/def2-TZVP
Electronic Energy = -1213.907946

C	-1.01390100	1.46187100	0.14074400
O	-0.28350700	1.99837200	0.93042100
C	-0.92244000	-0.03777800	-0.10157100
C	-2.12309800	-0.92828800	0.17506600
O	-3.08296200	-0.48305500	0.74171000
O	-1.91202300	-2.14675800	-0.25937700
O	-1.96300500	1.97488100	-0.59106500

C	-2.17800400	3.40405600	-0.45131200
H	-1.26760900	3.93446500	-0.73320300
H	-2.99226300	3.63285100	-1.13361000
H	-2.45482700	3.62521600	0.58007600
C	-2.97707400	-3.10688100	-0.02834700
H	-2.61412400	-4.03824400	-0.45455500
H	-3.14706800	-3.20226400	1.04439300
H	-3.87967300	-2.76623000	-0.53669700
N	0.18074800	-0.57011400	-0.45667200
O	1.24148100	0.19441300	-0.78713500
S	2.74370200	-0.34263100	-0.05754300
O	2.55273300	-1.76402200	0.11347100
O	3.70206900	0.21235400	-0.97025200
C	2.68258800	0.52968000	1.47298500
H	3.60553600	0.26931400	2.00127900
H	2.64364800	1.59686800	1.25004600
H	1.80999600	0.18501800	2.03003900
H	0.28521200	-1.58953900	-0.59795700

b

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1216.310786

Enthalpy = -1216.084303

Free Energy = -1216.149131

M06-2X/def2-TZVP

Electronic Energy = -1216.691672

C	0.40039200	1.62045000	0.35553800
O	0.35388900	2.11612900	1.45510300
C	0.57468000	0.13119500	0.12705300
O	0.32505400	2.27388100	-0.79243600
C	0.17380700	3.70335800	-0.69380400
H	1.02423700	4.13032200	-0.15879000
H	0.14544400	4.06222200	-1.72030600
H	-0.75592200	3.94409100	-0.17505600
N	-0.43882800	-0.63853300	0.03052800
O	-1.62713300	0.10628100	0.12581000
S	-2.92395900	-0.91130000	-0.04375500
O	-2.90926400	-1.44374400	-1.39387200
O	-2.92968700	-1.83167100	1.07800300
C	-4.16416600	0.33122400	0.13962700
H	-4.04884300	1.05899600	-0.66433700
H	-5.12241200	-0.18685000	0.05670500
H	-4.05662900	0.78951900	1.12330300
C	1.93973600	-0.42384900	0.04819500
C	3.03948900	0.43314500	0.16579400
C	2.14295800	-1.79780000	-0.14838200

C	4.33413000	-0.07791200	0.08876000
H	2.89799700	1.49967900	0.32108000
C	3.43592200	-2.30038900	-0.22354000
H	1.28955600	-2.46166300	-0.24152300
C	4.53376500	-1.44278300	-0.10536300
H	5.18242800	0.59247100	0.18137300
H	3.59025600	-3.36396300	-0.37528900
H	5.54188000	-1.84114400	-0.16489900

b^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1216.716168

Enthalpy = -1216.475939

Free Energy = -1216.539067

M06-2X/def2-TZVP

Electronic Energy = -1217.096176

C	-0.57660100	-0.09445600	-0.17120000
N	0.41572500	-0.92681700	-0.35514800
O	1.64956400	-0.49834200	-0.76166500
S	2.87943700	-1.16216500	0.22115000
O	2.85142200	-0.45296500	1.48144000
O	2.65473500	-2.59210200	0.19423300
C	4.21696100	-0.65329200	-0.80230800
H	4.20459500	0.43642300	-0.86175400
H	5.12327300	-1.00190000	-0.29991400
H	4.10512800	-1.12619400	-1.77857600
C	-0.38175700	1.35494100	-0.13059900
C	0.71634500	1.93850100	0.52389900
C	-1.34681100	2.16483200	-0.75312000
C	0.83927500	3.32147100	0.55104900
H	1.43970600	1.32091100	1.04466300
C	-1.19443600	3.54678500	-0.74639400
H	-2.19394700	1.71167700	-1.25800000
C	-0.10602600	4.12425900	-0.09230600
H	1.67285000	3.77512900	1.07672300
H	-1.92866600	4.17122700	-1.24411500
H	0.00385400	5.20411500	-0.07610200
H	0.28497800	-1.94167500	-0.38508100
C	-1.90382600	-0.70190700	-0.03817700
C	-2.24285000	-1.85586000	-0.76497900
C	-2.83183500	-0.12054200	0.84129400
C	-3.50117500	-2.42241800	-0.60624300
H	-1.54721100	-2.27927600	-1.48403400
C	-4.08144800	-0.70623400	1.00437800
H	-2.56330000	0.76550200	1.40755200
C	-4.41641300	-1.85232900	0.28111400

H	-3.77191100	-3.30116600	-1.18173000
H	-4.79466300	-0.26800600	1.69429700
H	-5.39794000	-2.29964300	0.40318800

c

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1219.495211

Enthalpy = -1219.230278

Free Energy = -1219.29458

M06-2X/def2-TZVP

Electronic Energy = -1219.860958

C	0.52166200	-0.10873400	-0.05040300
N	-0.52789400	-0.84464400	-0.10033100
O	-1.70822900	-0.07733700	0.00233500
S	-3.00332400	-1.09225800	0.00679900
O	-3.09943700	-1.73103900	-1.29483200
O	-2.93820800	-1.92766400	1.19386800
C	-4.23198600	0.16427600	0.18423900
H	-4.17090400	0.83637800	-0.67238000
H	-5.19311200	-0.35413800	0.20040200
H	-4.06169600	0.69030700	1.12423100
C	0.52398000	1.37799500	0.02465400
C	-0.16561500	2.14541200	-0.92101600
C	1.25537900	2.01070000	1.03558100
C	-0.12280000	3.53601900	-0.85151100
H	-0.72185800	1.65414500	-1.71344400
C	1.27719100	3.40195400	1.11422000
H	1.80116600	1.41305500	1.76068800
C	0.59189700	4.16554900	0.16894400
H	-0.64892600	4.12787200	-1.59416700
H	1.83595400	3.88813600	1.90778600
H	0.61844700	5.24963900	0.22389000
C	1.81419700	-0.84547400	-0.06666700
C	1.89954500	-2.14130200	0.46044400
C	2.95351000	-0.24781700	-0.61924900
C	3.10824900	-2.83035800	0.42582800
H	1.02054900	-2.59643500	0.90586300
C	4.16005300	-0.94444400	-0.65727700
H	2.89487200	0.75607800	-1.02948000
C	4.24022700	-2.23487500	-0.13456100
H	3.16859800	-3.83071600	0.84318100
H	5.03671700	-0.47728200	-1.09509400
H	5.18270300	-2.77349200	-0.15828300

c^+

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1219.913212
Enthalpy = -1219.634334
Free Energy = -1219.698041
M06-2X/def2-TZVP
Electronic Energy = -1220.279094

C	-0.57660100	-0.09445600	-0.17120000
N	0.41572500	-0.92681700	-0.35514800
O	1.64956400	-0.49834200	-0.76166500
S	2.87943700	-1.16216500	0.22115000
O	2.85142200	-0.45296500	1.48144000
O	2.65473500	-2.59210200	0.19423300
C	4.21696100	-0.65329200	-0.80230800
H	4.20459500	0.43642300	-0.86175400
H	5.12327300	-1.00190000	-0.29991400
H	4.10512800	-1.12619400	-1.77857600
C	-0.38175700	1.35494100	-0.13059900
C	0.71634500	1.93850100	0.52389900
C	-1.34681100	2.16483200	-0.75312000
C	0.83927500	3.32147100	0.55104900
H	1.43970600	1.32091100	1.04466300
C	-1.19443600	3.54678500	-0.74639400
H	-2.19394700	1.71167700	-1.25800000
C	-0.10602600	4.12425900	-0.09230600
H	1.67285000	3.77512900	1.07672300
H	-1.92866600	4.17122700	-1.24411500
H	0.00385400	5.20411500	-0.07610200
H	0.28497800	-1.94167500	-0.38508100
C	-1.90382600	-0.70190700	-0.03817700
C	-2.24285000	-1.85586000	-0.76497900
C	-2.83183500	-0.12054200	0.84129400
C	-3.50117500	-2.42241800	-0.60624300
H	-1.54721100	-2.27927600	-1.48403400
C	-4.08144800	-0.70623400	1.00437800
H	-2.56330000	0.76550200	1.40755200
C	-4.41641300	-1.85232900	0.28111400
H	-3.77191100	-3.30116600	-1.18173000
H	-4.79466300	-0.26800600	1.69429700
H	-5.39794000	-2.29964300	0.40318800

d

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -781.1559708
Enthalpy = -780.929783
Free Energy = -780.989816
M06-2X/def2-TZVP
Electronic Energy = -781.436967

C	2.26298800	-0.98000700	0.09525900
O	2.56106700	-2.14025200	0.23184500
C	0.84325200	-0.45249500	0.12229000
C	0.68411500	1.05644300	0.21946200
O	0.99500800	1.68969600	1.20033700
O	0.17045300	1.55930600	-0.89235000
O	3.11824900	0.01166600	-0.12971000
C	4.50472900	-0.35769700	-0.21419300
H	4.65723300	-1.04080000	-1.05213200
H	5.04612300	0.57266700	-0.37307800
H	4.82029800	-0.83255400	0.71668400
C	-0.06980000	2.97845300	-0.88609100
H	-0.49794300	3.20479600	-1.86030600
H	-0.77191900	3.23098500	-0.08887100
H	0.87010000	3.51507800	-0.74359600
N	-0.10204300	-1.29331500	0.05289700
C	-1.45541700	-0.88536300	0.08512400
C	-1.95545200	-0.02258700	1.06792400
C	-2.31340000	-1.43665600	-0.87276100
C	-3.30854500	0.31268900	1.06188000
H	-1.30078400	0.35365600	1.84881000
C	-3.65637100	-1.07223100	-0.88605000
H	-1.91149100	-2.13093000	-1.60439300
C	-4.15814900	-0.19779300	0.08059000
H	-3.69749100	0.97264100	1.83122500
H	-4.31603900	-1.48352400	-1.64384100
H	-5.20970100	0.07133000	0.07763500

d^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -781.576025

Enthalpy = -781.336339

Free Energy = -781.397803

M06-2X/def2-TZVP

Electronic Energy = -781.8586788

C	2.19955100	-1.03878400	0.07108600
O	2.25522000	-2.24325700	0.09780100
C	0.86234000	-0.31995900	0.12584900
C	0.81472000	1.19120000	0.22437100
O	1.19339300	1.75818400	1.21545800
O	0.34748700	1.71012800	-0.88519400
O	3.18061500	-0.18176100	-0.03673900
C	4.51164500	-0.74387900	-0.14079200
H	4.57451800	-1.35780000	-1.04041700
H	5.17756600	0.11275800	-0.20428200
H	4.72171100	-1.33912000	0.74856100

C	0.23305600	3.15395500	-0.91651800
H	-0.15354600	3.38551700	-1.90566300
H	-0.46251100	3.47775800	-0.14024300
H	1.21556500	3.60291300	-0.76529900
N	-0.16926800	-1.07685700	0.08062400
C	-1.55571200	-0.75513100	0.10447000
C	-2.03636200	0.37707700	0.76625100
C	-2.40345900	-1.64828500	-0.55412000
C	-3.40175300	0.63217400	0.72522600
H	-1.38415500	1.01996200	1.34776500
C	-3.76487700	-1.37161800	-0.59004000
H	-1.99527300	-2.52898700	-1.04122000
C	-4.26178200	-0.23138400	0.04276300
H	-3.79602000	1.49970700	1.24311100
H	-4.43601200	-2.04890100	-1.10667000
H	-5.32625400	-0.02199300	0.01952700
H	0.05134600	-2.08236800	-0.00142500

e

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -784.3386567
Enthalpy = -784.074217
Free Energy = -784.135249
M06-2X/def2-TZVP
Electronic Energy = -784.6088932

C	0.01640200	1.30430500	0.19534900
O	0.19786000	1.98055500	1.18135400
C	0.53076900	-0.12320800	0.04792500
O	-0.64426500	1.69630200	-0.88647400
C	-1.25356500	2.99619000	-0.81021700
H	-0.49478900	3.76130200	-0.63495900
H	-1.73619700	3.14899500	-1.77358700
H	-1.99242800	3.01125800	-0.00566600
N	-0.25720000	-1.12149300	-0.05021400
C	2.00167600	-0.30528200	0.03118100
C	2.85962200	0.79101400	-0.11706000
C	2.54203200	-1.59457400	0.13895000
C	4.23965200	0.60018200	-0.16371400
H	2.46112300	1.79823100	-0.19898700
C	3.91869600	-1.78035600	0.09745500
H	1.87248800	-2.44013400	0.25840200
C	4.77110900	-0.68342100	-0.05530200
H	4.89690100	1.45563000	-0.28295600
H	4.33038500	-2.78086000	0.18649300
H	5.84627200	-0.83131000	-0.08683500
C	-1.65770700	-0.96726300	0.03570300

C	-2.44634900	-1.53663500	-0.97118400
C	-2.26933700	-0.33383800	1.12502600
C	-3.83191600	-1.42072600	-0.91619700
H	-1.95966300	-2.05039600	-1.79487500
C	-3.65980100	-0.24062300	1.18090500
H	-1.65990800	0.05739000	1.93490800
C	-4.44484700	-0.77199100	0.15862800
H	-4.43687800	-1.84787600	-1.71041700
H	-4.12764800	0.24564600	2.03180900
H	-5.52661600	-0.69491300	0.20445000

e^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -784.7685961

Enthalpy = -784.489708

Free Energy = -784.549452

M06-2X/def2-TZVP

Electronic Energy = -785.0415244

C	0.03198000	1.27308200	0.40270700
O	-0.45226500	1.54716100	1.47010200
C	0.48047000	-0.14839000	0.08577200
O	0.29590300	2.09438800	-0.59026300
C	-0.07552400	3.47654300	-0.37775100
H	0.49182500	3.88323200	0.46095300
H	0.18096000	3.98792000	-1.30243200
H	-1.14675200	3.54178000	-0.17896500
N	-0.43186900	-1.06677000	0.00038700
C	1.90036100	-0.43422400	-0.00439100
C	2.81299400	0.49818100	0.52094800
C	2.36805400	-1.62189900	-0.59828100
C	4.17447700	0.22847500	0.48093200
H	2.46578400	1.42010200	0.97935800
C	3.73058800	-1.87445600	-0.64389000
H	1.68140300	-2.32860600	-1.05601900
C	4.63206100	-0.95492300	-0.09944400
H	4.87739900	0.94120100	0.89805500
H	4.09450800	-2.78197700	-1.11326500
H	5.69739900	-1.15951000	-0.13812300
H	-0.12107600	-2.04085400	-0.02182100
C	-1.85023200	-0.87955100	-0.05557600
C	-2.64772300	-1.75568500	0.67832700
C	-2.39593200	0.12617900	-0.85194900
C	-4.02868600	-1.59082200	0.64077800
H	-2.19153600	-2.53967900	1.27556500
C	-3.77948700	0.28026500	-0.87429800
H	-1.76155500	0.75219300	-1.47328700

C	-4.59344700	-0.57110100	-0.12717100
H	-4.66301700	-2.25878500	1.21371600
H	-4.21985900	1.05597100	-1.49179200
H	-5.67121700	-0.44803800	-0.15363900

f

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -787.5221627
Enthalpy = -787.219538
Free Energy = -787.280637
M06-2X/def2-TZVP
Electronic Energy = -787.7744114

C	0.54728400	-0.35662700	-0.06747500
N	-0.20556500	-1.39350700	-0.09773300
C	0.04741900	1.05543200	-0.07343600
C	-0.84115000	1.48453800	-1.06546000
C	0.46550000	1.95404400	0.91408400
C	-1.31010200	2.79674400	-1.06559200
H	-1.16199600	0.79059100	-1.83751500
C	-0.02072000	3.26044500	0.92430400
H	1.16280200	1.62599200	1.68076300
C	-0.90658300	3.68446000	-0.06711900
H	-1.99301400	3.12470900	-1.84328500
H	0.29698300	3.94783200	1.70241800
H	-1.27842900	4.70459900	-0.06379100
C	2.02448000	-0.57206400	-0.04488200
C	2.54135900	-1.77931300	0.44591700
C	2.90801000	0.40599600	-0.51891800
C	3.91422500	-2.00452100	0.45860500
H	1.85514900	-2.53221300	0.82041600
C	4.28314400	0.17398100	-0.51611500
H	2.52323900	1.34546500	-0.90417100
C	4.78924000	-1.02864400	-0.02476100
H	4.30392500	-2.93975000	0.84900500
H	4.95763600	0.93476600	-0.89679500
H	5.86059000	-1.20557900	-0.01574600
C	-1.60990200	-1.31500600	0.01031000
C	-2.23199400	-0.72320600	1.11829100
C	-2.39337800	-1.93938200	-0.96771300
C	-3.62106900	-0.73391900	1.22567900
H	-1.62274800	-0.26288200	1.89107200
C	-3.78270600	-1.92840300	-0.86284900
H	-1.90196300	-2.41937300	-1.80933000
C	-4.40358600	-1.32688400	0.23348500
H	-4.09275900	-0.27502600	2.08978100
H	-4.38151700	-2.40148300	-1.63566600

H	-5.48576100	-1.32911900	0.31885300

f^+

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -787.9670298
Enthalpy = -787.650103
Free Energy = -787.710902
M06-2X/def2-TZVP
Electronic Energy = -788.2197671

C	0.56117900	-0.27992600	-0.10158100
N	-0.29348500	-1.26724700	-0.19597600
C	0.11405200	1.12020700	-0.07500400
C	-0.88121300	1.56046500	-0.96108000
C	0.71749700	2.01959700	0.81460900
C	-1.26863500	2.89444200	-0.94996000
H	-1.32995400	0.86731500	-1.66632600
C	0.29990700	3.34713000	0.84034700
H	1.49207700	1.67553900	1.49326500
C	-0.68798100	3.78430100	-0.04225200
H	-2.02398500	3.24139200	-1.64721300
H	0.75145200	4.04055200	1.54207400
H	-1.00269700	4.82313700	-0.02921800
C	1.99138400	-0.60622400	-0.05123000
C	2.42948500	-1.79119000	0.56520300
C	2.92497300	0.27049600	-0.62783800
C	3.78488600	-2.09547700	0.59468700
H	1.71864100	-2.45009200	1.05676700
C	4.27743500	-0.05139600	-0.60844700
H	2.58905400	1.18227300	-1.11148800
C	4.70757800	-1.22993000	0.00325200
H	4.12320600	-3.00065600	1.08788900
H	4.99599600	0.61820900	-1.06922300
H	5.76561000	-1.47193100	0.02613100
C	-1.71816700	-1.24242000	-0.02709500
C	-2.28853800	-0.57107700	1.05345900
C	-2.49276700	-1.95350300	-0.94011700
C	-3.67258100	-0.59408800	1.19853400
H	-1.66131700	-0.04688300	1.76789600
C	-3.87699600	-1.96931000	-0.78111600
H	-2.01689300	-2.47563400	-1.76505100
C	-4.46702800	-1.28665100	0.28244900
H	-4.12978400	-0.07681300	2.03568000
H	-4.49131900	-2.51444000	-1.49019900
H	-5.54531700	-1.30086300	0.40427900
H	0.09281900	-2.19305000	-0.38436600

g

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -856.3613801

Enthalpy = -856.129908

Free Energy = -856.193182

M06-2X/def2-TZVP

Electronic Energy = -856.6735138

C	-0.97077300	1.39180100	0.18206800
O	-1.22541500	2.05690800	1.15834200
C	-1.28186600	-0.09258700	0.08199700
C	-2.76016500	-0.37772900	0.01285300
O	-3.56317300	0.51110500	-0.17607200
O	-3.06051200	-1.65738900	0.15211100
O	-0.39508400	1.83968000	-0.92369400
C	-0.01262100	3.22657800	-0.91430400
H	0.72641000	3.40164900	-0.12912600
H	0.41926100	3.41547300	-1.89495700
H	-0.88907700	3.85587000	-0.75005400
C	-4.45716200	-1.97929200	0.04683800
H	-4.51903200	-3.05630500	0.18862200
H	-5.02157900	-1.45764400	0.82239300
H	-4.83288500	-1.69956100	-0.93938100
N	-0.44016400	-1.04004000	0.01388600
C	0.95268200	-0.82837500	0.06644700
C	1.57153300	0.09787400	0.91615300
C	1.74593500	-1.65816000	-0.73784100
C	2.95670700	0.21983100	0.92782100
H	0.98408200	0.69618500	1.60644900
C	3.12575100	-1.51752800	-0.75374500
H	1.26076400	-2.40069800	-1.36400400
C	3.73405300	-0.57451000	0.08077700
H	3.43642400	0.92445100	1.60195500
H	3.74491800	-2.14090800	-1.39082800
O	5.08776500	-0.48702200	0.04332600
H	5.39877700	0.18808400	0.66525600

g^+

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -856.7819569

Enthalpy = -856.536622

Free Energy = -856.600099

M06-2X/def2-TZVP

Electronic Energy = -857.095568

C	1.06676600	1.49112500	-0.19465600
O	1.39191600	2.11612600	-1.16956400
C	1.32097700	0.00185600	-0.09267000

C	2.76733400	-0.42645300	-0.03244500
O	3.64718700	0.38691100	0.08369400
O	2.88567700	-1.73632200	-0.09546800
O	0.49245600	1.93869700	0.89818700
C	0.17924100	3.35221500	0.91330800
H	-0.52697400	3.57480000	0.11126800
H	-0.26804400	3.53410200	1.88732200
H	1.09537800	3.93054100	0.78813200
C	4.23101600	-2.26187800	0.01104500
H	4.11946800	-3.34233300	-0.03143000
H	4.82696400	-1.89668300	-0.82612400
H	4.66726600	-1.94947000	0.96063800
N	0.38995900	-0.88268200	-0.03184600
C	-1.01531500	-0.74010500	-0.08175900
C	-1.63662200	0.32374100	-0.74584100
C	-1.76652900	-1.73895200	0.55201800
C	-3.01694600	0.40889800	-0.73377500
H	-1.06937800	1.05209600	-1.31656200
C	-3.14414700	-1.64486800	0.57355400
H	-1.26431200	-2.57022900	1.03880800
C	-3.77345900	-0.56562200	-0.06386600
H	-3.51556100	1.21706000	-1.25959300
H	-3.74819400	-2.39565200	1.07074400
O	-5.11424400	-0.52626900	-0.01872500
H	-5.45827300	0.24562900	-0.49677000
H	0.71411000	-1.85397800	0.08201400

h

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -859.5460172

Enthalpy = -859.276259

Free Energy = -859.339753

M06-2X/def2-TZVP

Electronic Energy = -859.8439506

C	-0.42978900	1.35623300	0.16775900
O	-0.67280200	2.04439200	1.13330000
C	-0.88168000	-0.09258400	0.03033800
O	0.24904300	1.75848700	-0.89835900
C	0.81148200	3.07917200	-0.82370300
H	1.50141500	3.14029300	0.02118600
H	1.34314500	3.22265500	-1.76231400
H	0.01886100	3.82189600	-0.71373900
N	-0.05842200	-1.06200400	-0.07834900
C	1.33796700	-0.87281300	0.00472100
C	1.94583300	-0.14069500	1.03119300
C	2.14507000	-1.51792300	-0.94147900

C	3.33289800	-0.01940000	1.08580500
H	1.34004300	0.31094000	1.81203500
C	3.52613600	-1.38049200	-0.90508500
H	1.67366600	-2.11417300	-1.71709200
C	4.12348200	-0.62726400	0.10996600
H	3.79932100	0.53913400	1.89353000
H	4.15454200	-1.86227100	-1.64756000
O	5.48198300	-0.53719200	0.10762100
H	5.78195800	0.00137800	0.85489400
C	-2.34486100	-0.33528400	0.03367300
C	-3.25235100	0.71969700	-0.12482200
C	-2.82910500	-1.64389000	0.17517800
C	-4.62336700	0.46812000	-0.15050700
H	-2.89860300	1.74130700	-0.23033800
C	-4.19692100	-1.89017600	0.15431600
H	-2.12284300	-2.45730600	0.30532100
C	-5.09818000	-0.83473700	-0.00989100
H	-5.31864000	1.29186100	-0.27788600
H	-4.56307900	-2.90568300	0.26971300
H	-6.16631000	-1.02927200	-0.02458000

h^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -859.9779064

Enthalpy = -859.695565

Free Energy = -859.758441

M06-2X/def2-TZVP

Electronic Energy = -860.2789518

C	-0.47195100	1.39378000	0.20283600
O	-0.78556100	2.03422500	1.17408700
C	-0.92306200	-0.04846900	0.01547200
O	0.24660600	1.80060200	-0.82094300
C	0.78407700	3.13816300	-0.72389100
H	1.43227200	3.20571100	0.15197900
H	1.35209900	3.28550500	-1.63923400
H	-0.03102300	3.85987800	-0.65124900
N	-0.02363400	-0.97176500	-0.14159800
C	1.39458000	-0.84409400	-0.03205300
C	1.97139000	-0.08912700	0.98839900
C	2.18264500	-1.52029500	-0.96539700
C	3.35388200	0.02773000	1.04860600
H	1.35932100	0.37865500	1.75458500
C	3.56177200	-1.40540200	-0.90266200
H	1.71503800	-2.11554700	-1.74407500
C	4.14946600	-0.62350900	0.09980600
H	3.81583600	0.60566500	1.84371400

H	4.19655600	-1.91169300	-1.62185800
O	5.49765400	-0.54839200	0.11105700
H	5.80453700	0.01238500	0.84069000
C	-2.34622900	-0.33730600	0.03152600
C	-3.25284400	0.68926800	-0.28755600
C	-2.81974700	-1.62465600	0.34334500
C	-4.61440600	0.41708000	-0.32772300
H	-2.89898400	1.68901700	-0.52317900
C	-4.18260900	-1.88138200	0.31305100
H	-2.13686400	-2.41232100	0.64785700
C	-5.07856900	-0.86454000	-0.02882900
H	-5.31299500	1.20510300	-0.58674400
H	-4.54953100	-2.86971200	0.56839400
H	-6.14397900	-1.07139200	-0.04997700
H	-0.35679500	-1.91383000	-0.36292300

i

M06-2X/6-31+G(d,p)[LANL2DZ]
Electronic Energy = -781.9252419
Enthalpy = -781.708116
Free Energy = -781.764171
M06-2X/def2-TZVP
Electronic Energy = -782.1905636

C	1.97475400	-0.71027000	-0.12954100
C	2.43064200	0.59881000	0.07202000
C	3.79063900	0.88730500	0.14155700
C	4.68454900	-0.17271200	0.00646700
C	4.22786700	-1.48546700	-0.19621500
C	2.86622000	-1.77075200	-0.27002400
H	4.13595900	1.90513900	0.29328400
H	5.75241000	0.01522600	0.05623900
H	4.95155900	-2.28819600	-0.29681700
H	2.50749300	-2.78318400	-0.42747900
C	1.28119400	1.53027200	0.16934700
C	0.49054700	-0.75489200	-0.16903600
C	0.02517700	0.68182600	0.05709200
N	-1.12400700	1.21809600	0.07314400
C	-2.33228000	0.49231700	0.05611100
C	-2.58230900	-0.57056200	0.93304400
C	-3.34364000	0.95571400	-0.79390800
C	-3.82985000	-1.18626700	0.92684200
H	-1.80796400	-0.89523000	1.62089100
C	-4.57607100	0.30832100	-0.81937000
H	-3.14412900	1.80925800	-1.43482600
C	-4.82434000	-0.76017800	0.04337500
H	-4.02538500	-2.00441300	1.61325800

H	-5.34981200	0.65345400	-1.49813100
H	-5.79291800	-1.25031700	0.03835500
O	1.31490500	2.73124500	0.31719100
O	-0.19712500	-1.72489400	-0.39761100

i^{+}

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -782.3491778

Enthalpy = -782.118175

Free Energy = -782.173644

M06-2X/def2-TZVP

Electronic Energy = -782.6159735

C	-2.45134200	0.64735300	0.06929200
C	-2.12275500	-0.71385200	-0.06450500
C	-3.10972700	-1.68417900	-0.20190500
C	-4.43549000	-1.25614900	-0.19524600
C	-4.76336800	0.10391200	-0.06158600
C	-3.77506200	1.07643900	0.07240800
H	-2.85086200	-2.73273500	-0.30689600
H	-5.23338400	-1.98477600	-0.29546800
H	-5.80763500	0.39840000	-0.06451000
H	-4.02256700	2.12826700	0.17083100
C	-0.66028500	-0.93356200	-0.05215000
C	-1.22603600	1.44951900	0.17052200
C	-0.07382900	0.46179300	0.10496500
N	1.11763700	0.93674800	0.08129500
C	2.40566500	0.34896100	0.04504200
C	3.43265900	1.16696700	-0.44341400
C	2.65032300	-0.94470200	0.51538300
C	4.72251000	0.65811600	-0.50538200
H	3.21370900	2.17719900	-0.77785100
C	3.95054300	-1.43019400	0.45692000
H	1.85593000	-1.54591700	0.93669000
C	4.98061000	-0.63963400	-0.05864500
H	5.52564200	1.27499400	-0.89327900
H	4.16144300	-2.42810400	0.82561700
H	5.99151000	-1.03223500	-0.09835500
H	1.13218100	1.97116400	0.08544900
O	-1.05552500	2.64119200	0.27762400
O	-0.06146400	-1.97221900	-0.18530900

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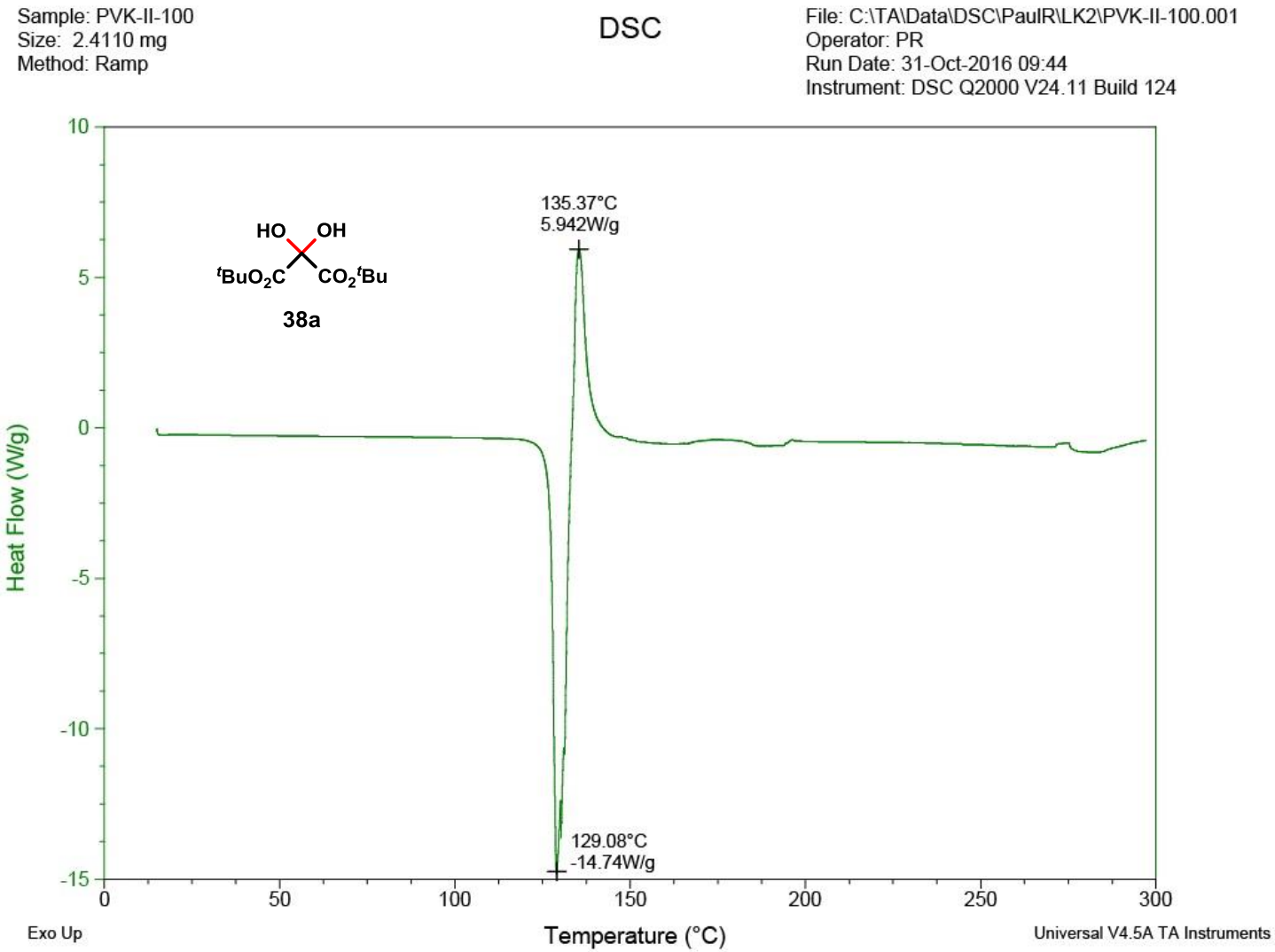
26. DSC (Differential Scanning Calorimetry) Analysis Data of the Starting Materials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Operator: PR
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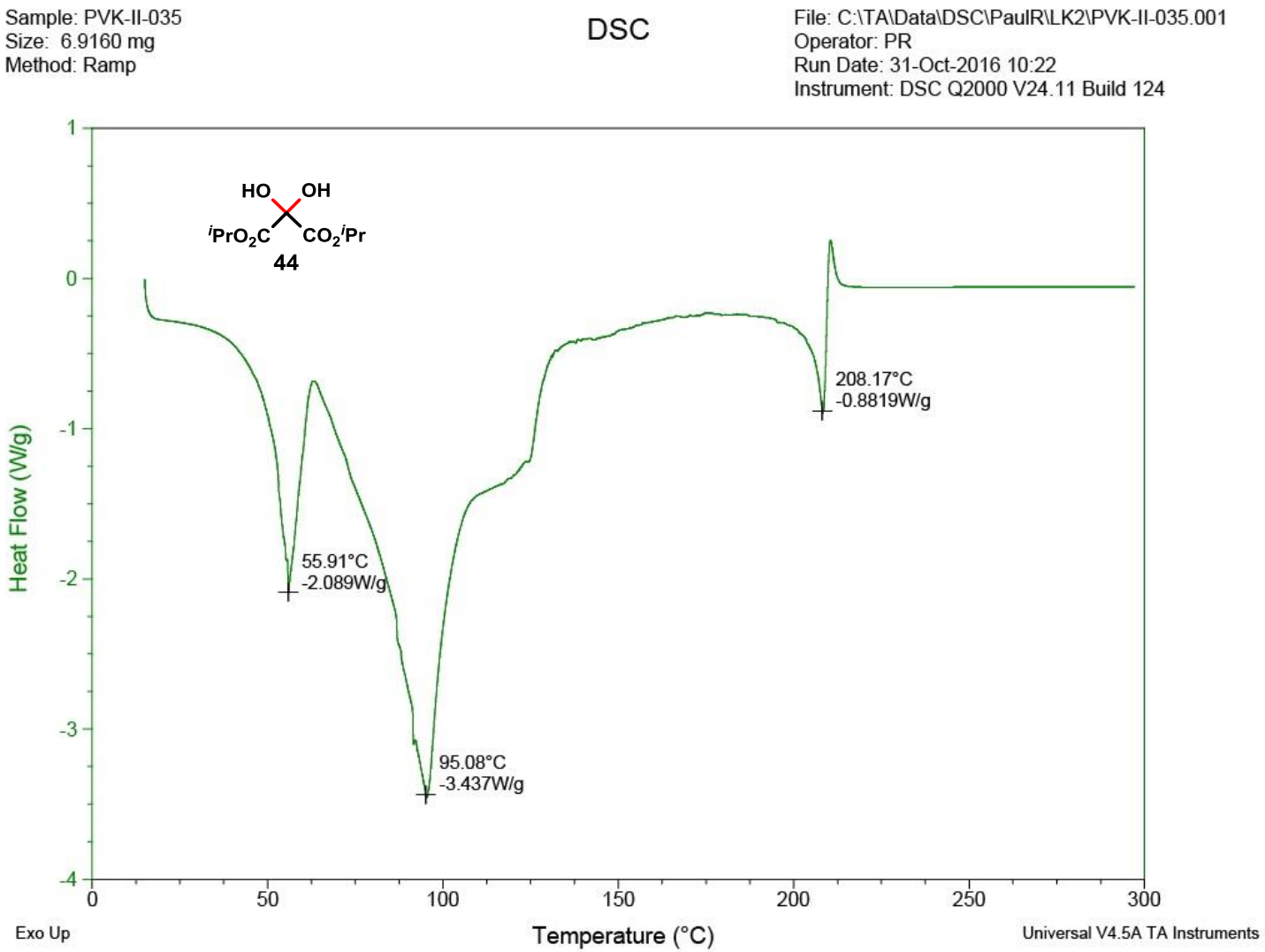
Instrument: DSC Q2000 V24.11 Build 124
HO OH
tBuO2C CO2tBu
38a
135.37°C
5.942W/g
129.08°C
-14.74W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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Size: 6.9160 mg
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Operator: PR
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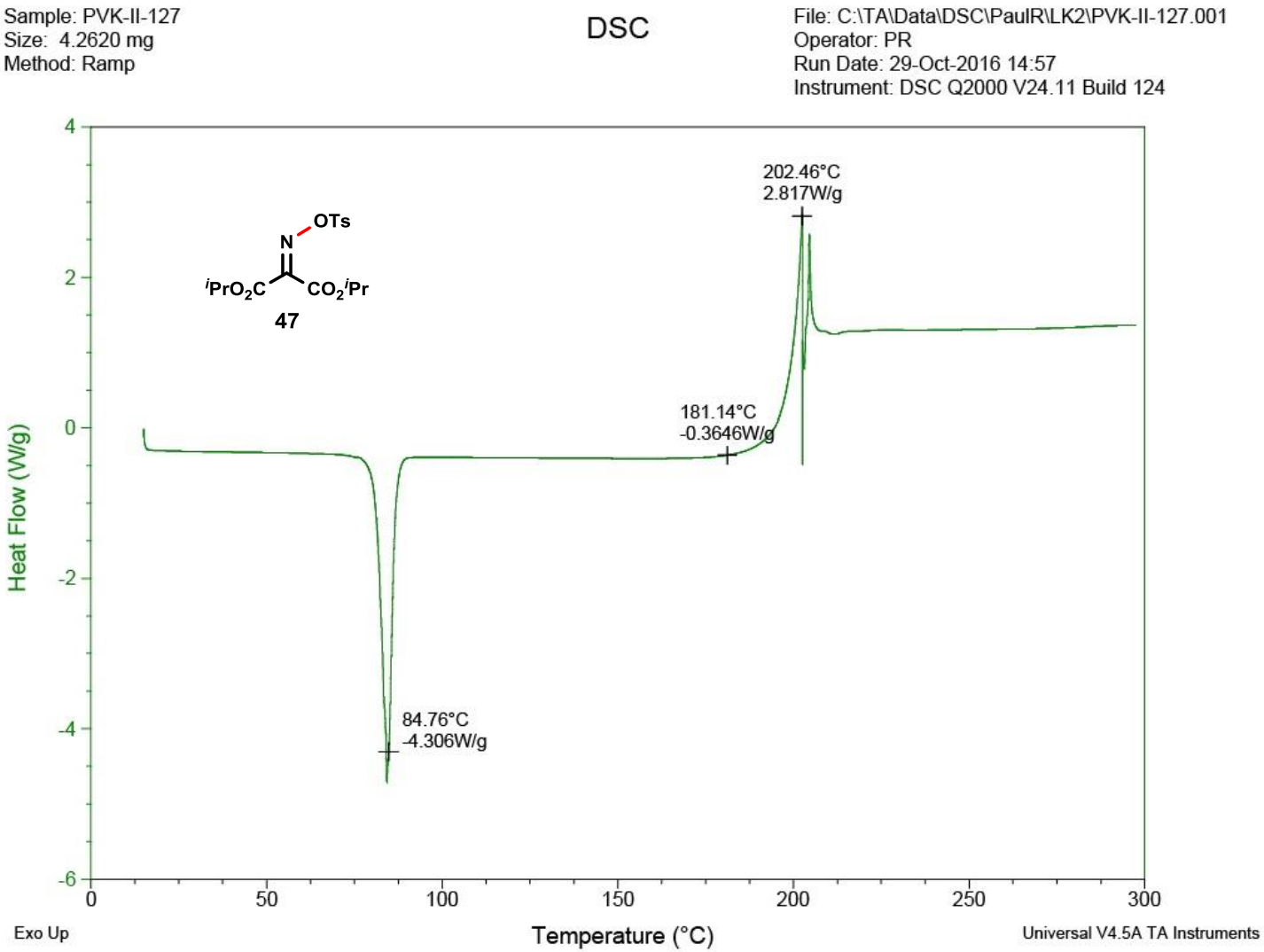
Instrument: DSC Q2000 V24.11 Build 124
HO
OH
iPrO2C
CO2iPr
44
208.17°C
-0.8819W/g
55.91°C
-2.089W/g
95.08°C
-3.437W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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Operator: PR
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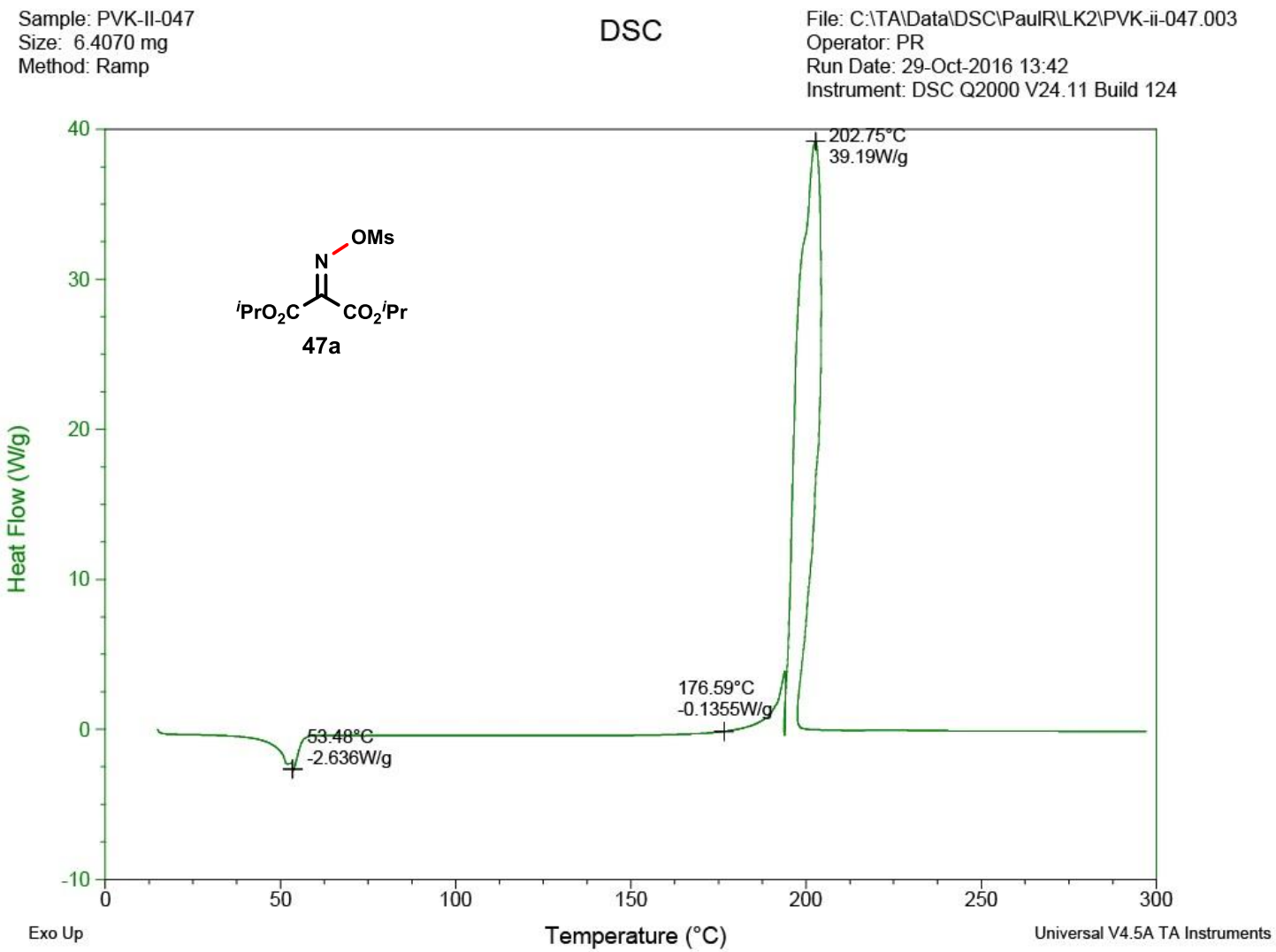
Instrument: DSC Q2000 V24.11 Build 124
OTs
N
iPrO2C
CO2iPr
47
202.46°C
2.817W/g
181.14°C
-0.3646W/g
84.76°C
-4.306W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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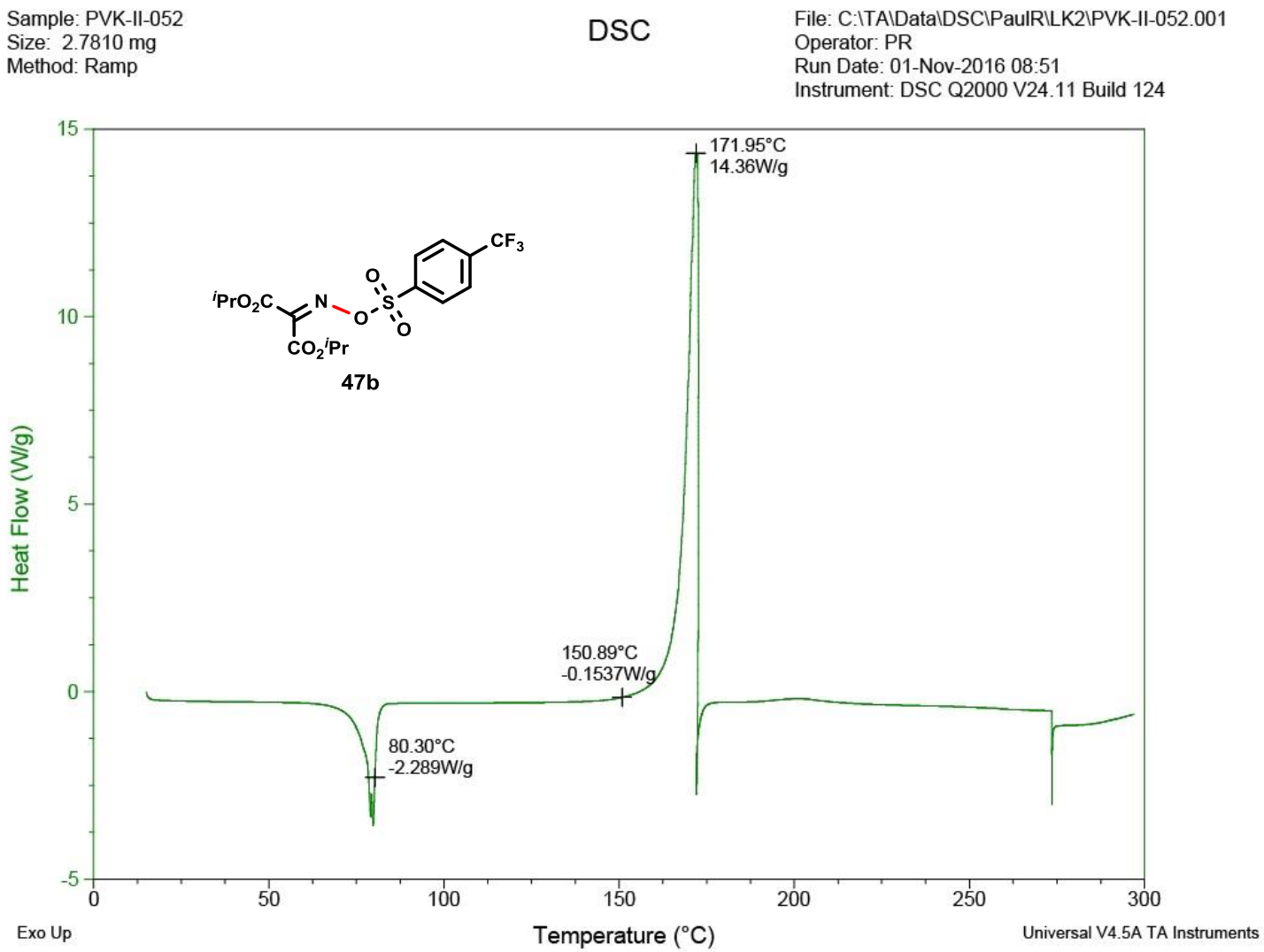
OMs
N
iPrO2C
CO2iPr
47a
202.75°C
39.19W/g
176.59°C
-0.1355W/g
53.48°C
-2.636W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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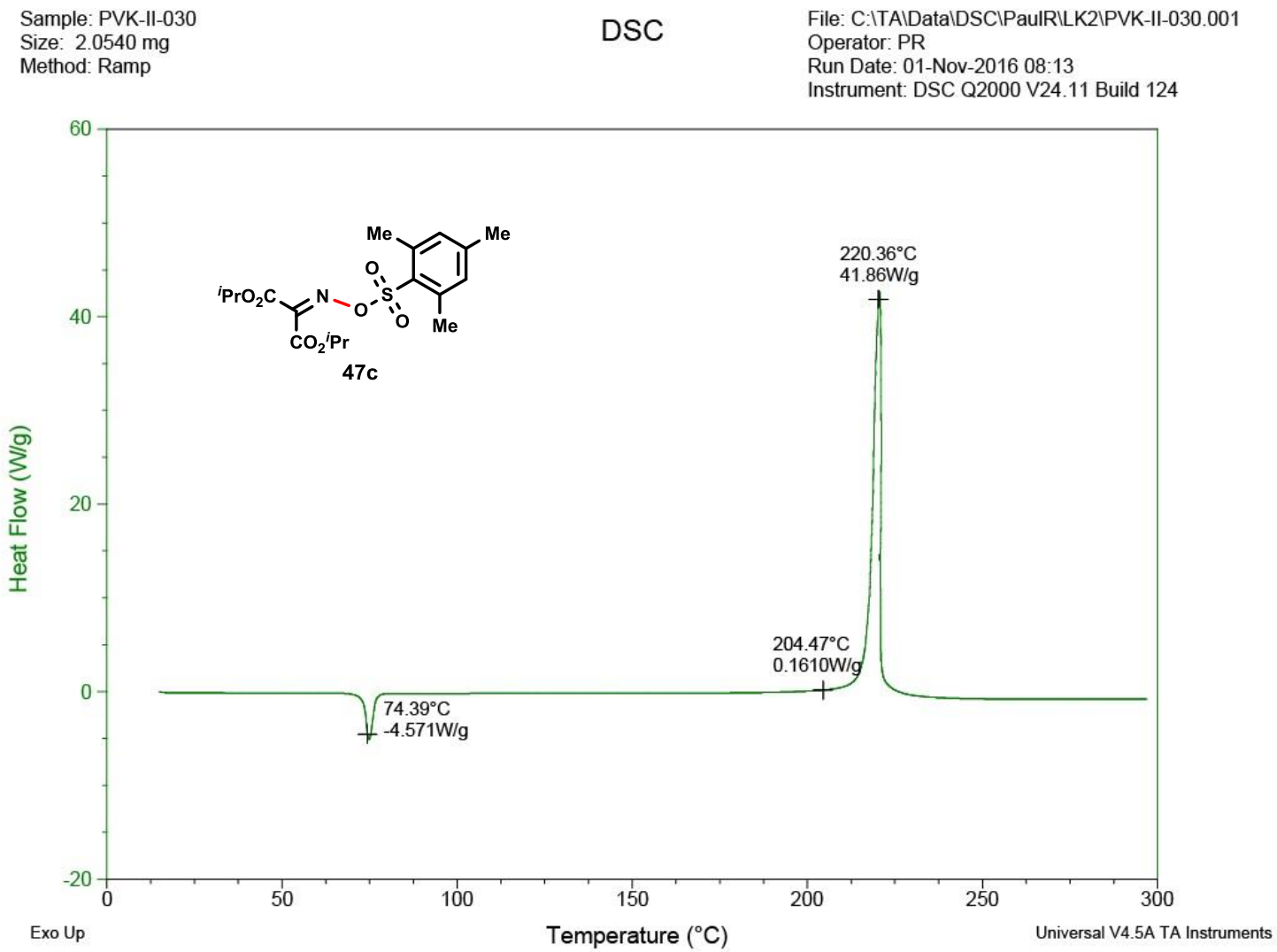
171.95°C
14.36W/g
150.89°C
-0.1537W/g
80.30°C
-2.289W/g
47b
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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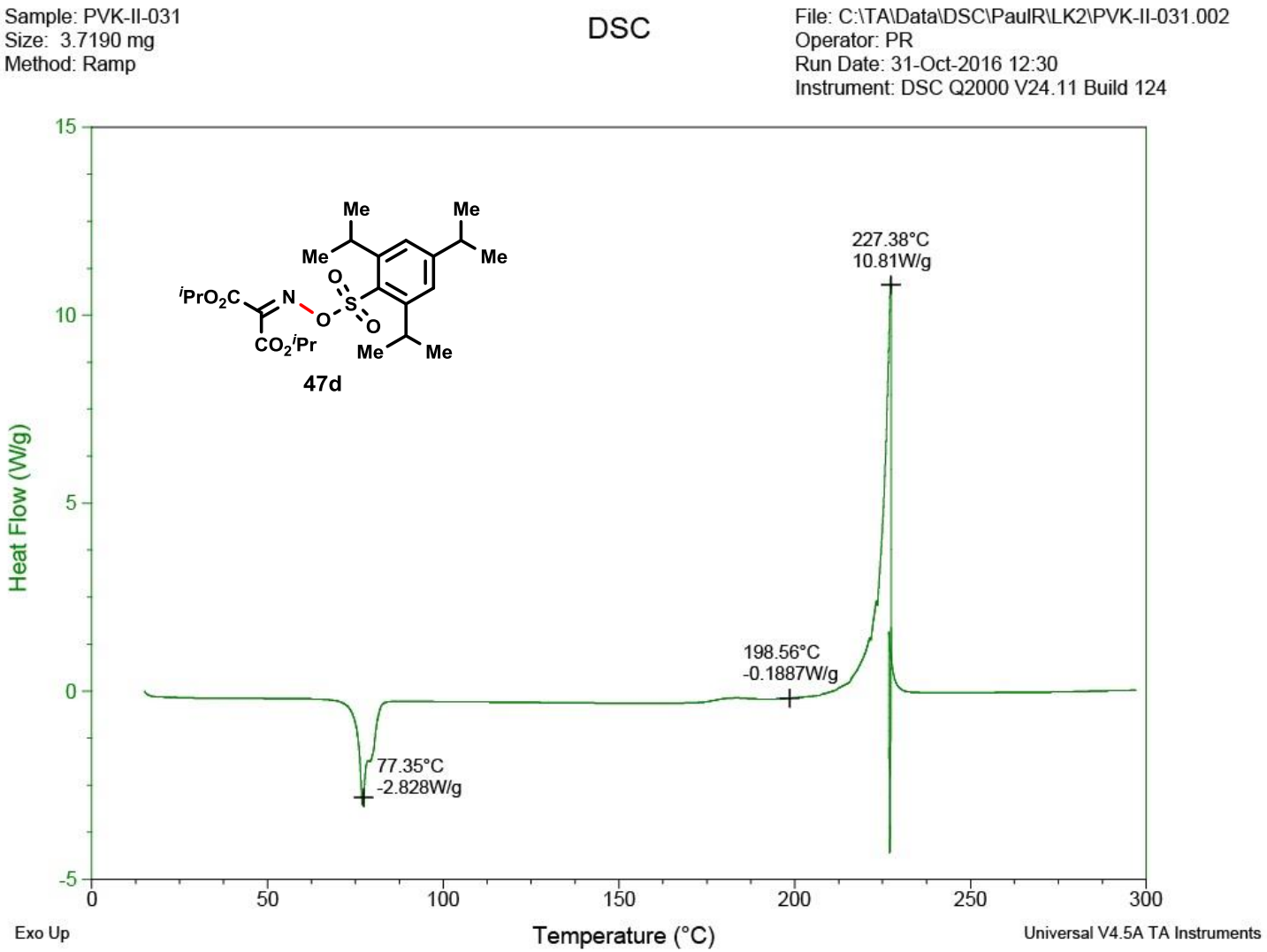
Instrument: DSC Q2000 V24.11 Build 124
47c
220.36°C
41.86W/g
204.47°C
0.1610W/g
74.39°C
-4.571W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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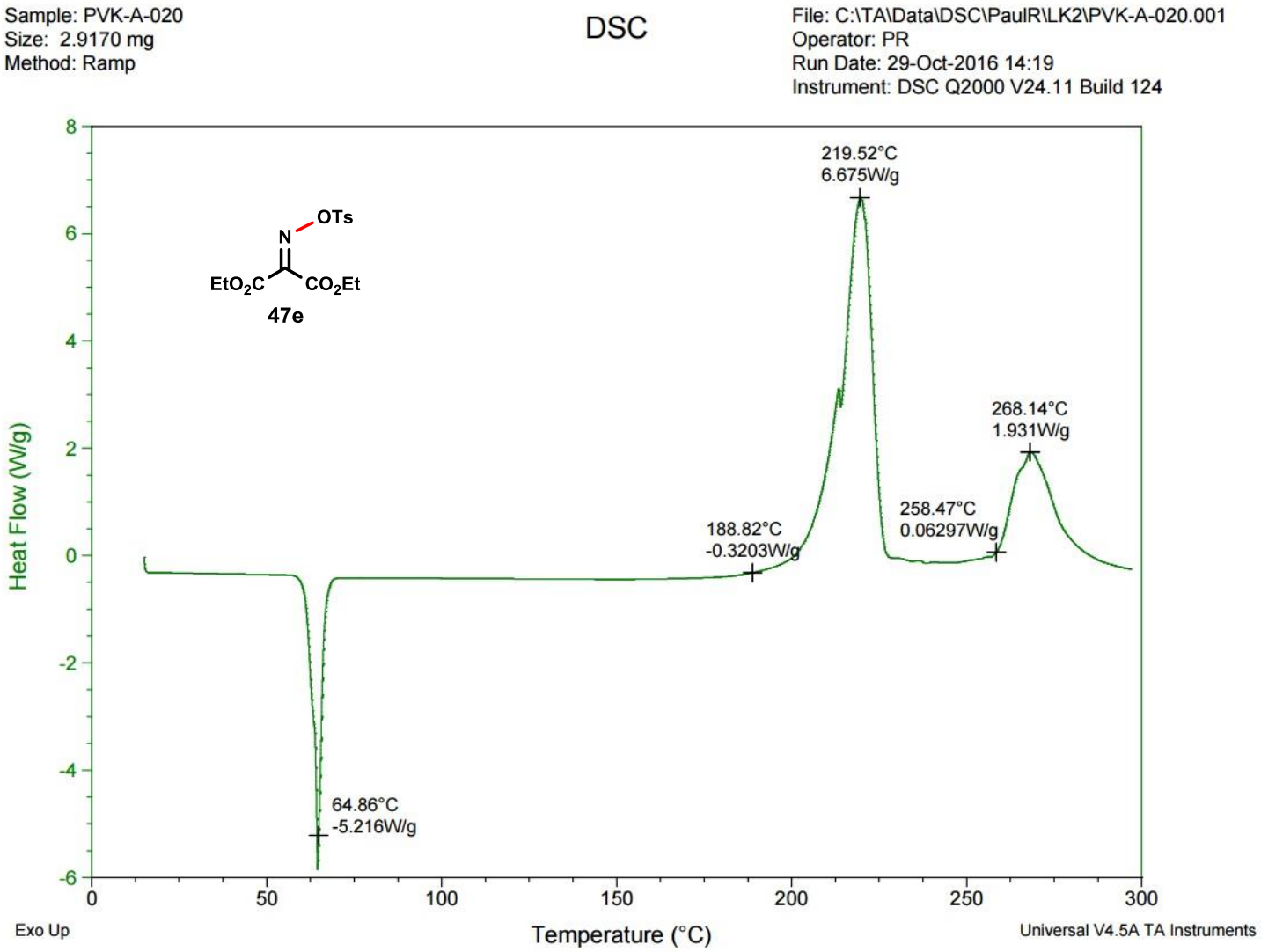
Instrument: DSC Q2000 V24.11 Build 124
47d
227.38°C
10.81W/g
198.56°C
-0.1887W/g
77.35°C
-2.828W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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Size: 2.9170 mg
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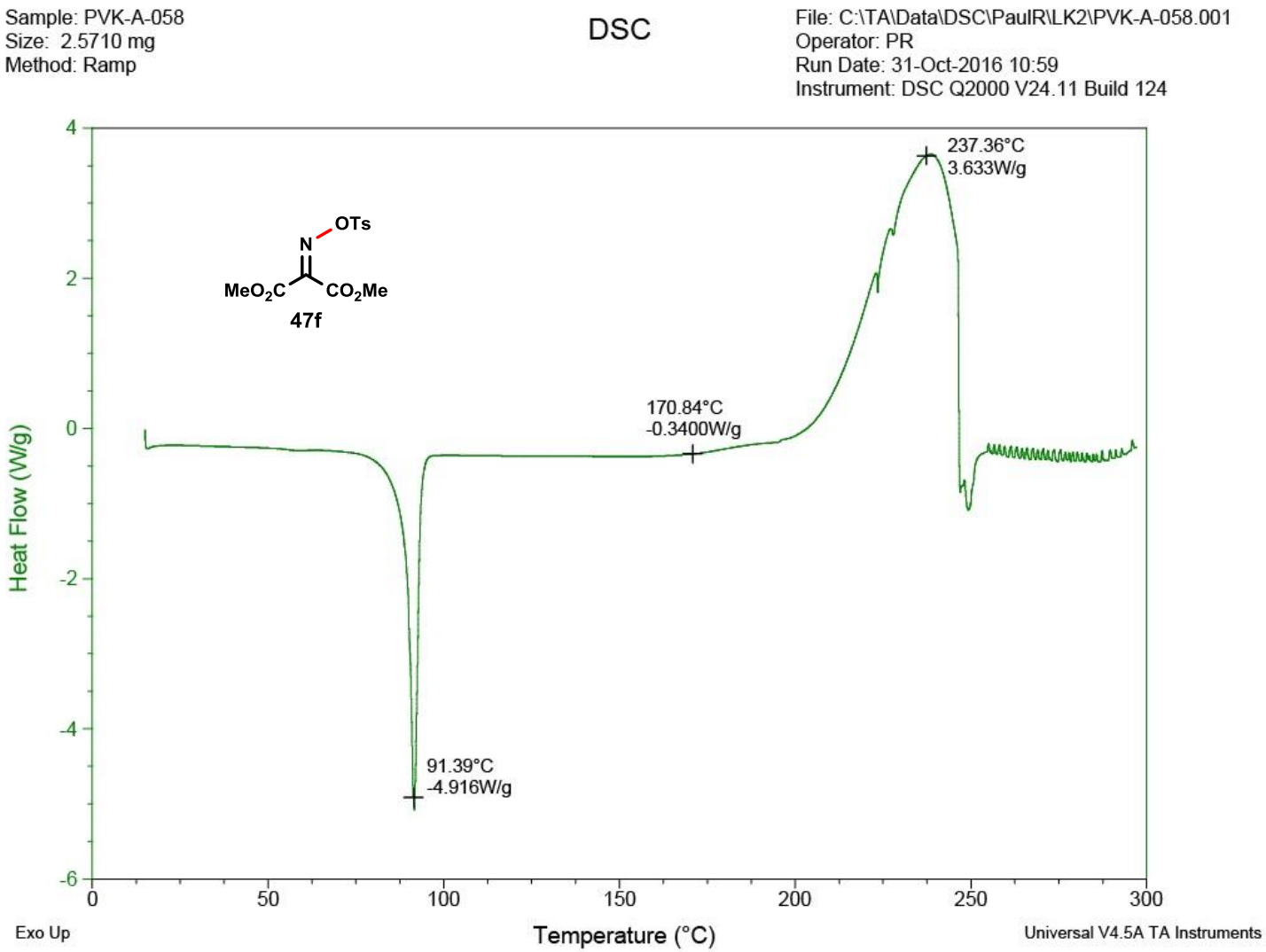
Operator: PR
Run Date: 29-Oct-2016 14:19
Instrument: DSC Q2000 V24.11 Build 124
OTs
N
EtO2C
CO2Et
47e
219.52°C
6.675W/g
268.14°C
1.931W/g
258.47°C
0.06297W/g
188.82°C
-0.3203W/g
64.86°C
-5.216W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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Size: 2.5710 mg
Method: Ramp
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Operator: PR
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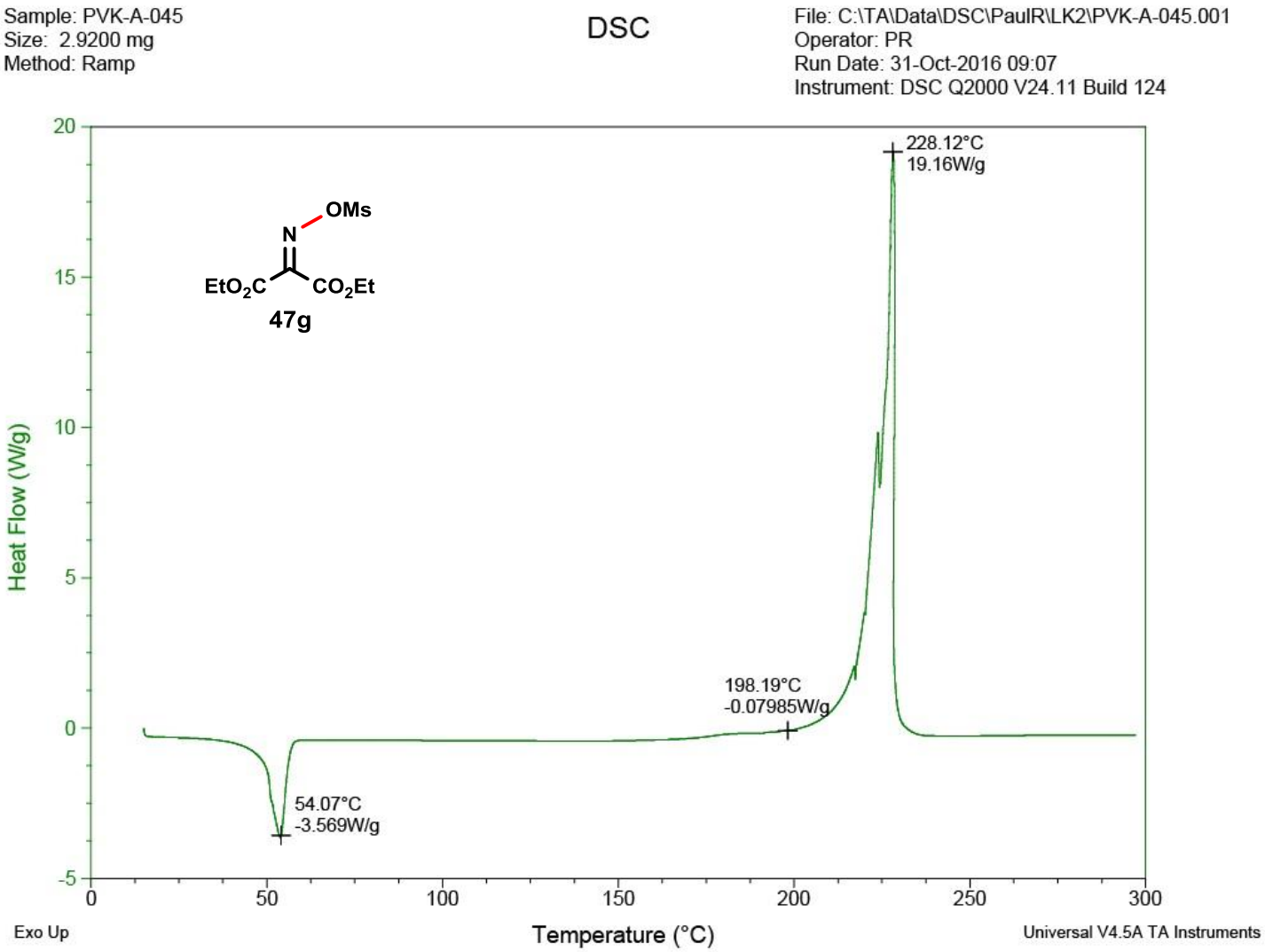
Instrument: DSC Q2000 V24.11 Build 124
OTs
N
MeO2C
CO2Me
47f
237.36°C
3.633W/g
170.84°C
-0.3400W/g
91.39°C
-4.916W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments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Size: 2.9200 mg
Method: Ramp
DSC
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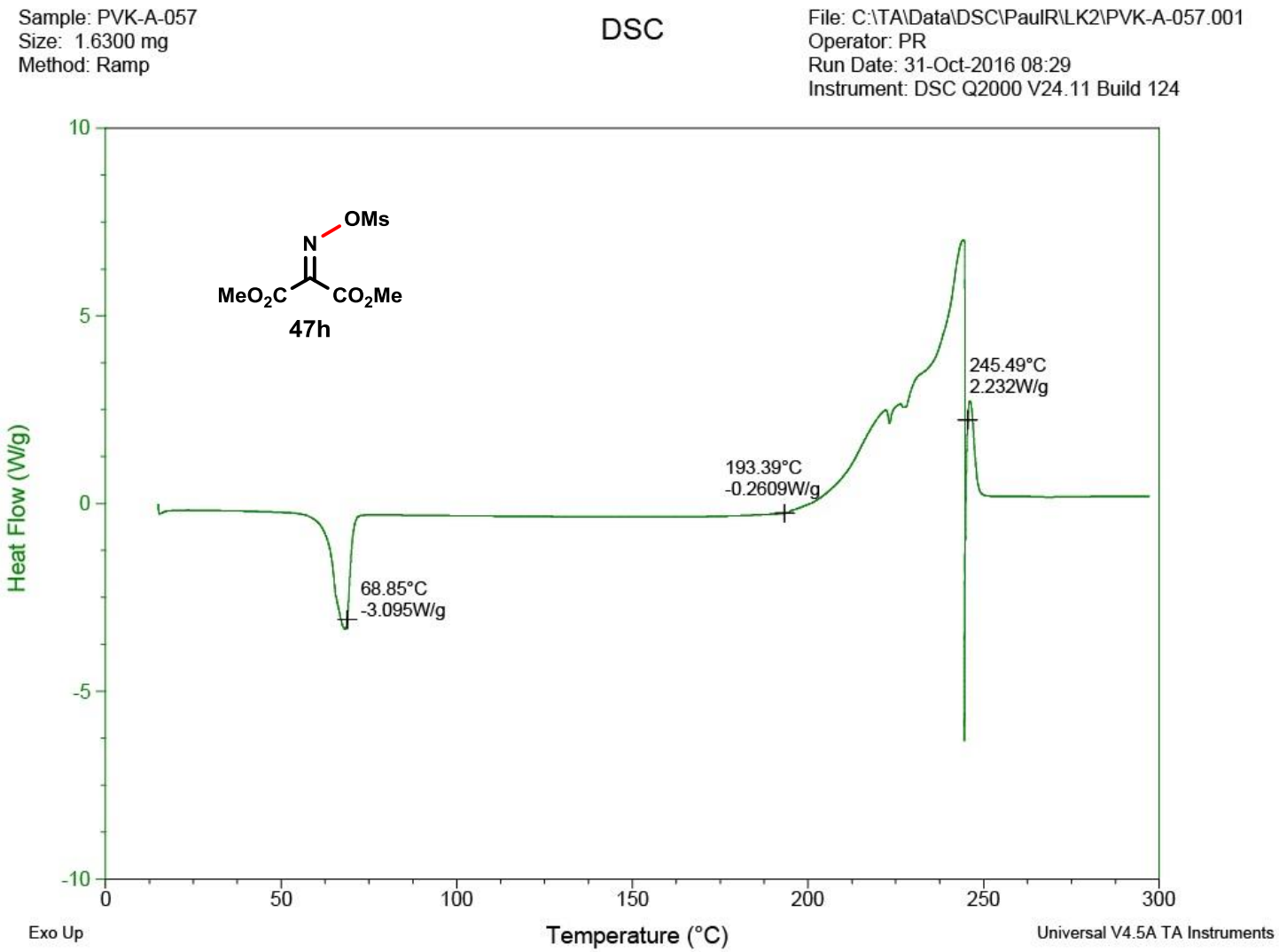
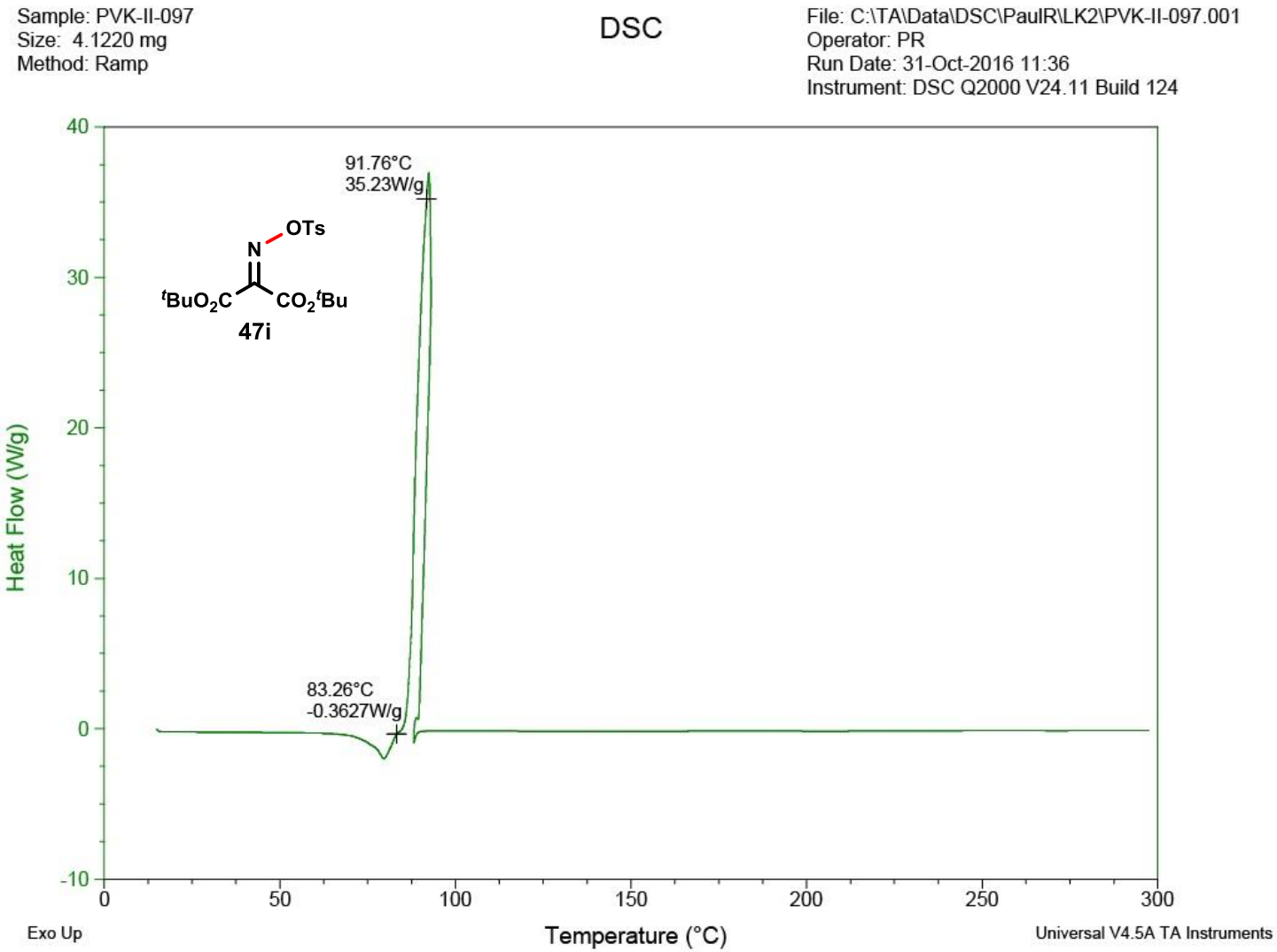
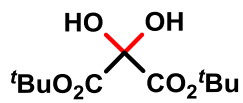
Operator: PR
Run Date: 31-Oct-2016 09:07
Instrument: DSC Q2000 V24.11 Build 124
OMs
N
EtO2C
CO2Et
47g
228.12°C
19.16W/g
198.19°C
-0.07985W/g
54.07°C
-3.569W/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments


Sample: PVK-A-057
Size: 1.6300 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\PaulR\LK2\PVK-A-057.001
Operator: PR
Run Date: 31-Oct-2016 08:29
Instrument: DSC Q2000 V24.11 Build 124
OMs
N
MeO2C
CO2Me
47h
245.49°C
2.232W/g
193.39°C
-0.2609W/g
68.85°C
-3.095W/g
Heat Flow (W/g)
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

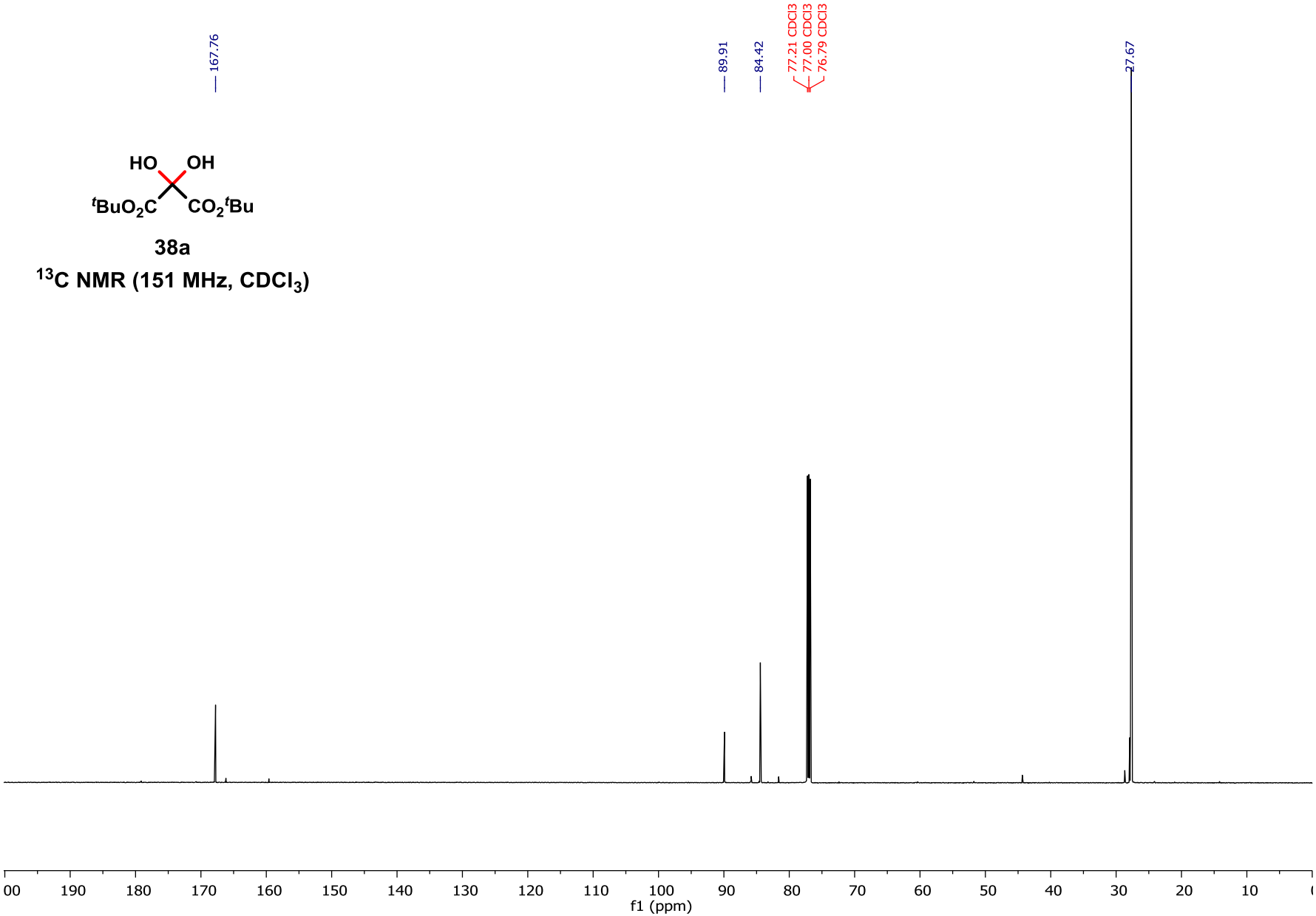

Sample: PVK-II-097
Size: 4.1220 mg
Method: Ramp
DSC
File: C:\TA\Data\DSC\PaulR\LK2\PVK-II-097.001
Operator: PR
Run Date: 31-Oct-2016 11:36
Instrument: DSC Q2000 V24.11 Build 124
91.76°C
35.23W/g
83.26°C
-0.3627W/g
OTs
N
tBuO2C
CO2tBu
47i
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

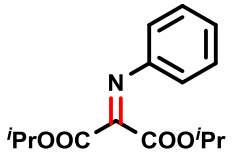
27. ^{1}H-, ^{13}C- and ^{19}F-NMR Spectra of All the Compounds



38a

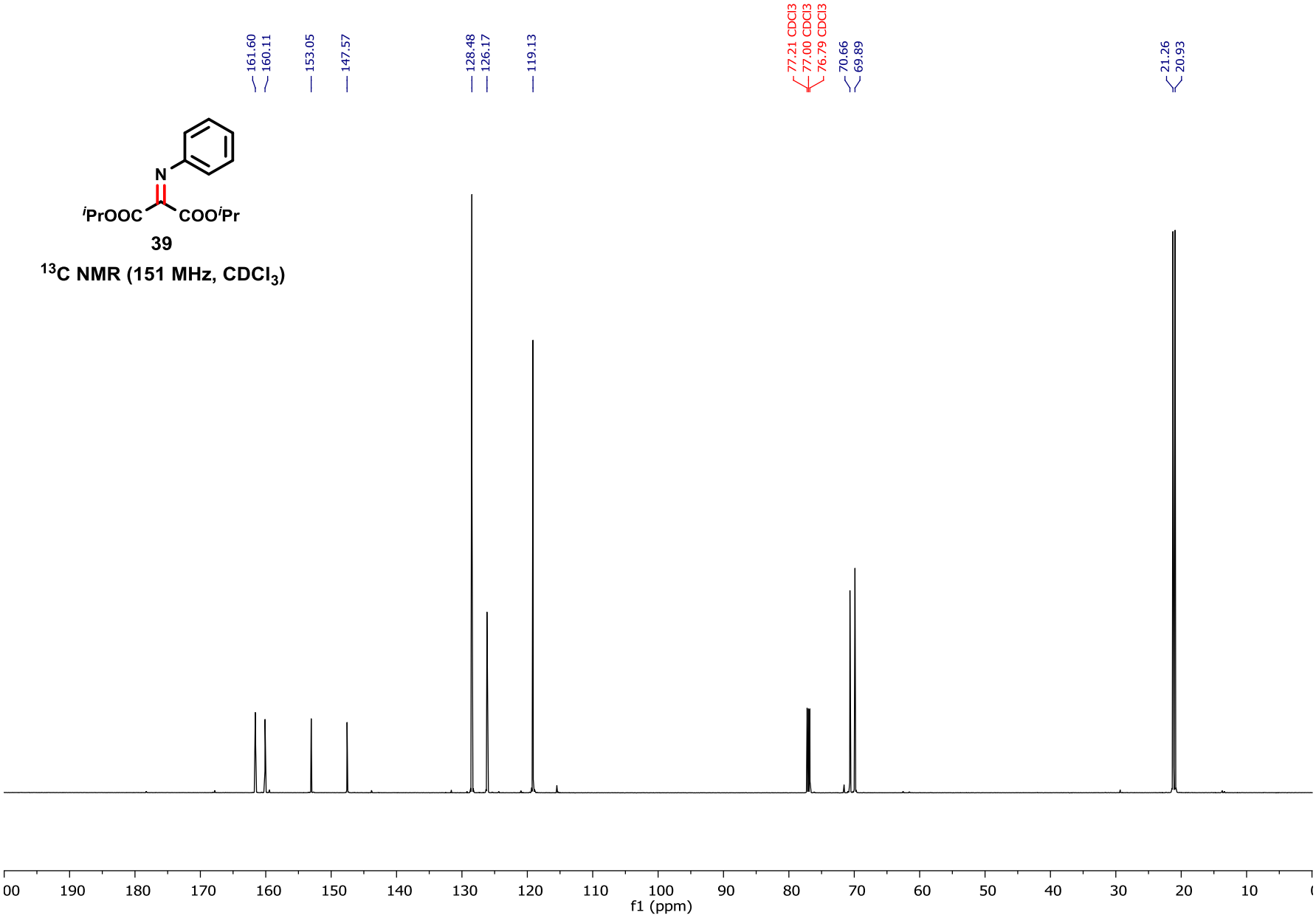
^{1}H NMR (600 MHz, $CDCl_3$)

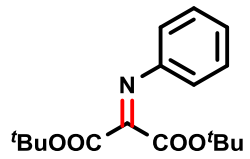

167.76
89.91
84.42
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
27.67
HO
OH
tBuO2C
CO2tBu
38a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



39

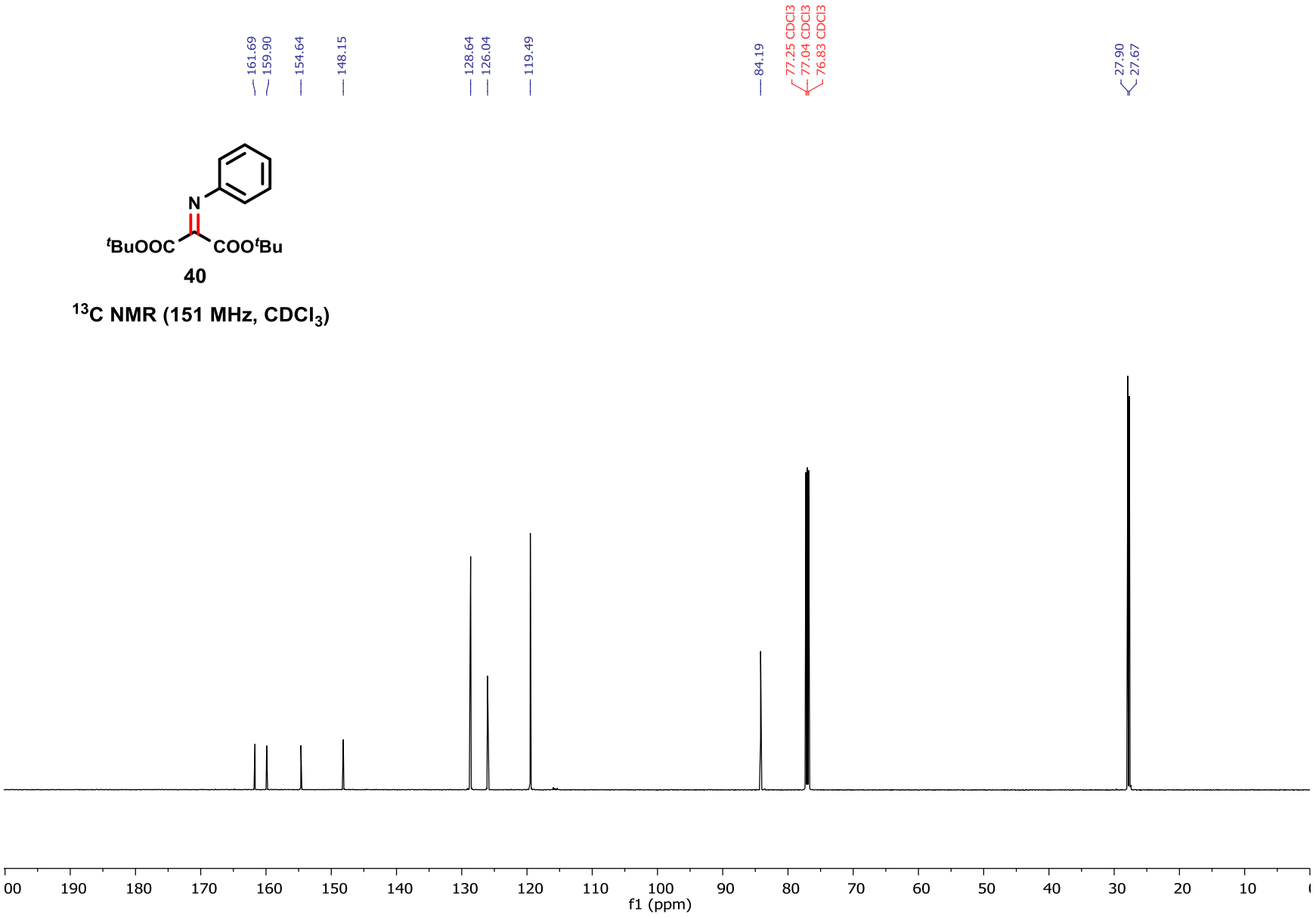
^{1}H NMR (600 MHz, $CDCl_3$)

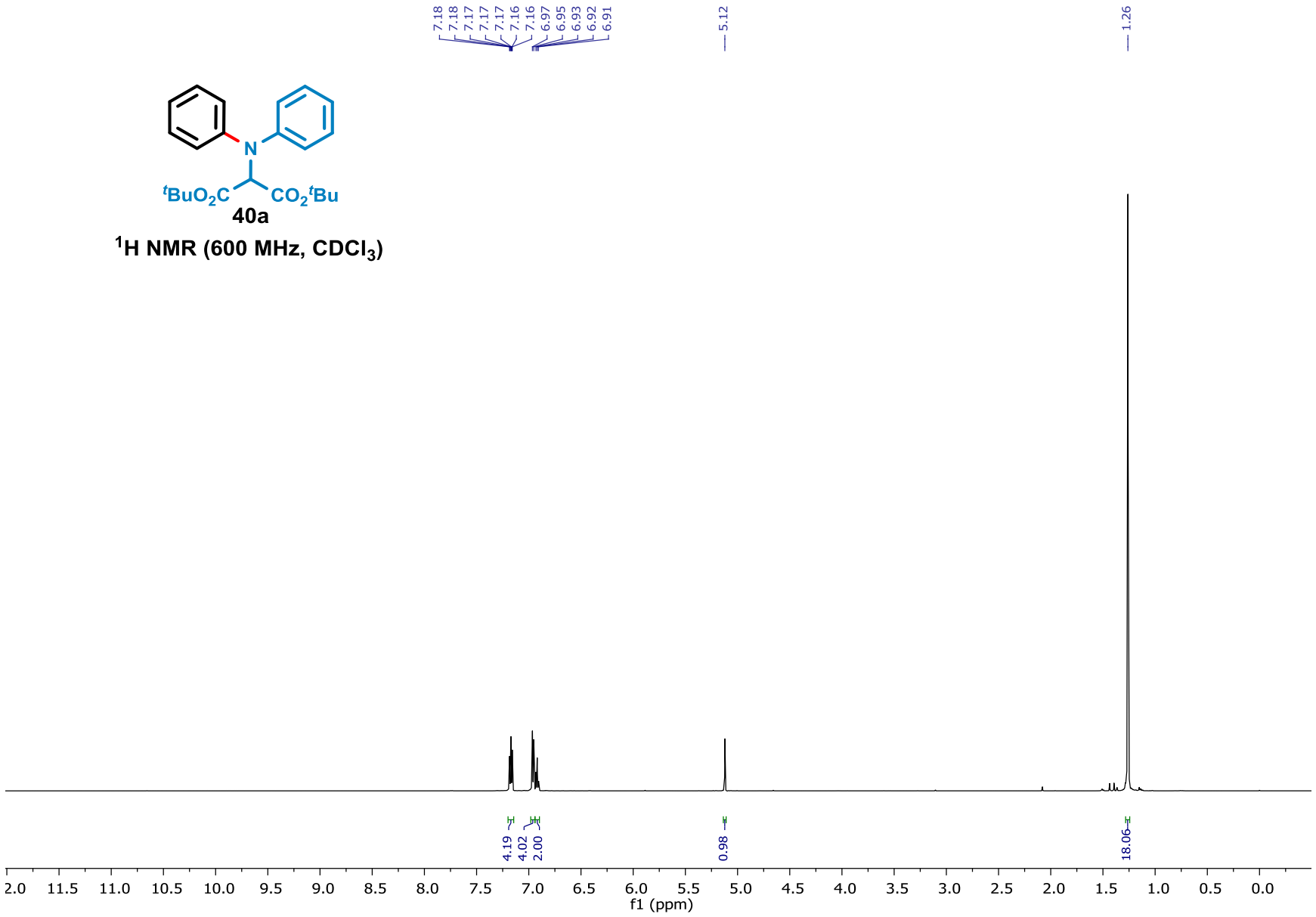

161.60
160.11
153.05
147.57
128.48
126.17
119.13
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.66
69.89
21.26
20.93
N
iPrOOC
COOiPr
39
13C NMR (151 MHz, CDCl3)
f1 (ppm)

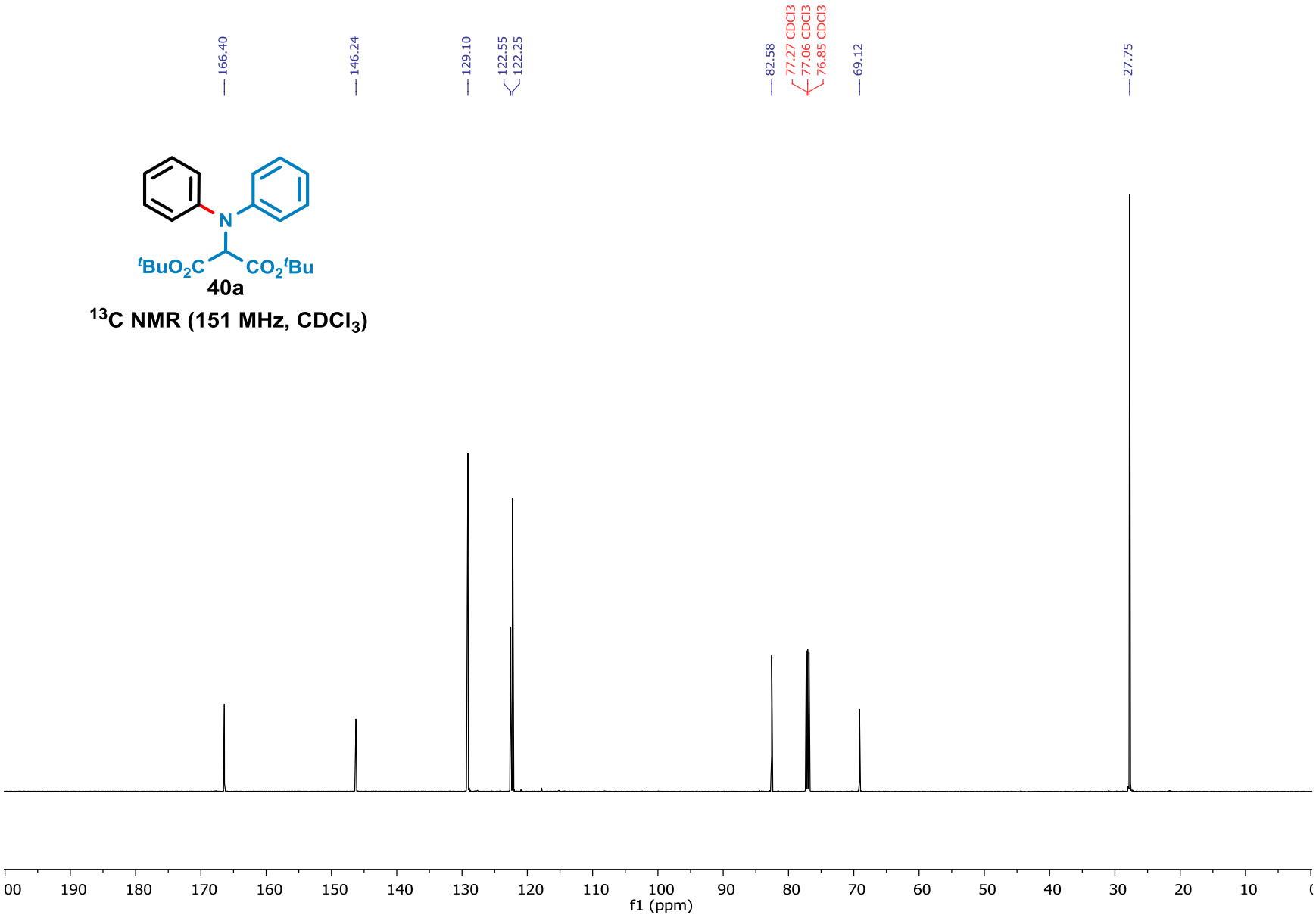


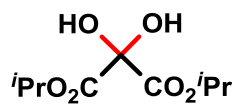
40

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


161.69
159.90
154.64
148.15
128.64
126.04
119.49
84.19
77.25 CDCl3
77.04 CDCl3
76.83 CDCl3
27.90
27.67
N
tBuOOC
COOtBu
40
13C NMR (151 MHz, CDCl3)
f1 (ppm)

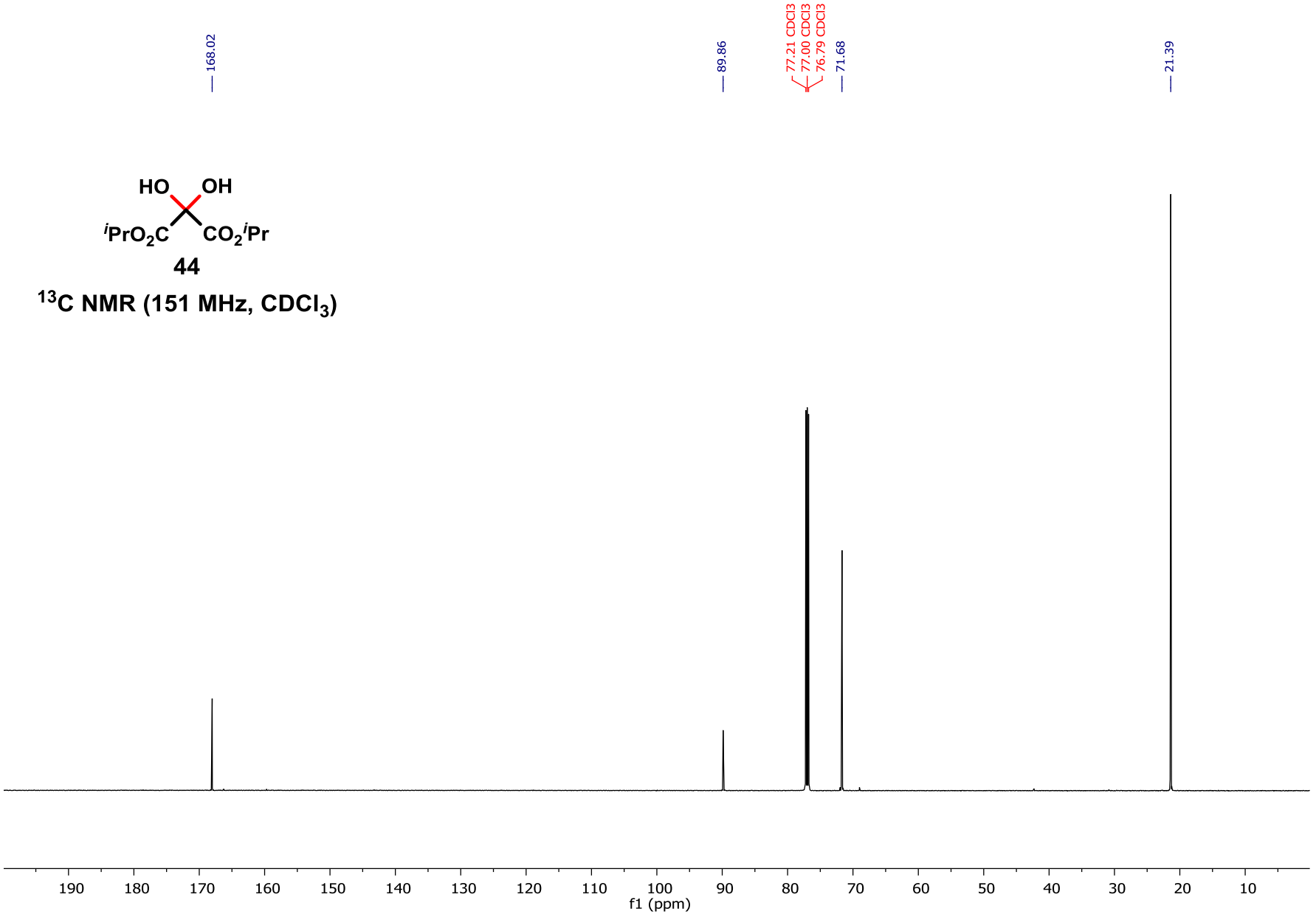

7.18
7.18
7.17
7.17
7.17
7.16
7.16
6.97
6.95
6.93
6.92
6.91
5.12
1.26
N
tBuO2C
CO2tBu
40a
1H NMR (600 MHz, CDCl3)
4.19
4.02
2.00
0.98
18.06
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

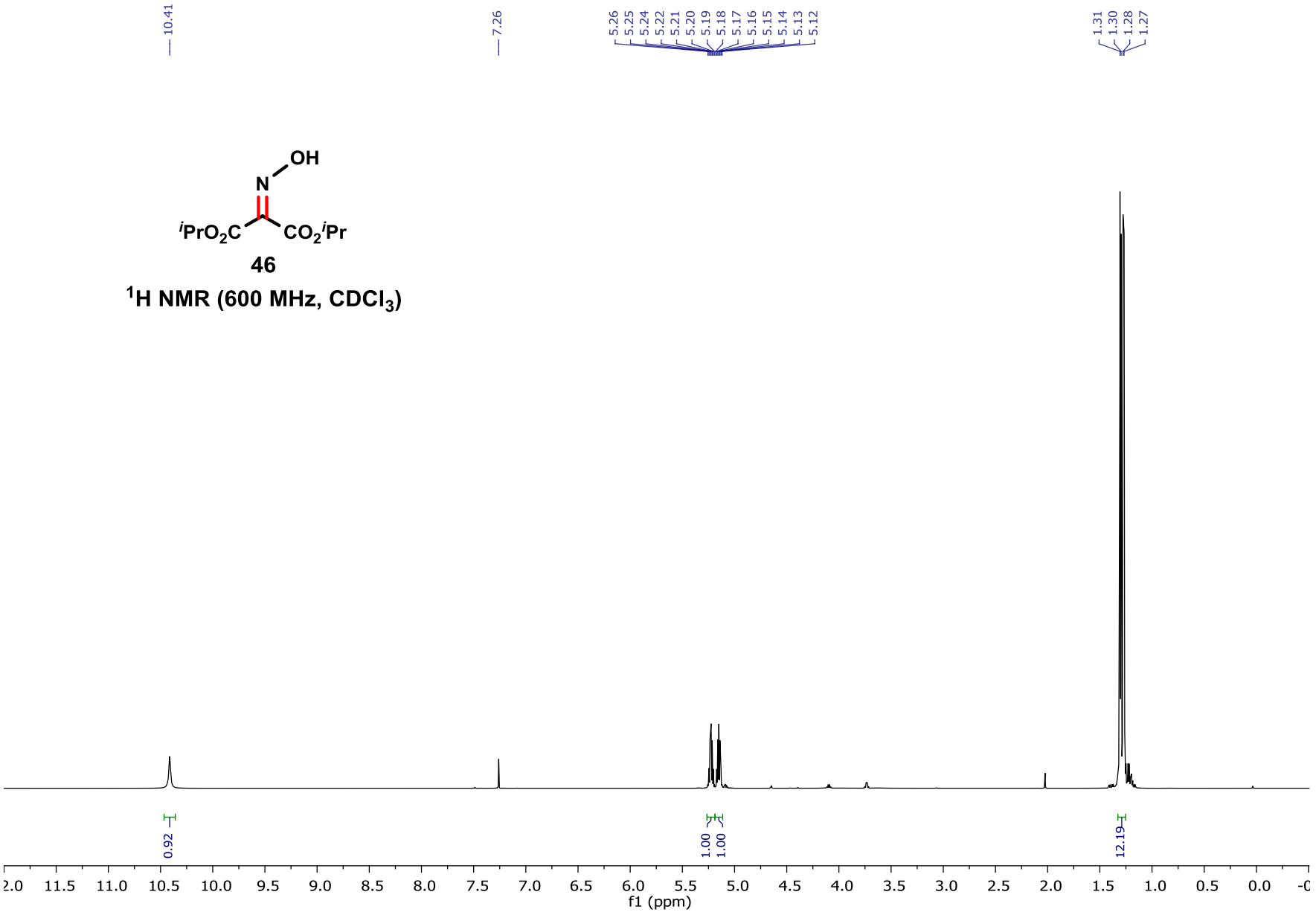

166.40
146.24
129.10
122.55
122.25
82.58
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
69.12
27.75
N
tBuO2C
CO2tBu
40a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

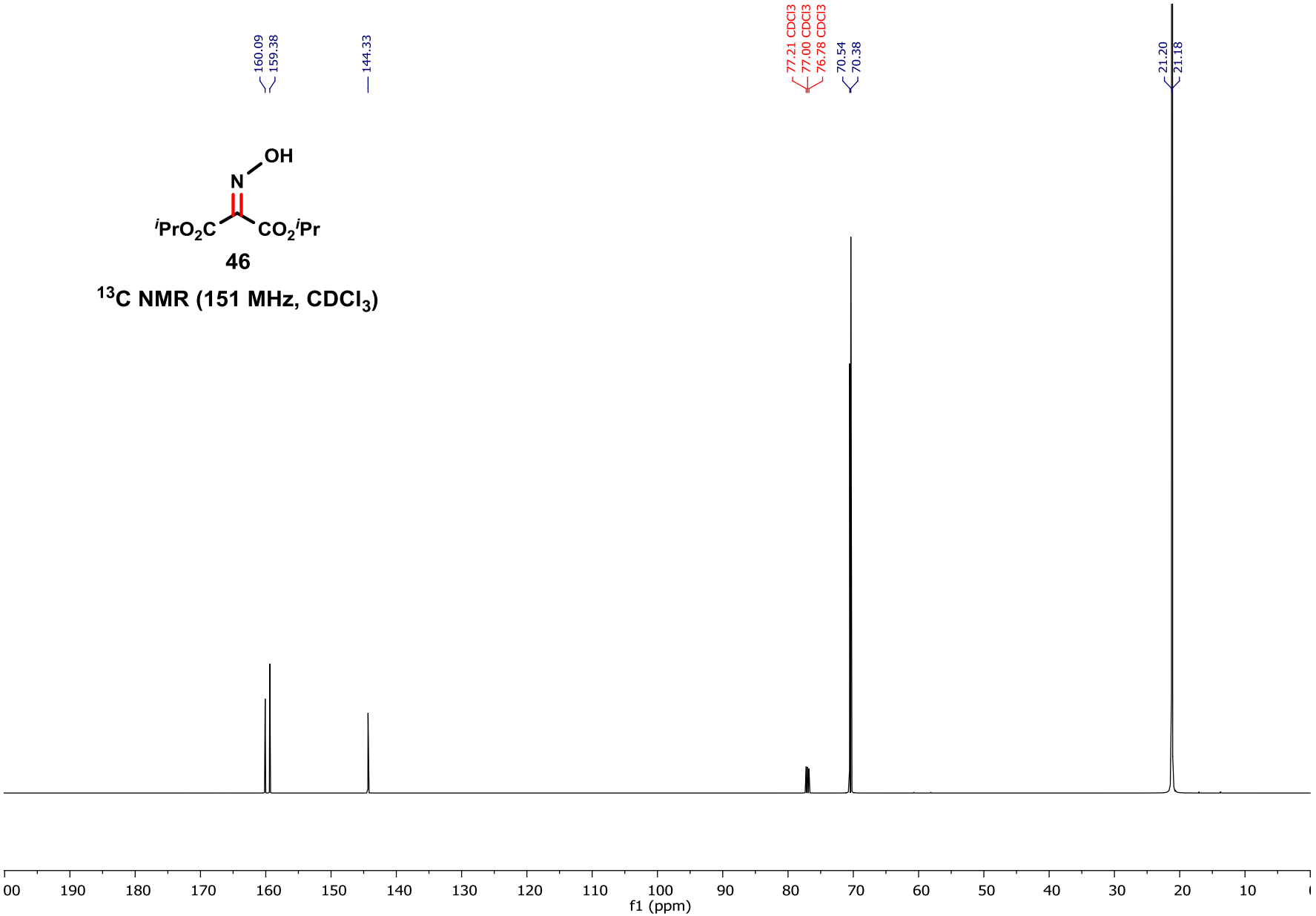


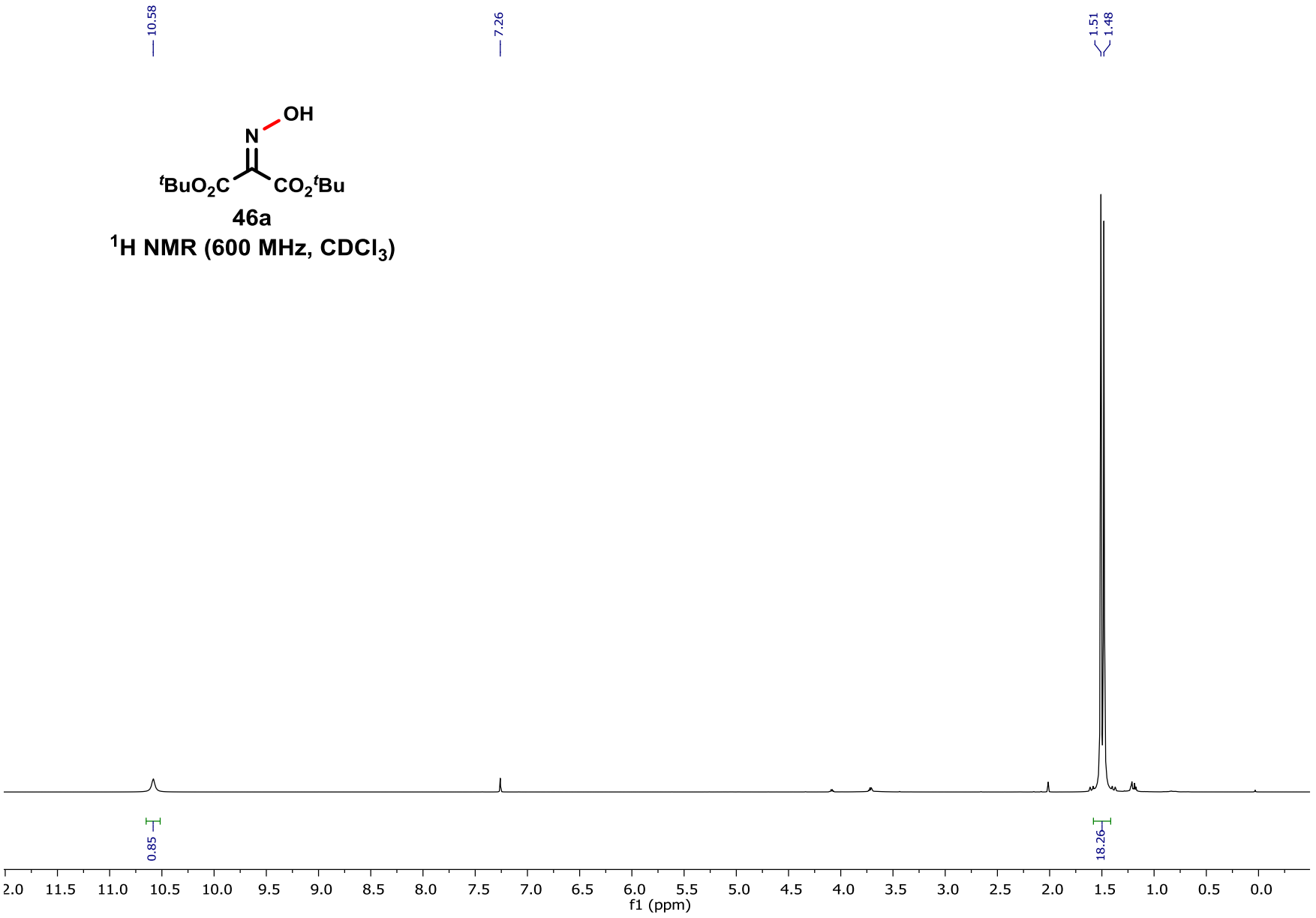
44

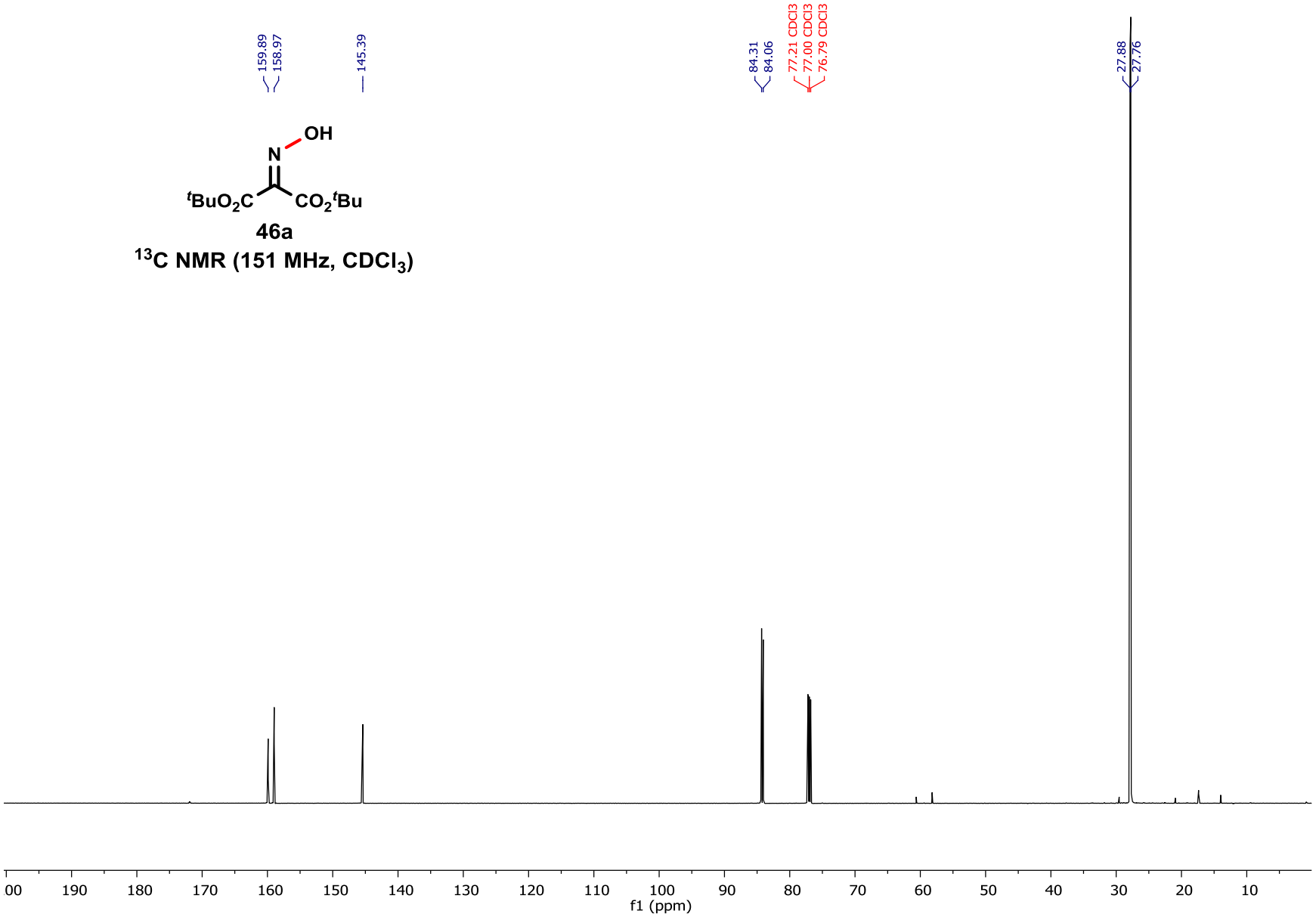
^{1}H NMR (600 MHz, $CDCl_3$)

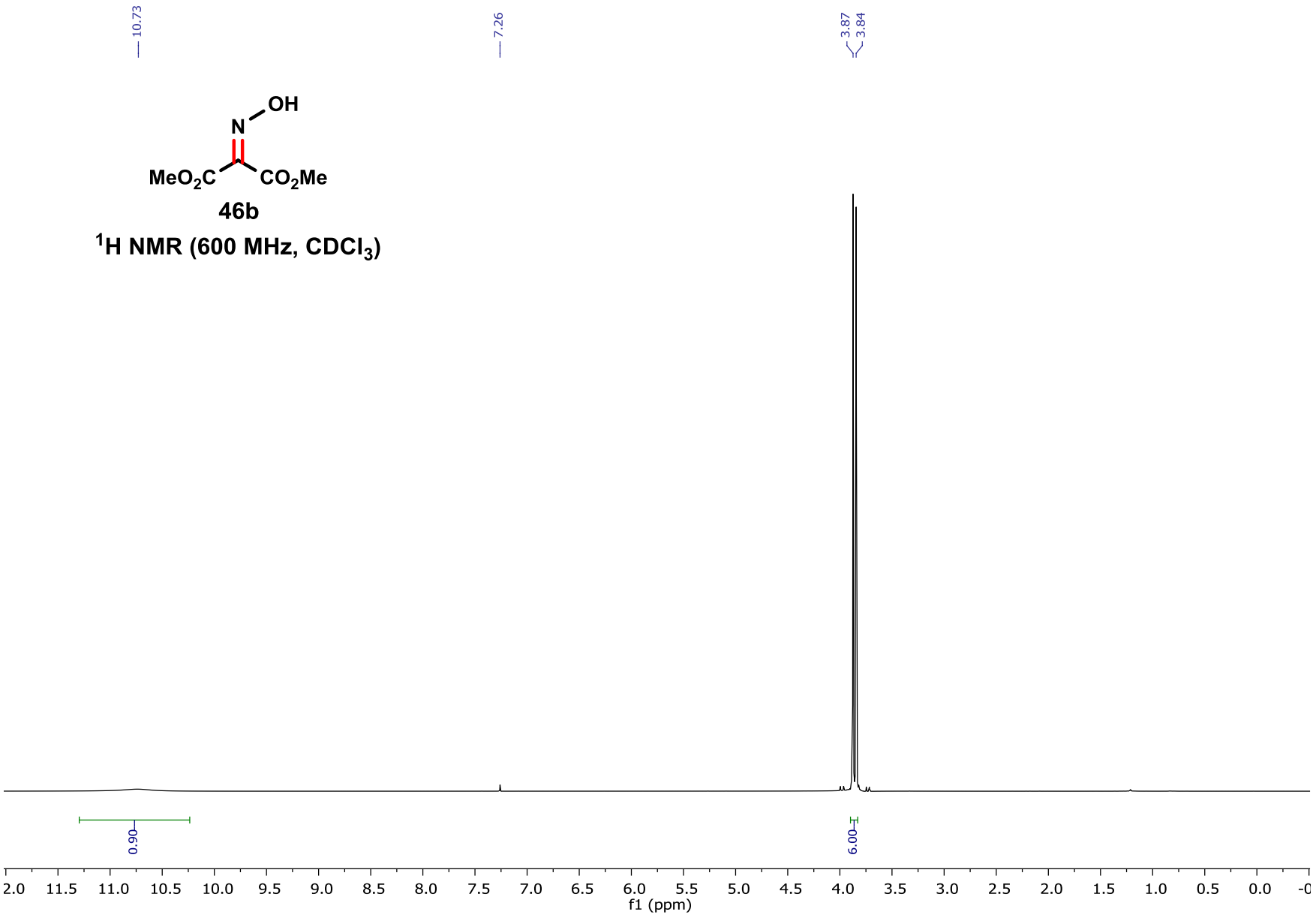

168.02
89.86
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.68
21.39
HO
OH
iPrO2C
CO2iPr
44
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

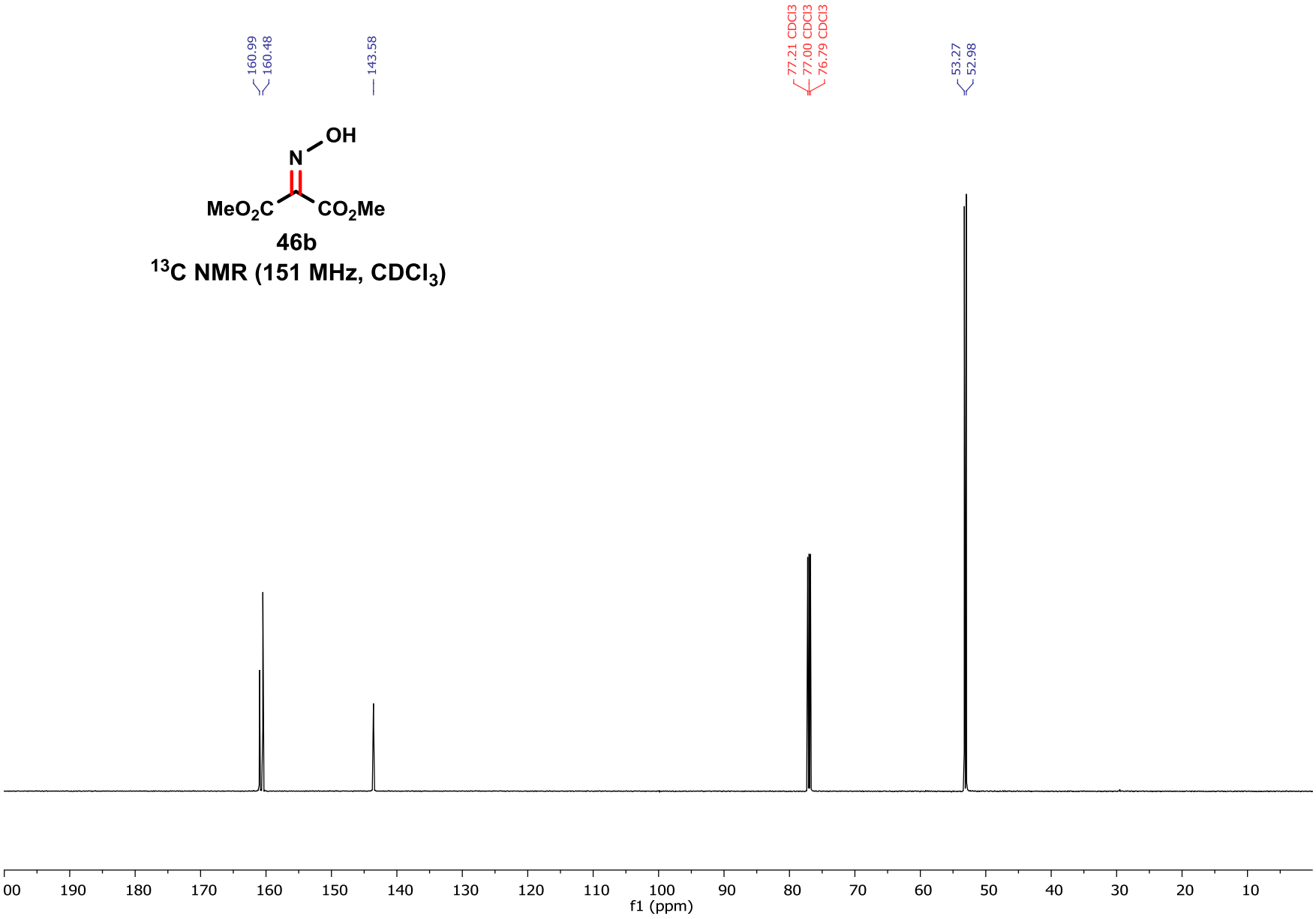

10.41
7.26
5.26
5.25
5.24
5.22
5.21
5.20
5.19
5.18
5.17
5.16
5.15
5.14
5.13
5.12
1.31
1.30
1.28
1.27
OH
N
iPrO2C
CO2iPr
46
1H NMR (600 MHz, CDCl3)
0.92
1.00
1.00
12.19
f1 (ppm)

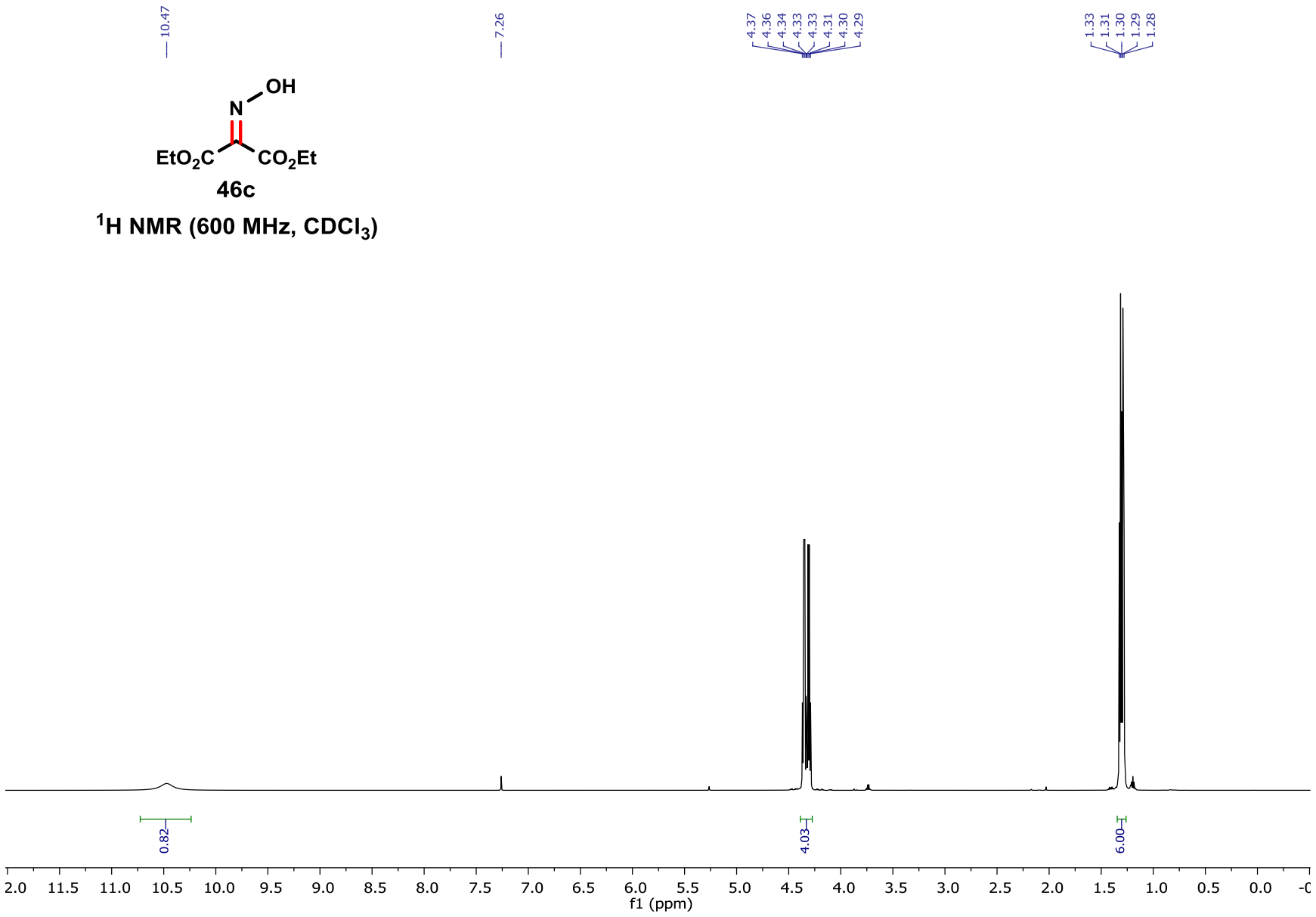

160.09
159.38
144.33
77.21 CDCl3
77.00 CDCl3
76.78 CDCl3
70.54
70.38
21.20
21.18
OH
N
iPrO2C
CO2iPr
46
13C NMR (151 MHz, CDCl3)
f1 (ppm)

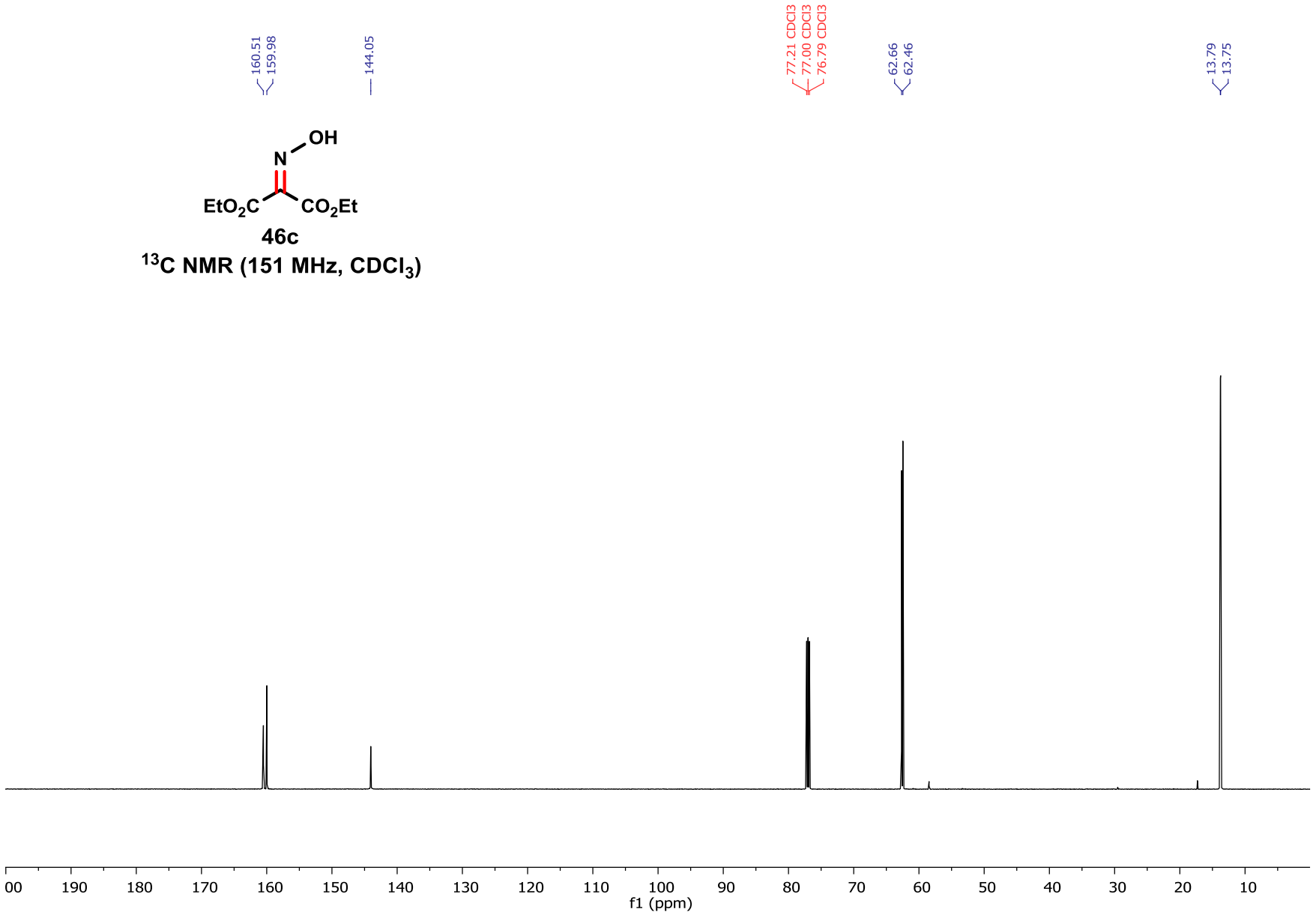

10.58
7.26
1.51
1.48
OH
N
tBuO2C
CO2tBu
46a
1H NMR (600 MHz, CDCl3)
0.85
18.26
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

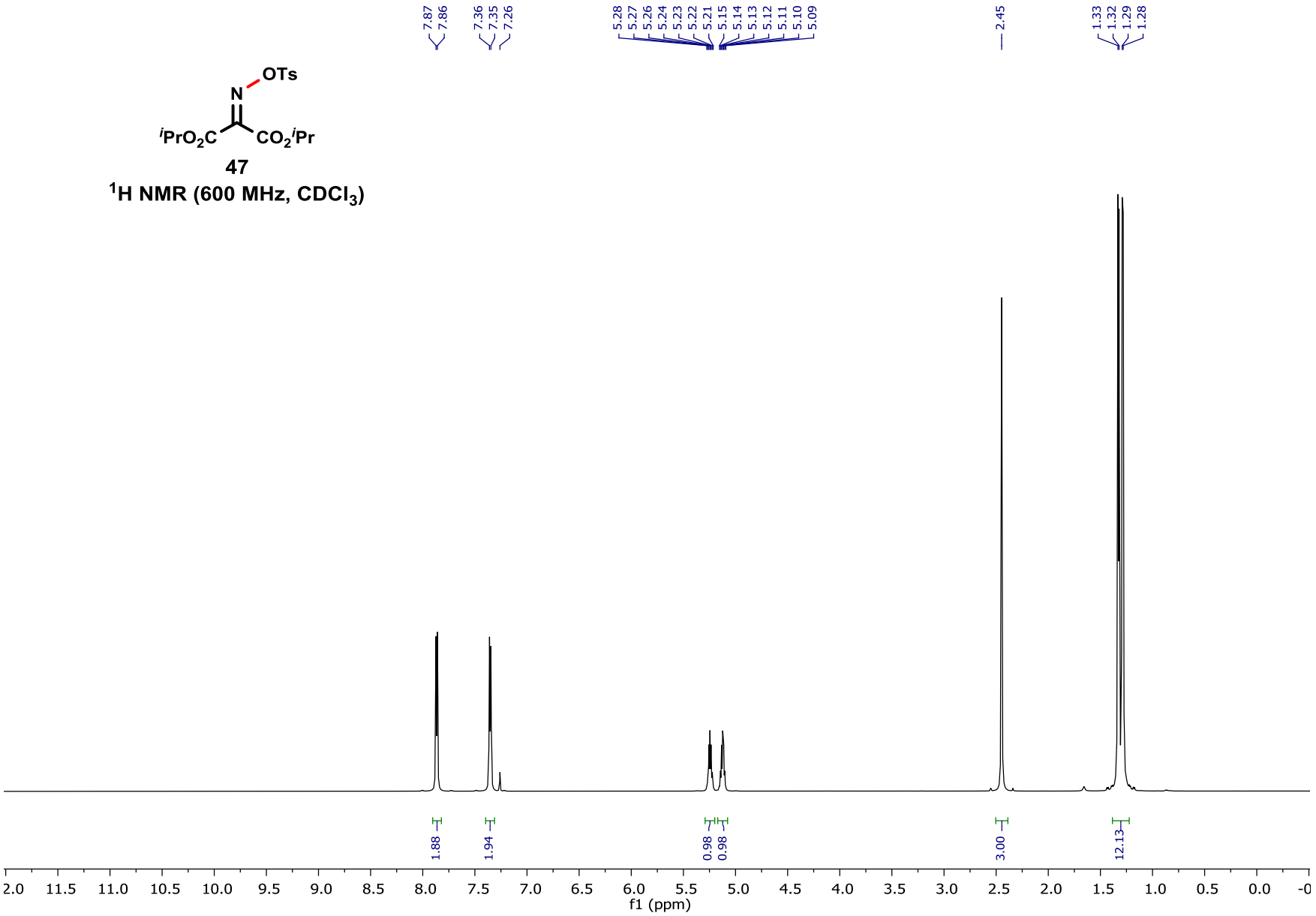

159.89
158.97
145.39
84.31
84.06
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
27.88
27.76
OH
N
tBuO2C
CO2tBu
46a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

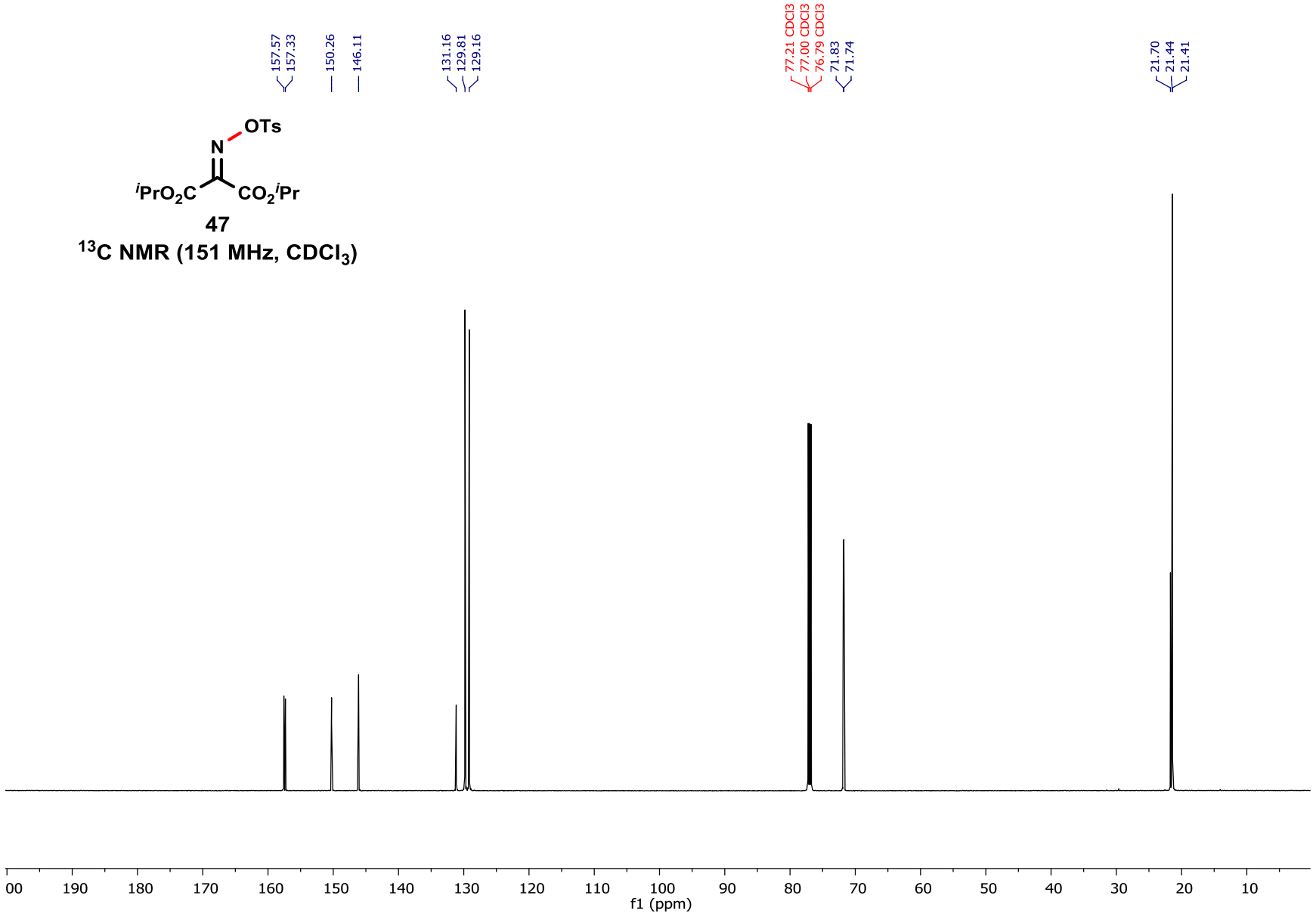

10.73
7.26
3.87
3.84
OH
N
MeO2C
CO2Me
46b
1H NMR (600 MHz, CDCl3)
0.90
6.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

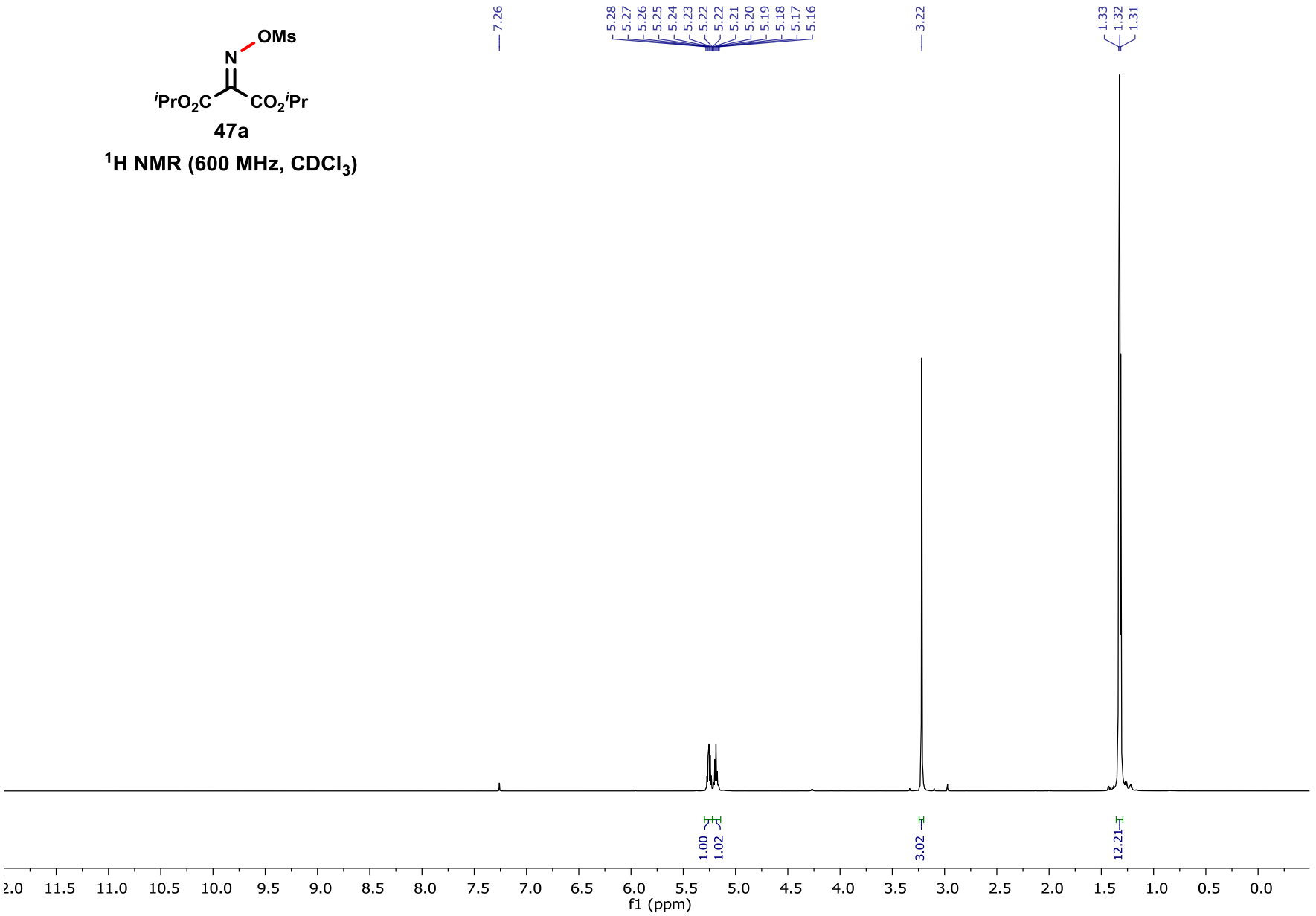

160.99
160.48
143.58
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
53.27
52.98
OH
N
MeO2C
CO2Me
46b
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

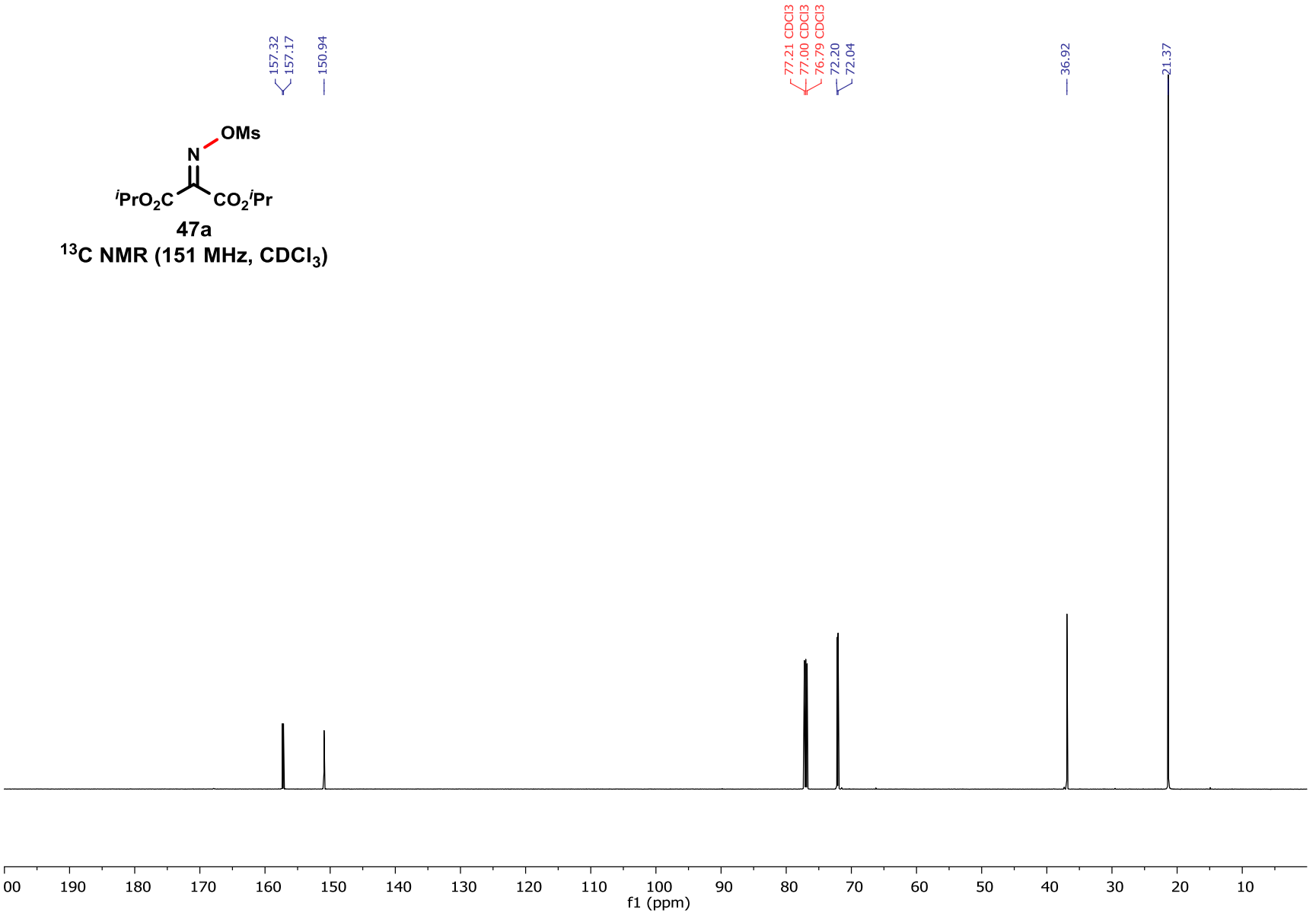

10.47
7.26
4.37
4.36
4.34
4.33
4.33
4.31
4.30
4.29
1.33
1.31
1.30
1.29
1.28
OH
N
EtO2C
CO2Et
46c
1H NMR (600 MHz, CDCl3)
0.82
4.03
6.00
f1 (ppm)

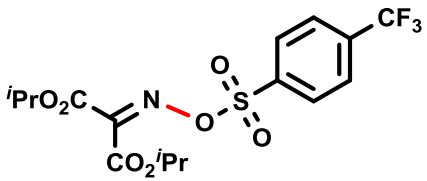

160.51
159.98
144.05
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
62.66
62.46
13.79
13.75
OH
N
EtO2C
CO2Et
46c
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OTs
N
iPrO2C
CO2iPr
47
1H NMR (600 MHz, CDCl3)
7.87
7.86
7.36
7.35
7.26
5.28
5.27
5.26
5.24
5.23
5.22
5.21
5.15
5.14
5.13
5.12
5.11
5.10
5.09
2.45
1.33
1.32
1.29
1.28
1.88
1.94
0.98
0.98
3.00
12.13
f1 (ppm)


157.57
157.33
150.26
146.11
131.16
129.81
129.16
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.83
71.74
21.70
21.44
21.41
OTs
N
iPrO2C
CO2iPr
47
13C NMR (151 MHz, CDCl3)
f1 (ppm)

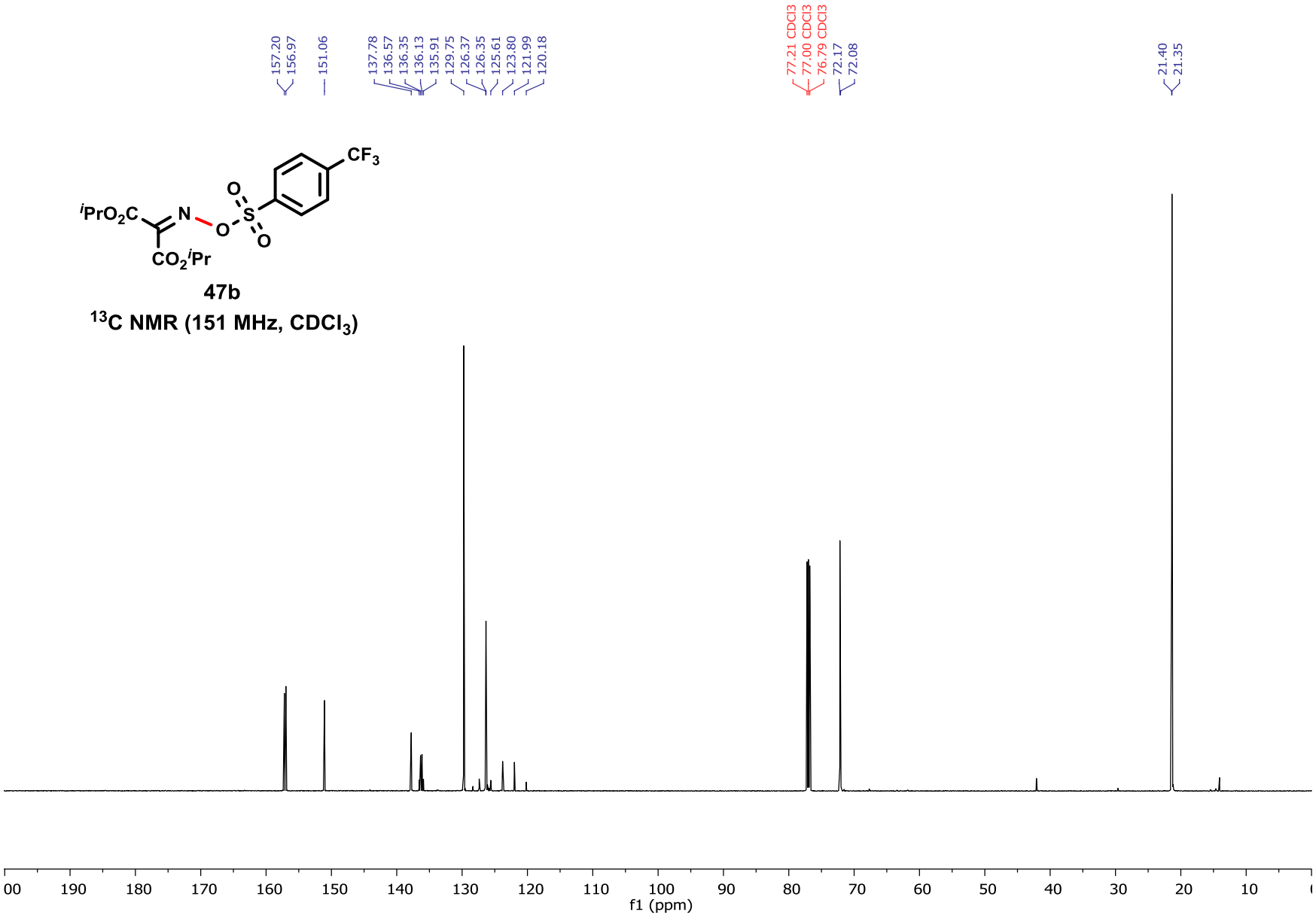

OMs
N
iPrO2C
CO2iPr
47a
1H NMR (600 MHz, CDCl3)
7.26
5.28
5.27
5.26
5.25
5.24
5.23
5.22
5.22
5.21
5.20
5.19
5.18
5.17
5.16
3.22
1.33
1.32
1.31
1.00
1.02
3.02
12.21
f1 (ppm)

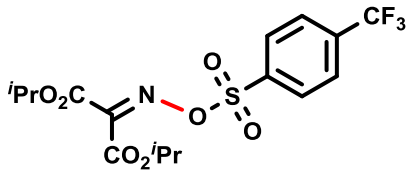

157.32
157.17
150.94
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
72.20
72.04
36.92
21.37
OMs
N
iPrO2C
CO2iPr
47a
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



47b

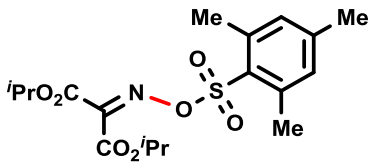
^{1}H NMR (600 MHz, $CDCl_3$)


157.20
156.97
151.06
137.78
136.57
136.35
136.13
135.91
129.75
126.37
126.35
125.61
123.80
121.99
120.18
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
72.17
72.08
21.40
21.35
CF3
iPrO2C
N
O
S
O
O
CO2iPr
47b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



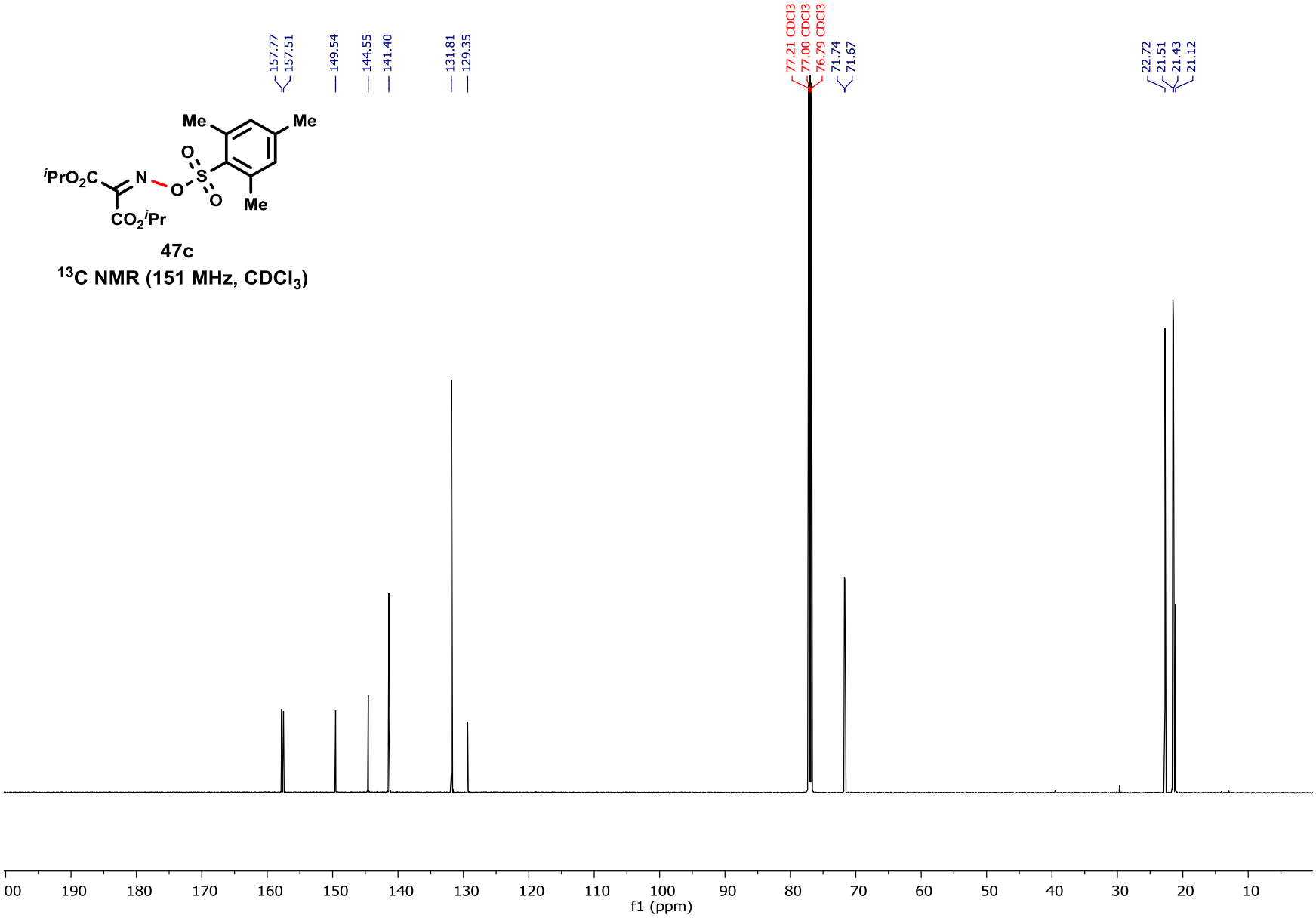
47b

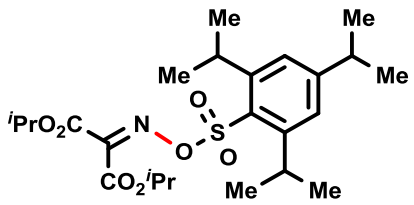
^{19}F NMR (471 MHz, $CDCl_3$)



47c

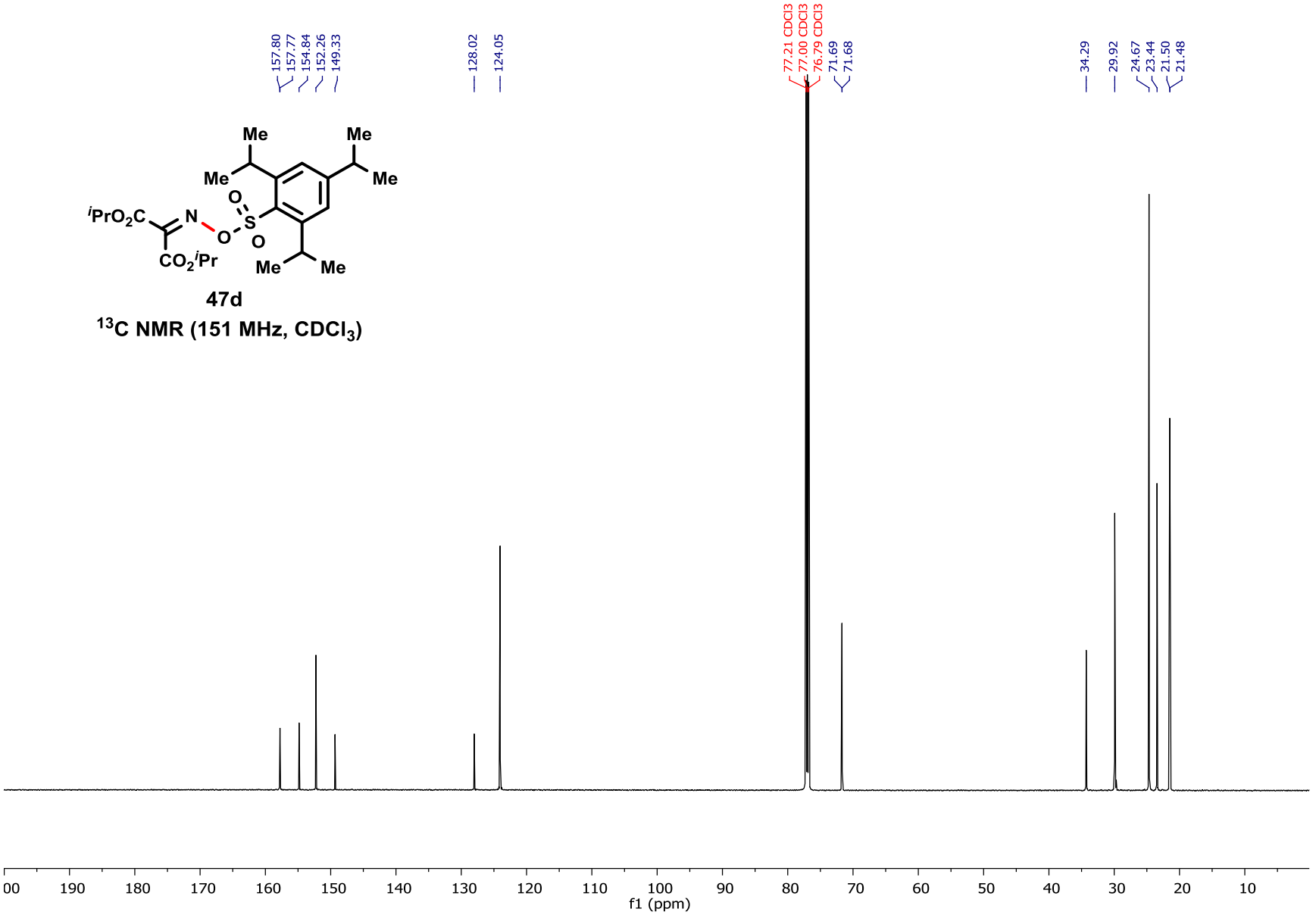
^{1}H NMR (600 MHz, $CDCl_3$)

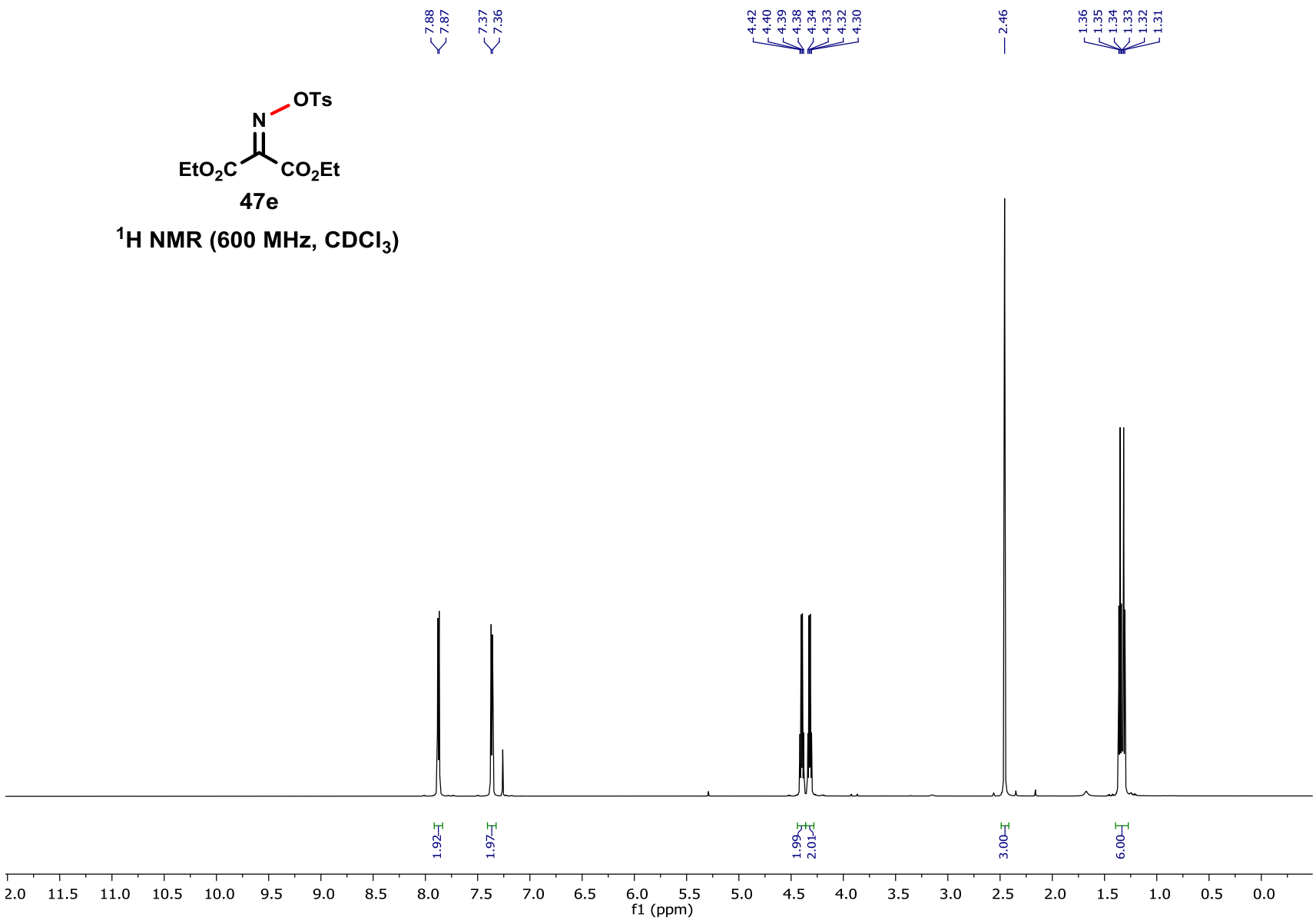

157.77
157.51
149.54
144.55
141.40
131.81
129.35
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.74
71.67
22.72
21.51
21.43
21.12
Me
Me
Me
O
S
O
O
N
O
$^{i}PrO_2C$
$CO_2{}^{i}Pr$
47c
^{13}C NMR (151 MHz, $CDCl_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

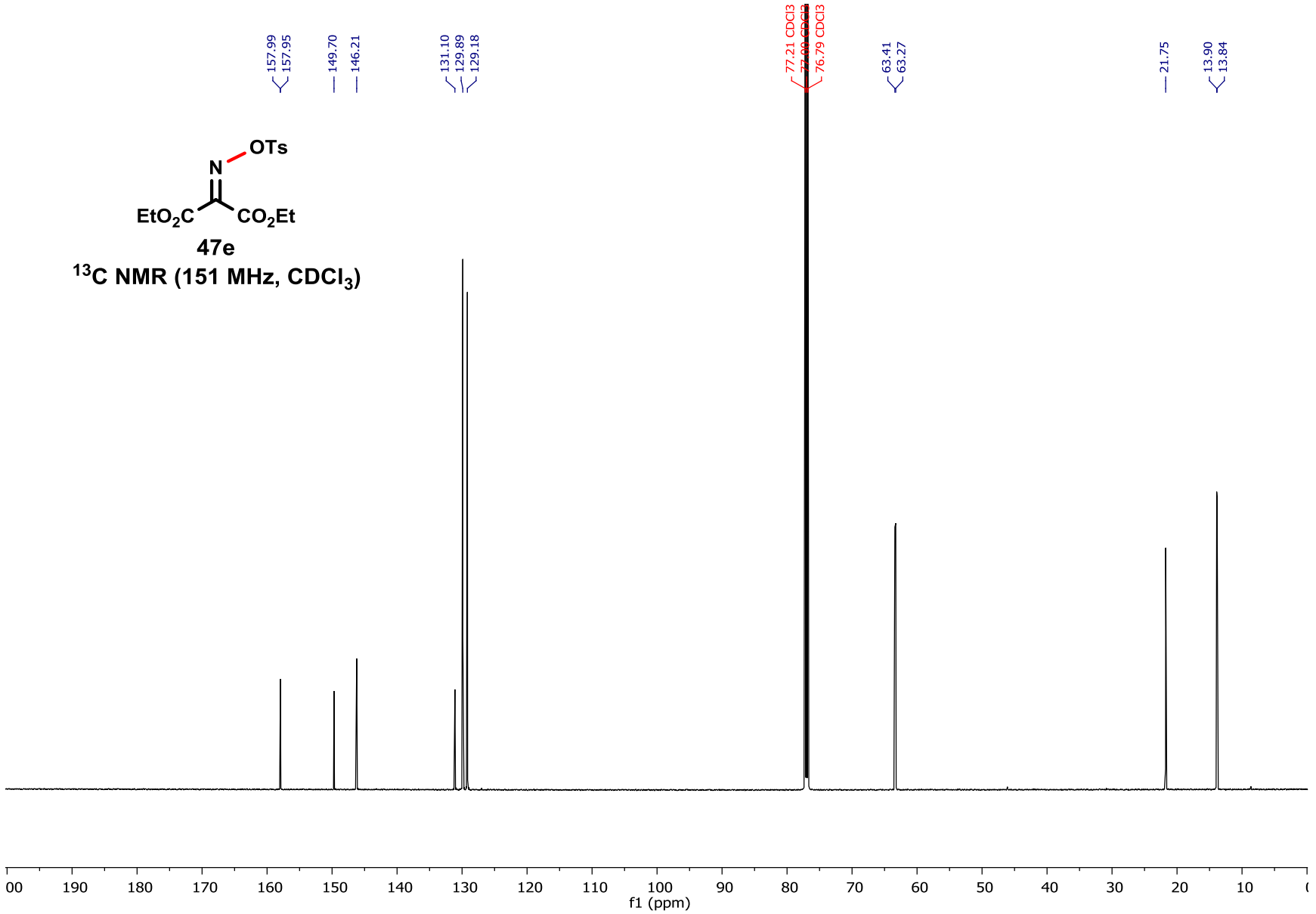


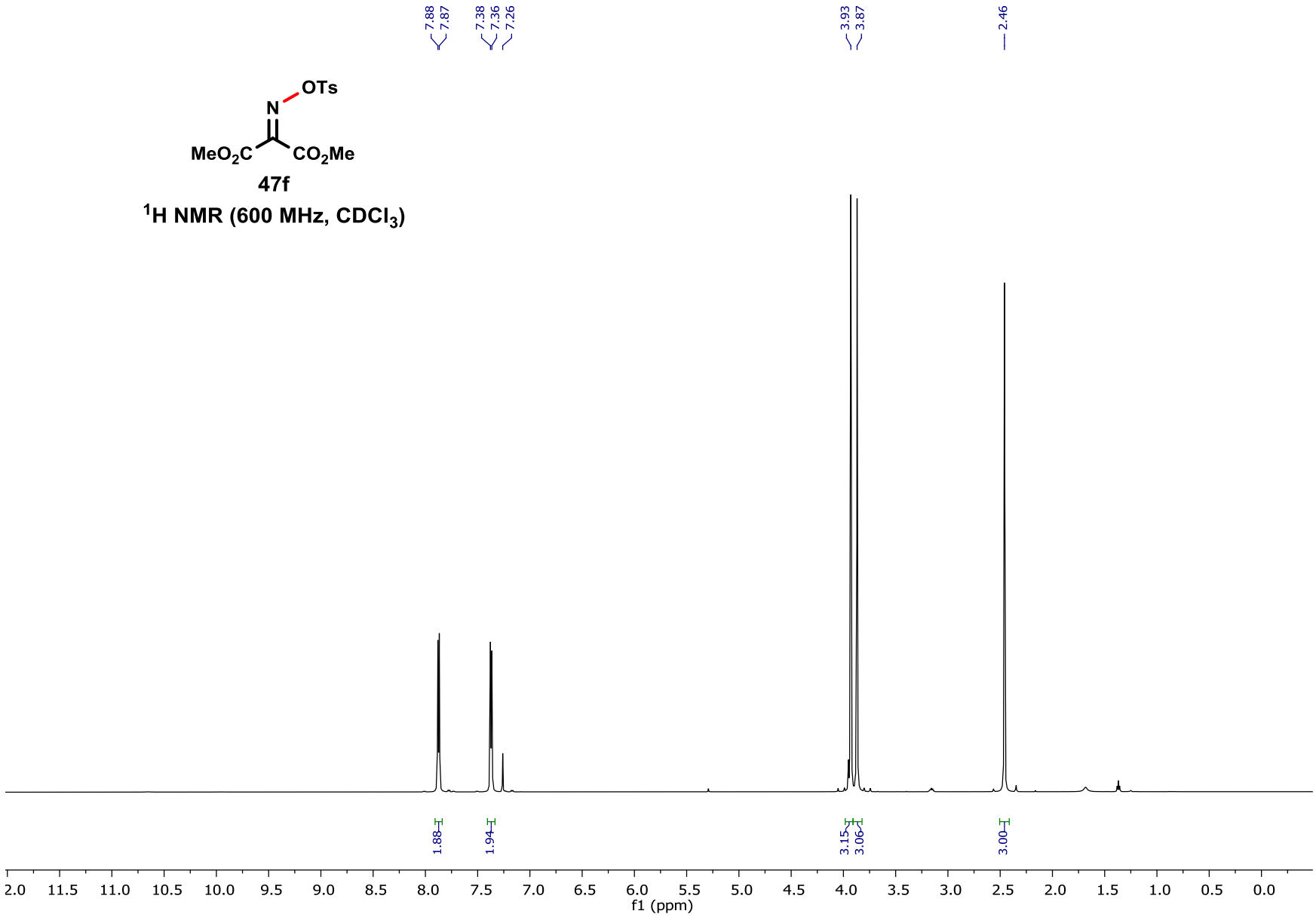
47d

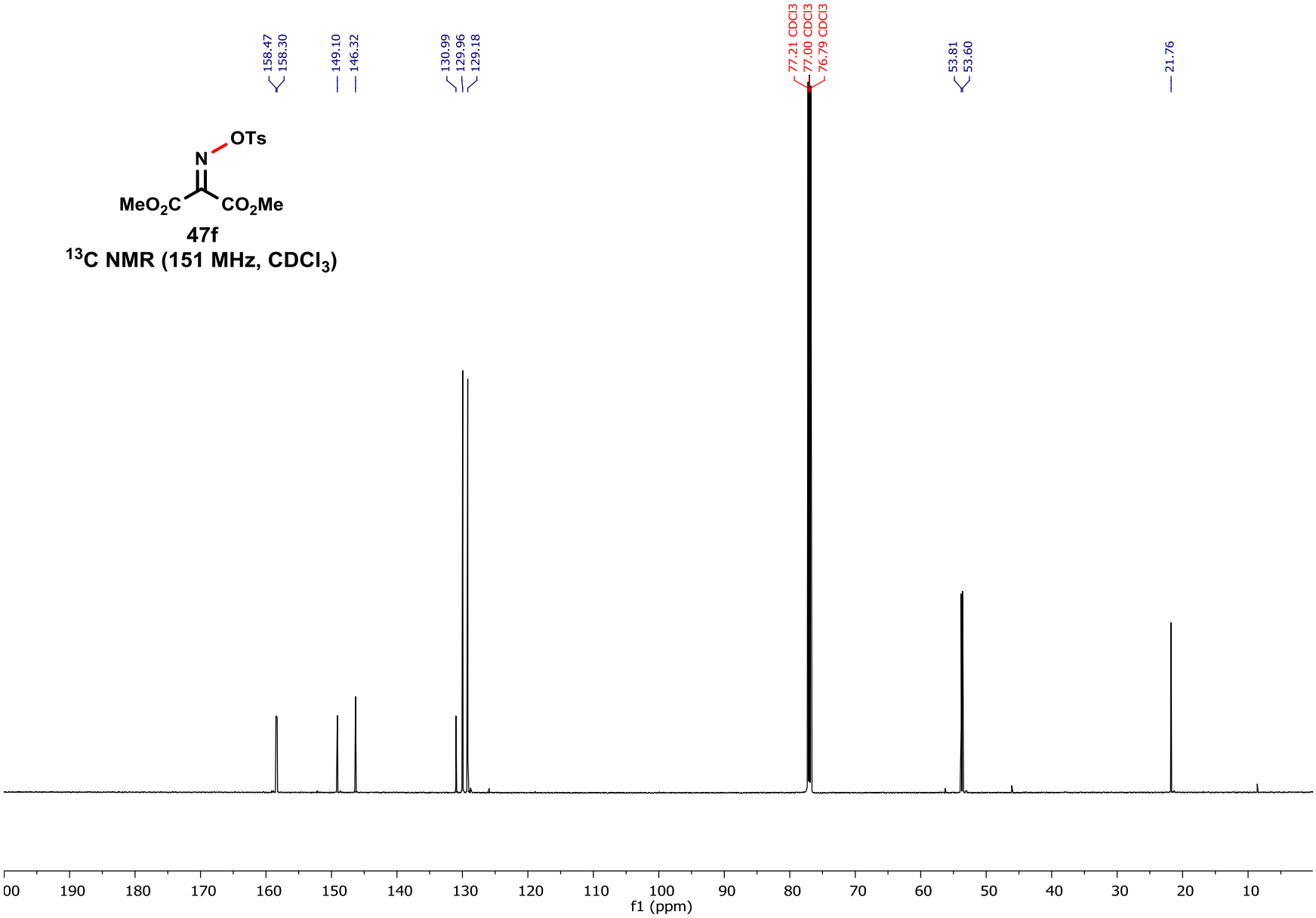
^{1}H NMR (600 MHz, $CDCl_3$)

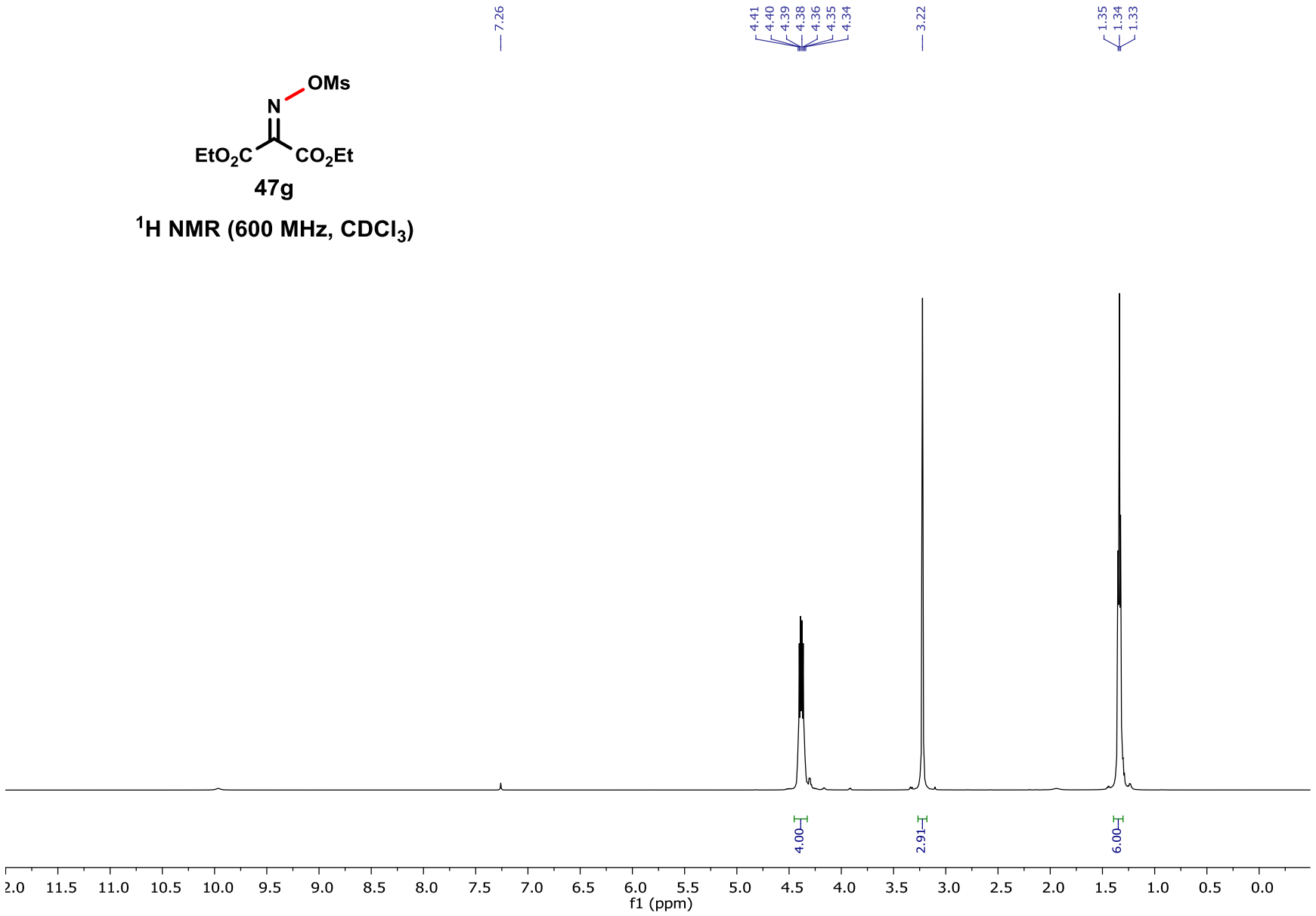

157.80
157.77
154.84
152.26
149.33
128.02
124.05
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.69
71.68
34.29
29.92
24.67
23.44
21.50
21.48
Me
Me
Me
Me
Me
Me
iPrO2C
N
O
S
O
O
CO2iPr
47d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

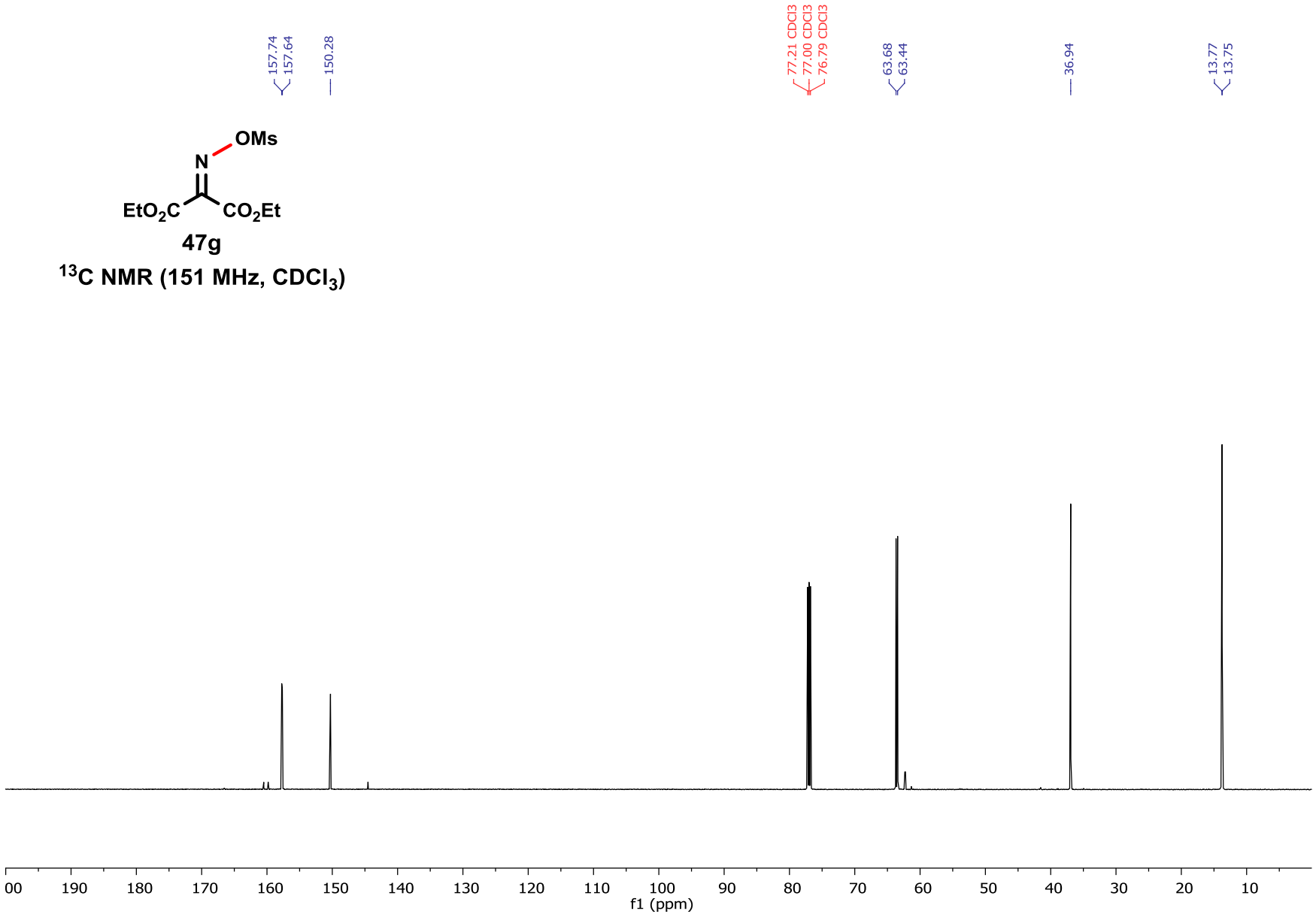

7.88
7.87
7.37
7.36
4.42
4.40
4.39
4.38
4.34
4.33
4.32
4.30
2.46
1.36
1.35
1.34
1.33
1.32
1.31
OTs
N
EtO2C
CO2Et
47e
1H NMR (600 MHz, CDCl3)
1.92
1.97
1.99
2.01
3.00
6.00
f1 (ppm)

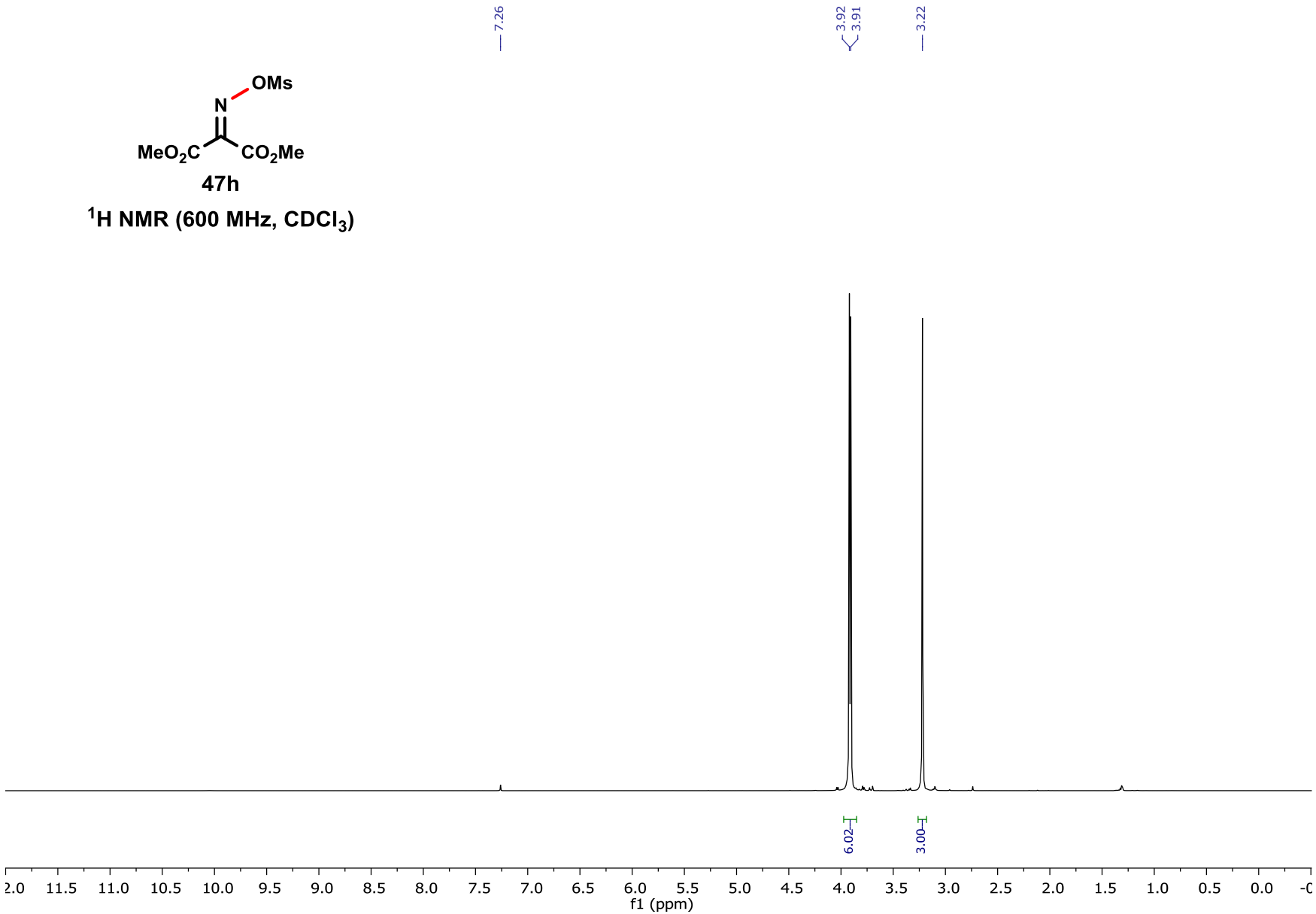

157.99
157.95
149.70
146.21
131.10
129.89
129.18
77.21 CDCl3
76.79 CDCl3
63.41
63.27
21.75
13.90
13.84
OTs
N
EtO2C
CO2Et
47e
13C NMR (151 MHz, CDCl3)
f1 (ppm)

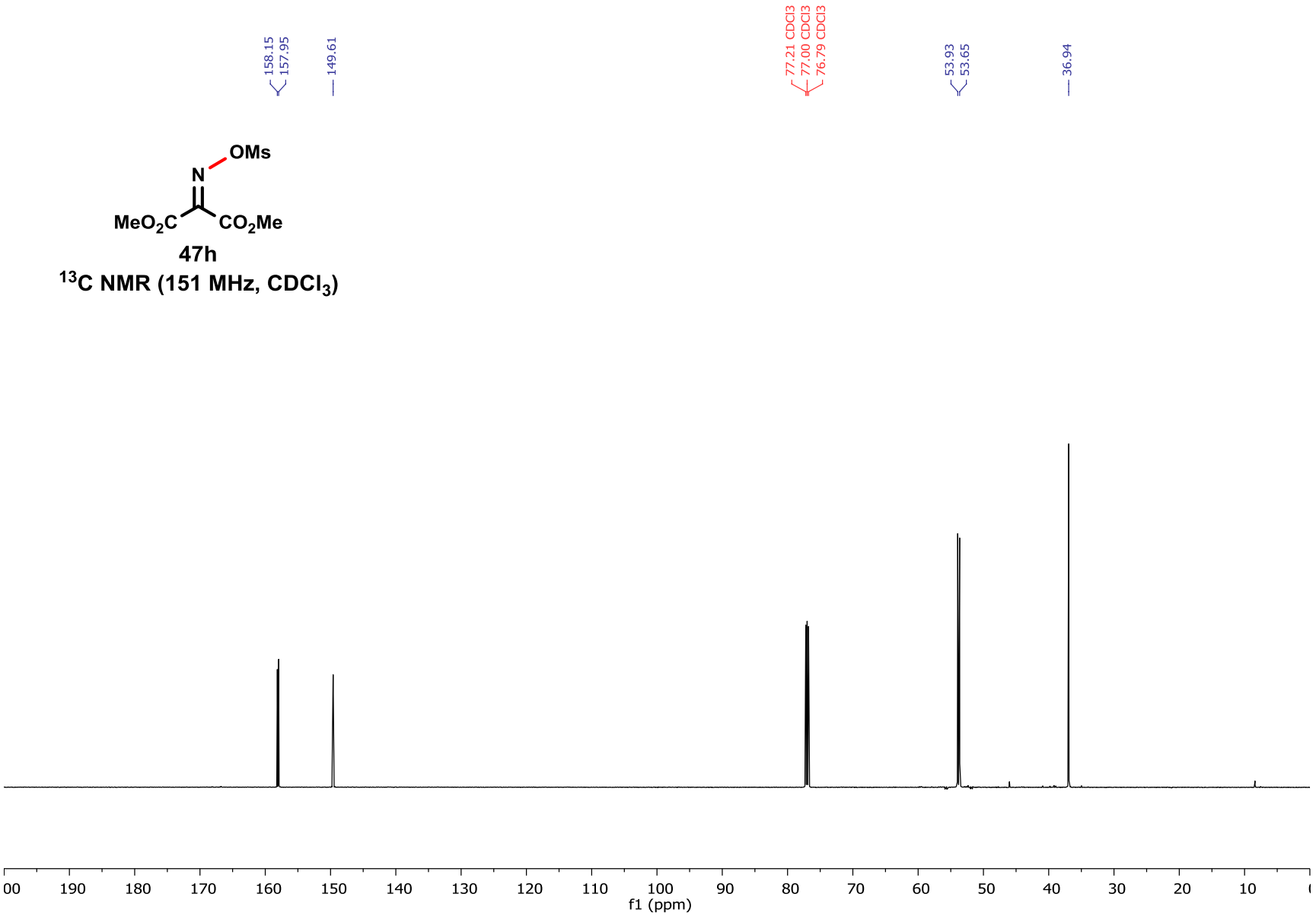

7.88
7.87
7.38
7.36
7.26
3.93
3.87
2.46
OTs
N
MeO2C
CO2Me
47f
1H NMR (600 MHz, CDCl3)
1.88
1.94
3.15
3.06
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

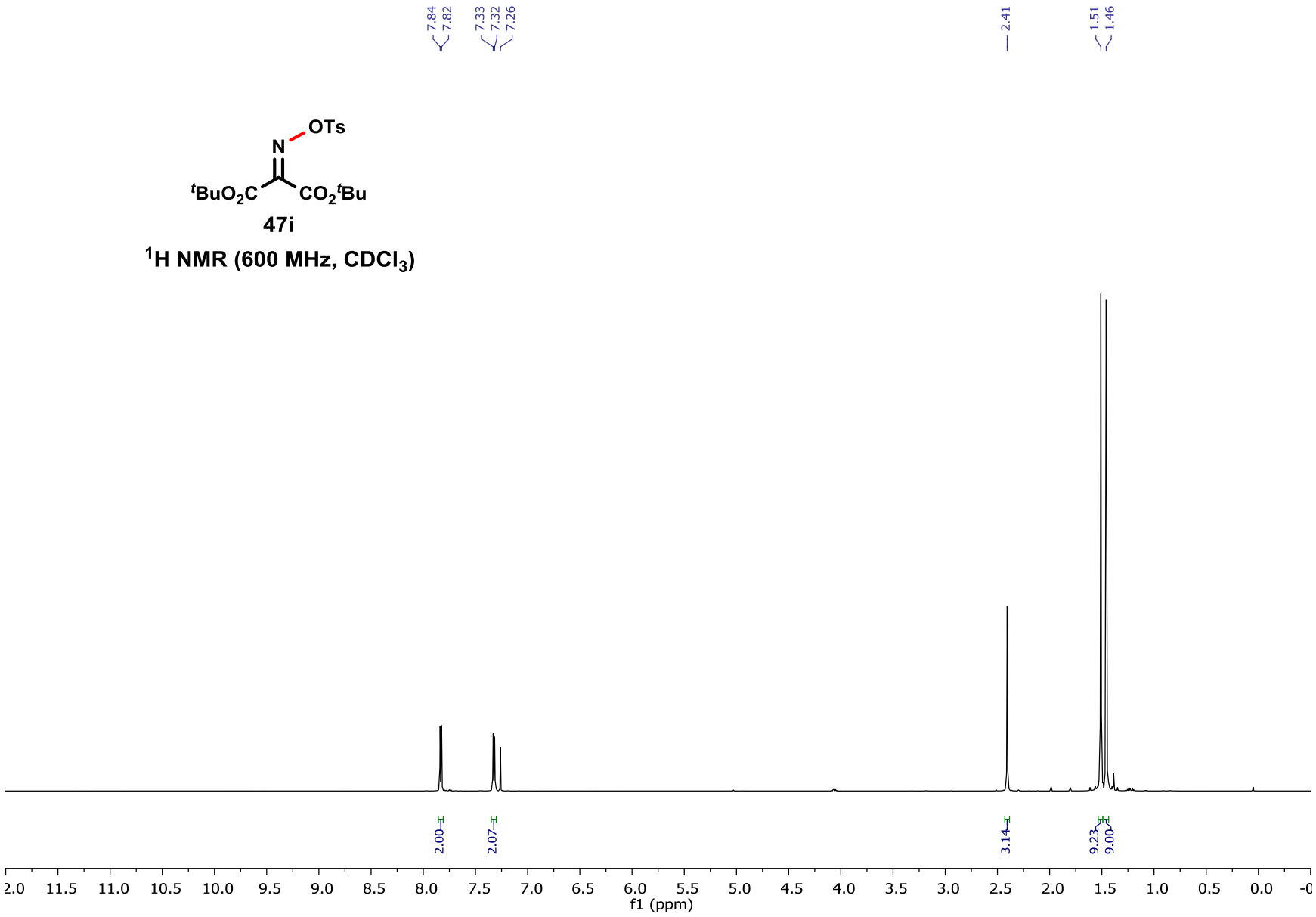

158.47
158.30
149.10
146.32
130.99
129.96
129.18
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
53.81
53.60
21.76
OTs
N
MeO2C
CO2Me
47f
13C NMR (151 MHz, CDCl3)
f1 (ppm)

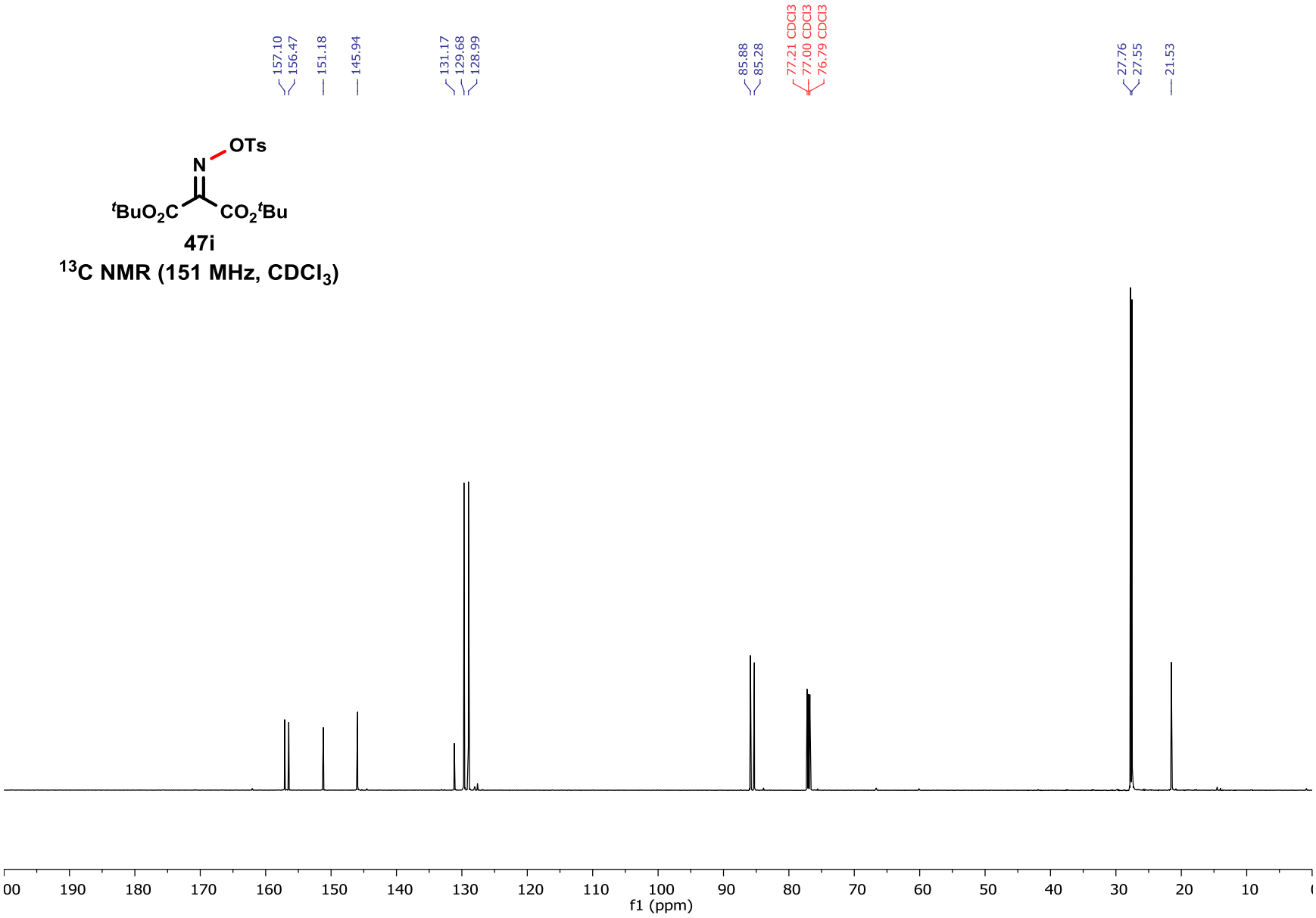

OMs
N
EtO2C
CO2Et
47g
1H NMR (600 MHz, CDCl3)
7.26
4.41
4.40
4.39
4.38
4.36
4.35
4.34
3.22
1.35
1.34
1.33
4.00
2.91
6.00
f1 (ppm)

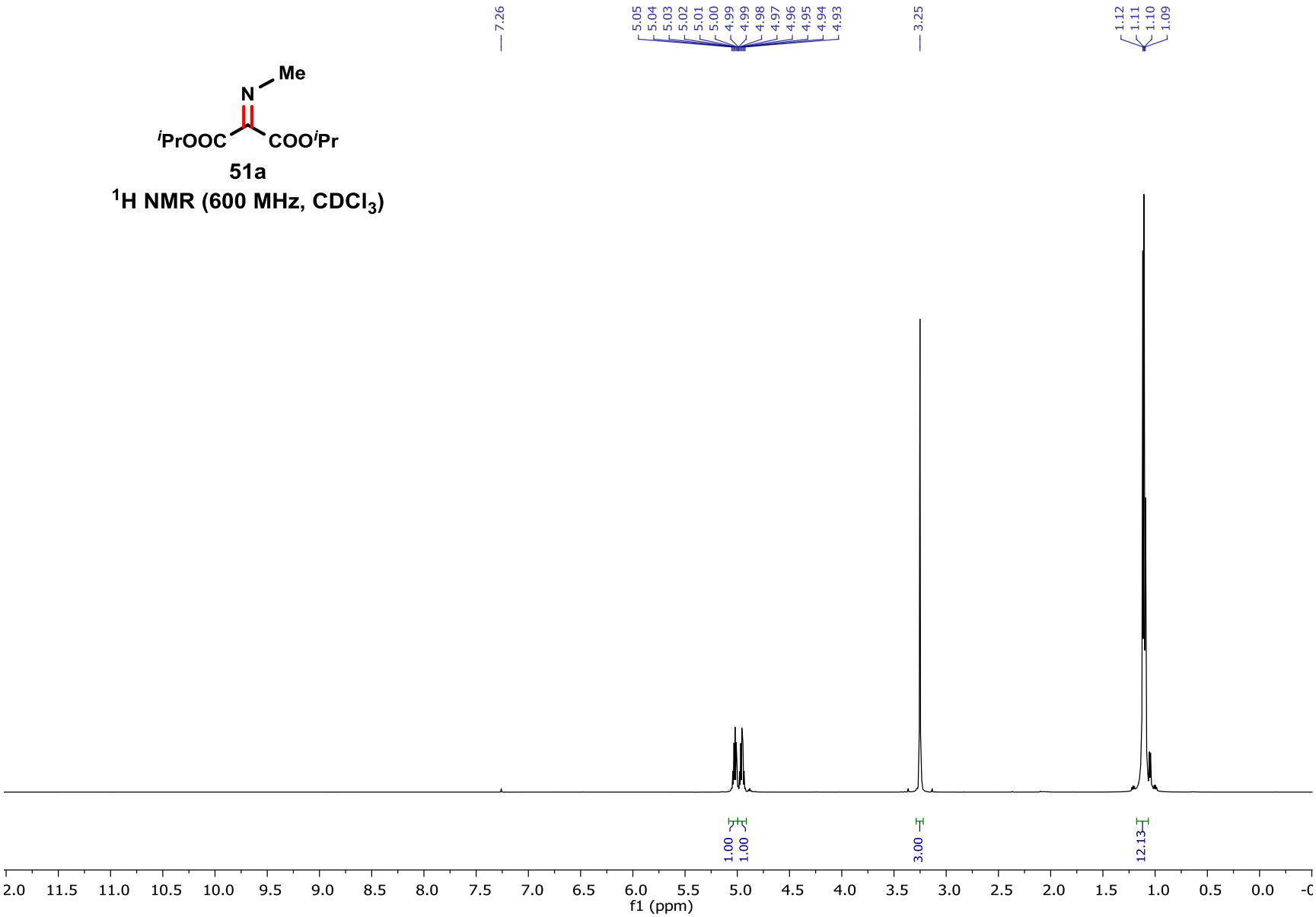

157.74
157.64
150.28
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
63.68
63.44
36.94
13.77
13.75
OMs
N
EtO2C
CO2Et
47g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

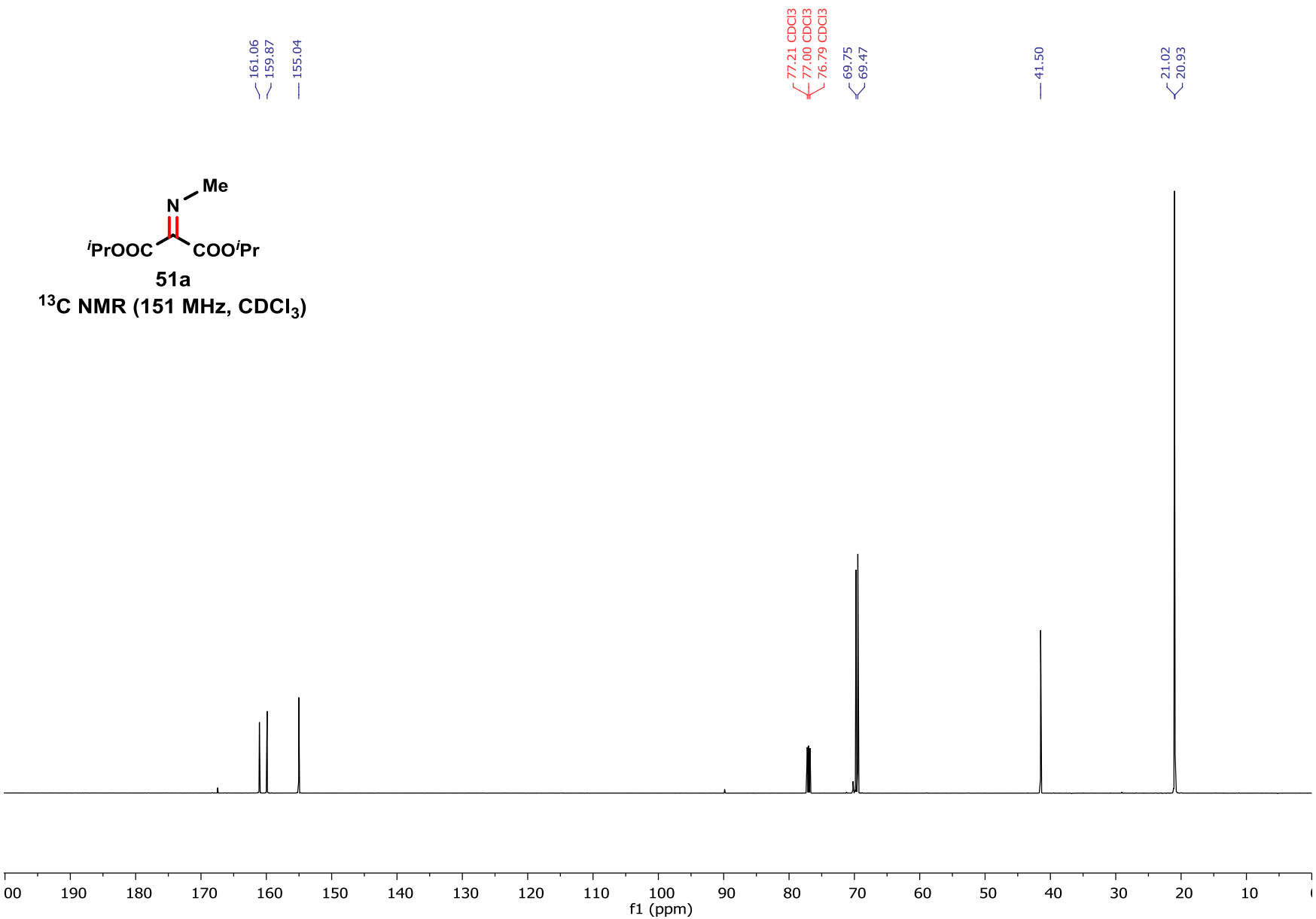

OMs
N
MeO2C
CO2Me
47h
1H NMR (600 MHz, CDCl3)
7.26
3.92
3.91
3.22
6.02
3.00
f1 (ppm)

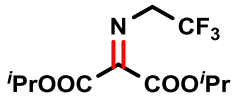

158.15
157.95
149.61
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
53.93
53.65
36.94
OMs
N
MeO2C
CO2Me
47h
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.84
7.82
7.33
7.32
7.26
2.41
1.51
1.46
OTs
N
tBuO2C
CO2tBu
47i
1H NMR (600 MHz, CDCl3)
2.00
2.07
3.14
9.23
9.00
f1 (ppm)


157.10
156.47
151.18
145.94
131.17
129.68
128.99
85.88
85.28
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
27.76
27.55
21.53
OTs
N
tBuO2C
CO2tBu
47i
13C NMR (151 MHz, CDCl3)
f1 (ppm)

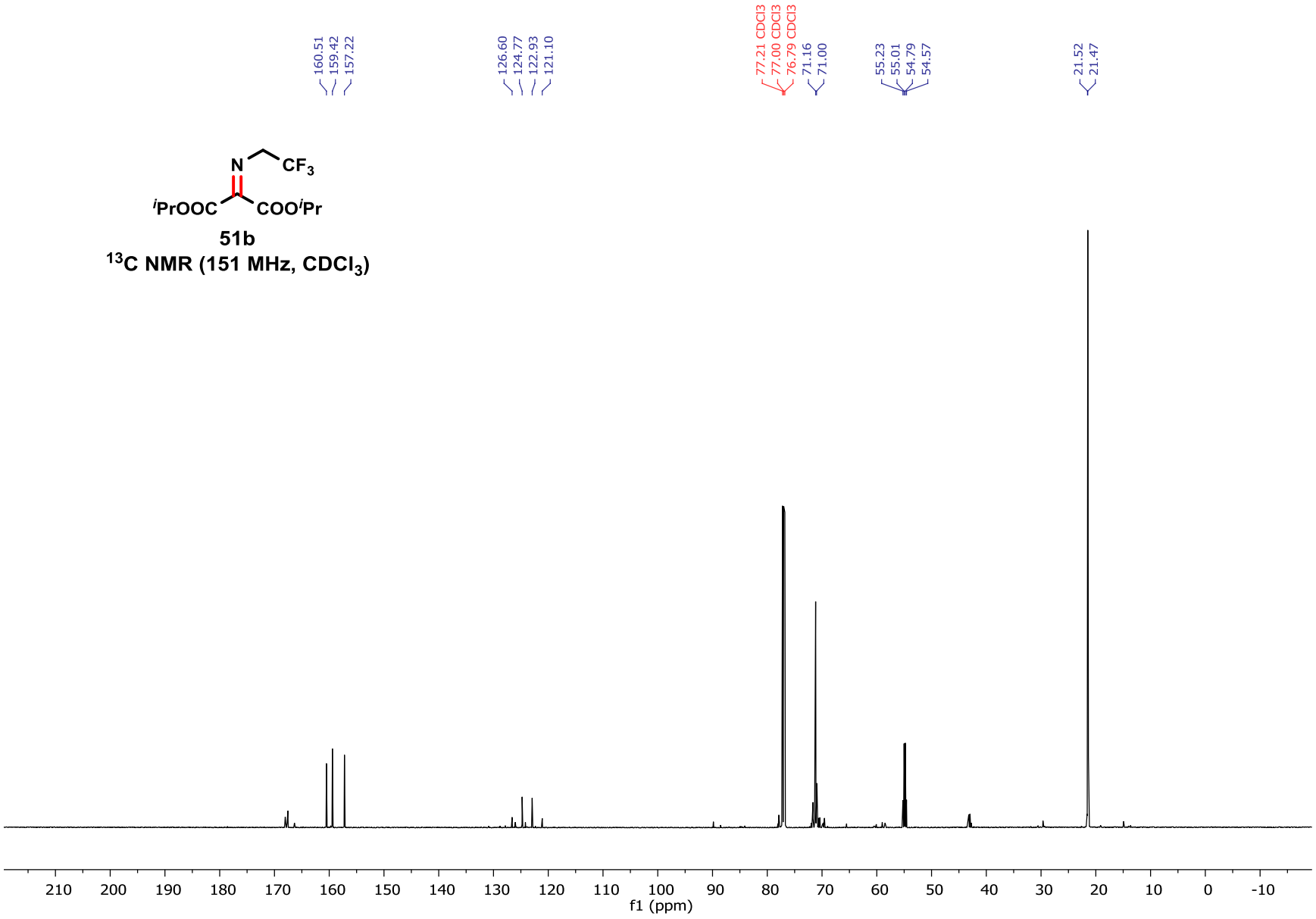

Me
N
iPrOOC
COOiPr
51a
1H NMR (600 MHz, CDCl3)
7.26
5.05
5.04
5.03
5.02
5.01
5.00
4.99
4.99
4.98
4.97
4.96
4.95
4.94
4.93
3.25
1.12
1.11
1.10
1.09
1.00
1.00
3.00
12.13
f1 (ppm)

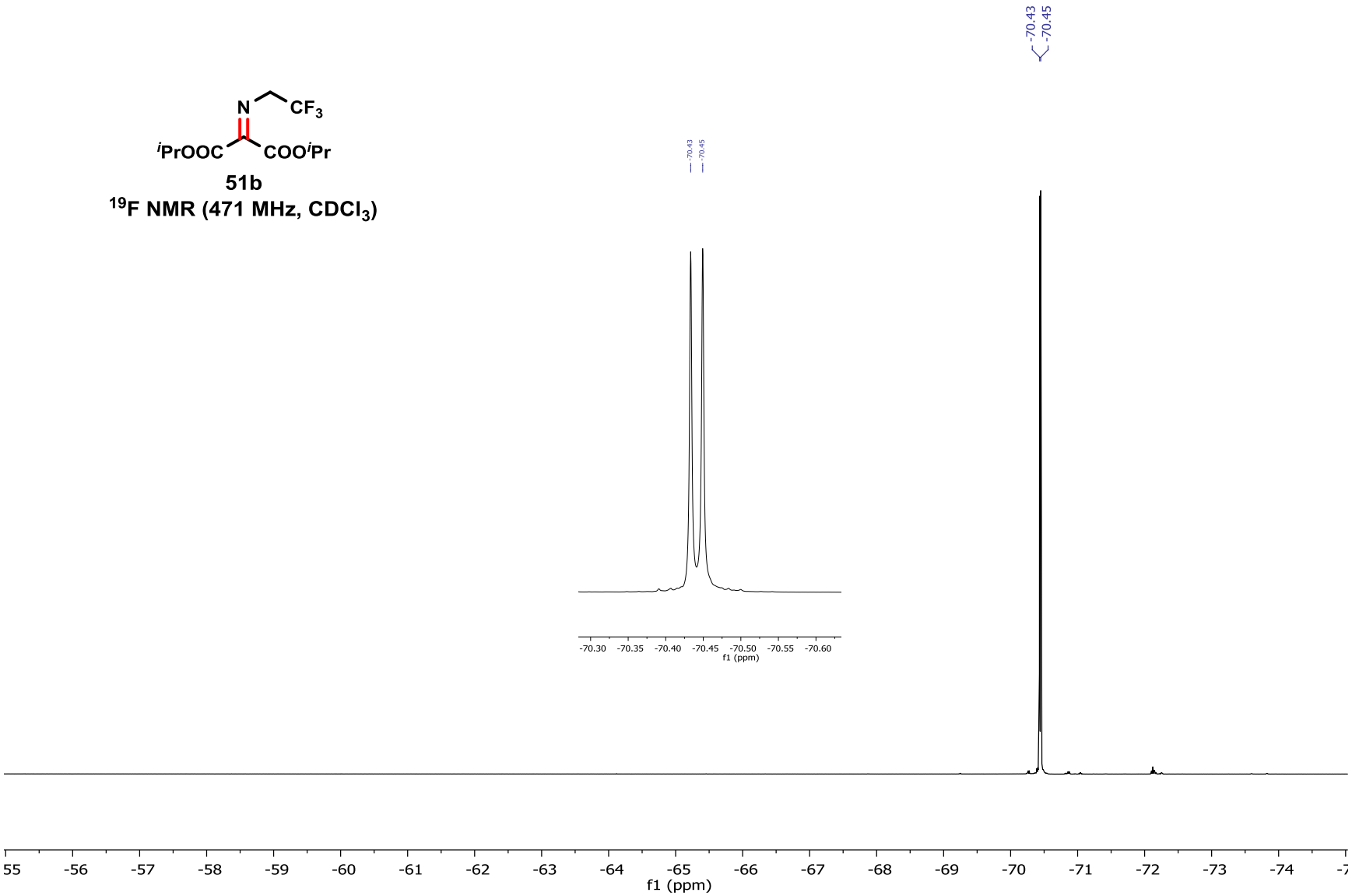

161.06
159.87
155.04
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.75
69.47
41.50
21.02
20.93
Me
N
iPrOOC
COOiPr
51a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

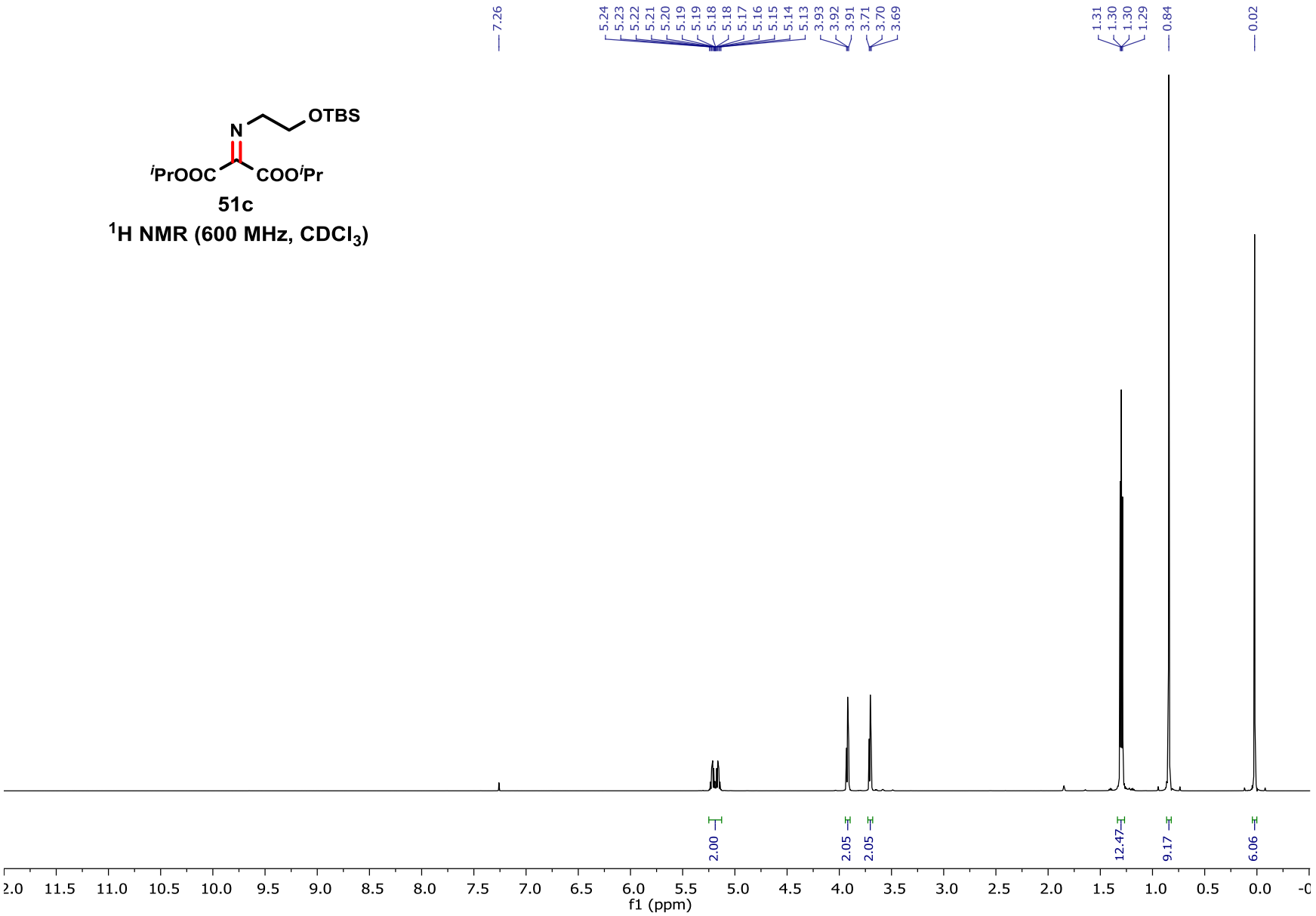


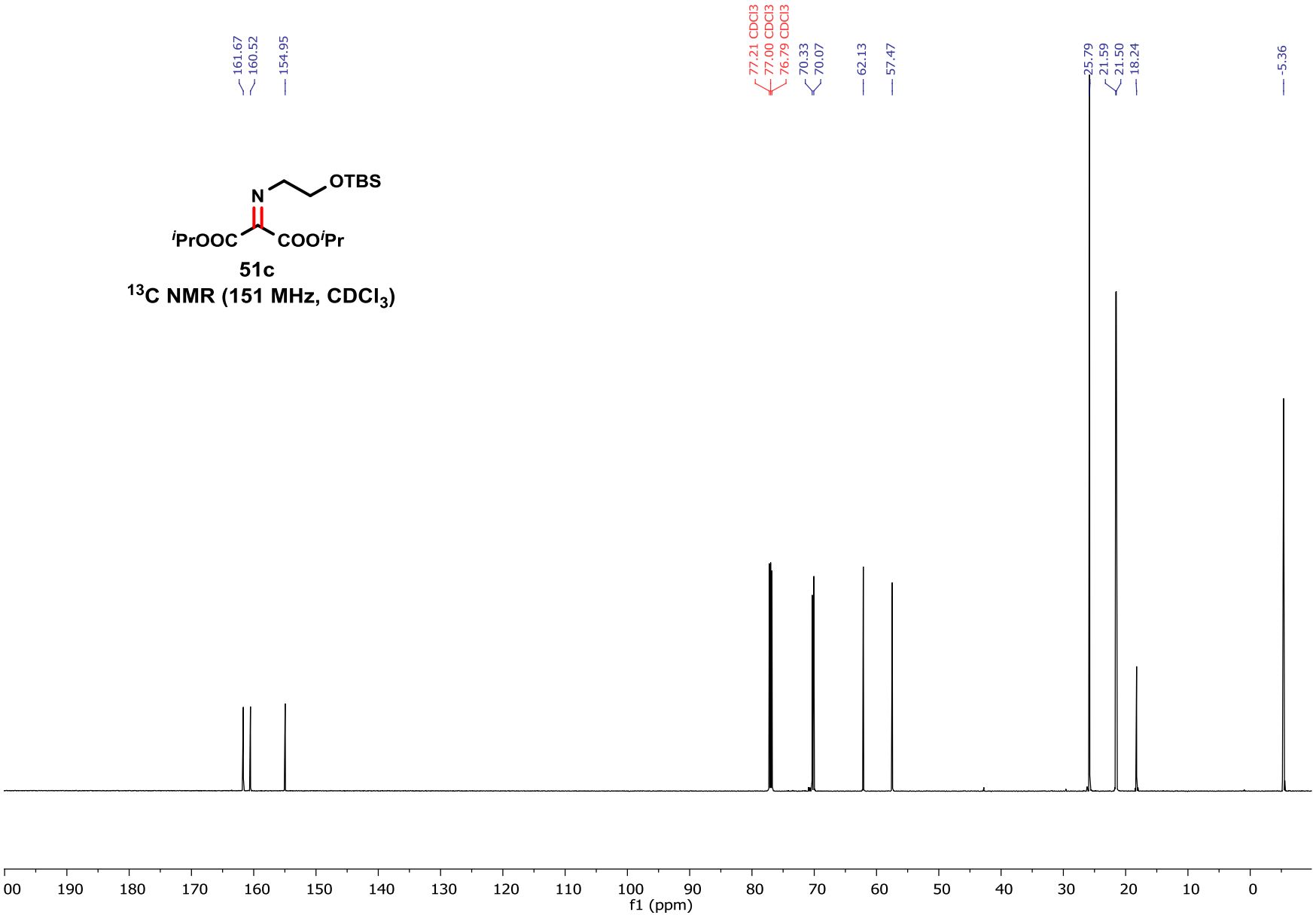
51b

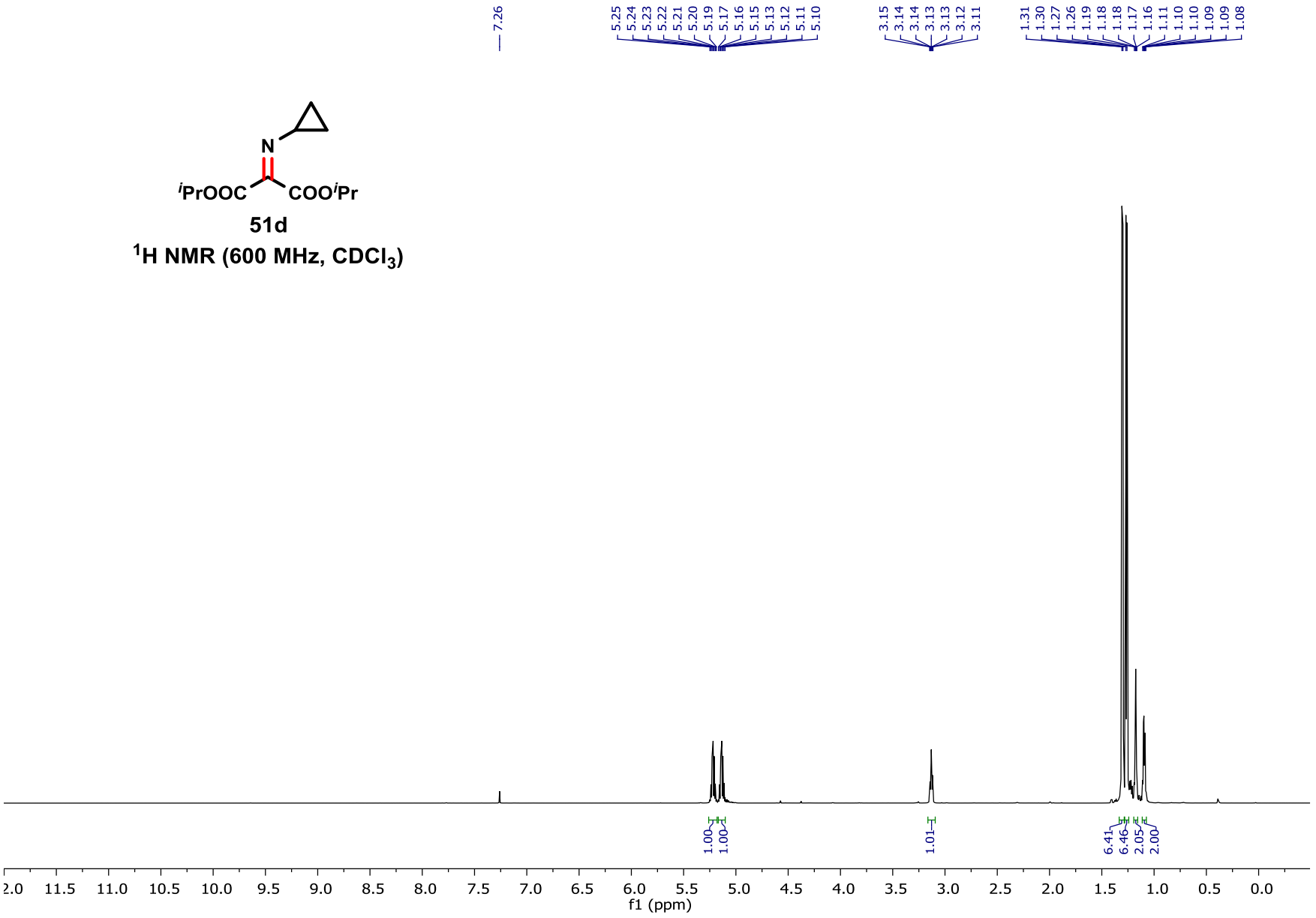
^{1}H NMR (600 MHz, $CDCl_3$)

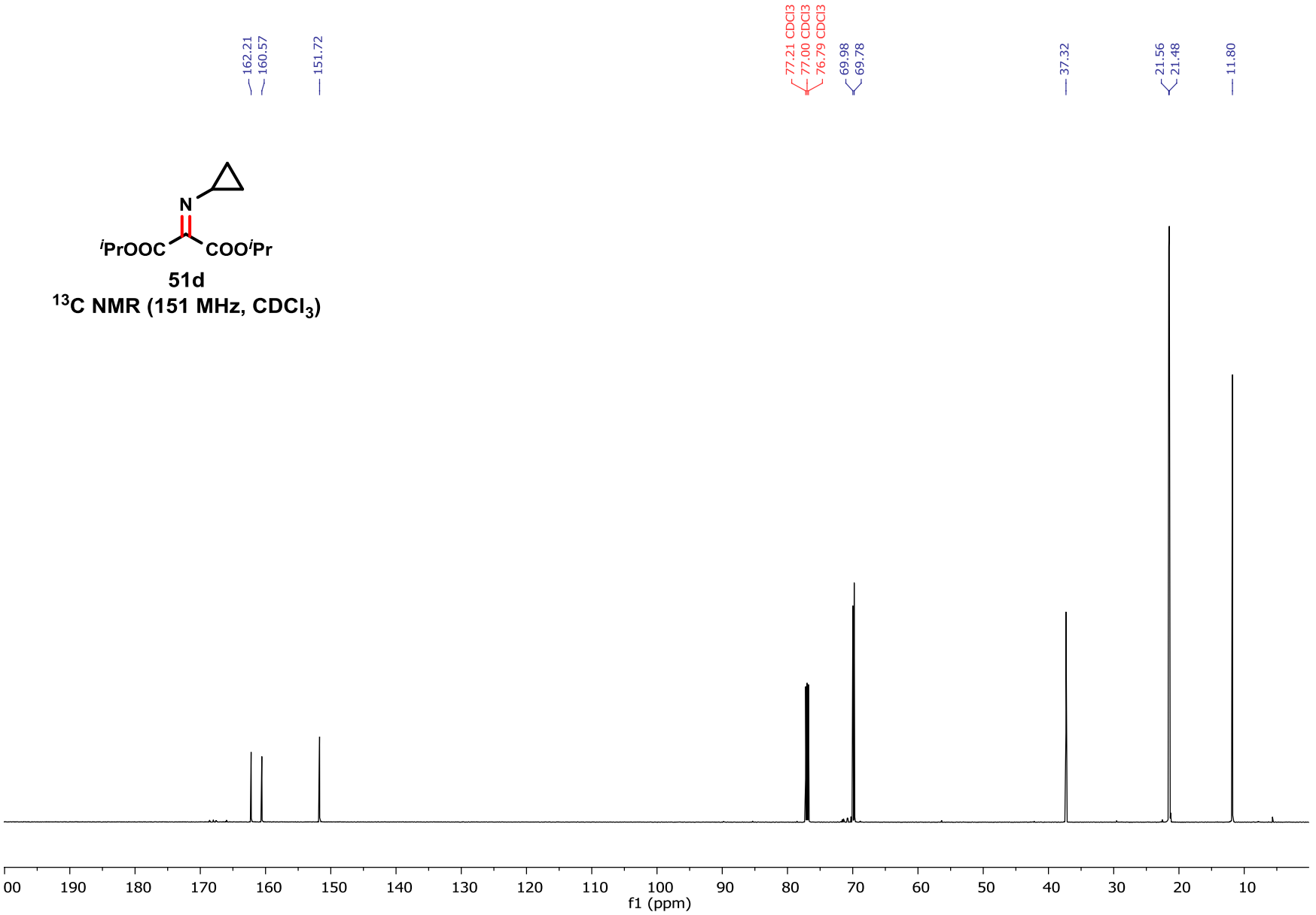

160.51
159.42
157.22
126.60
124.77
122.93
121.10
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.16
71.00
55.23
55.01
54.79
54.57
21.52
21.47
N
CF3
iPrOOC
COOiPr
51b
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

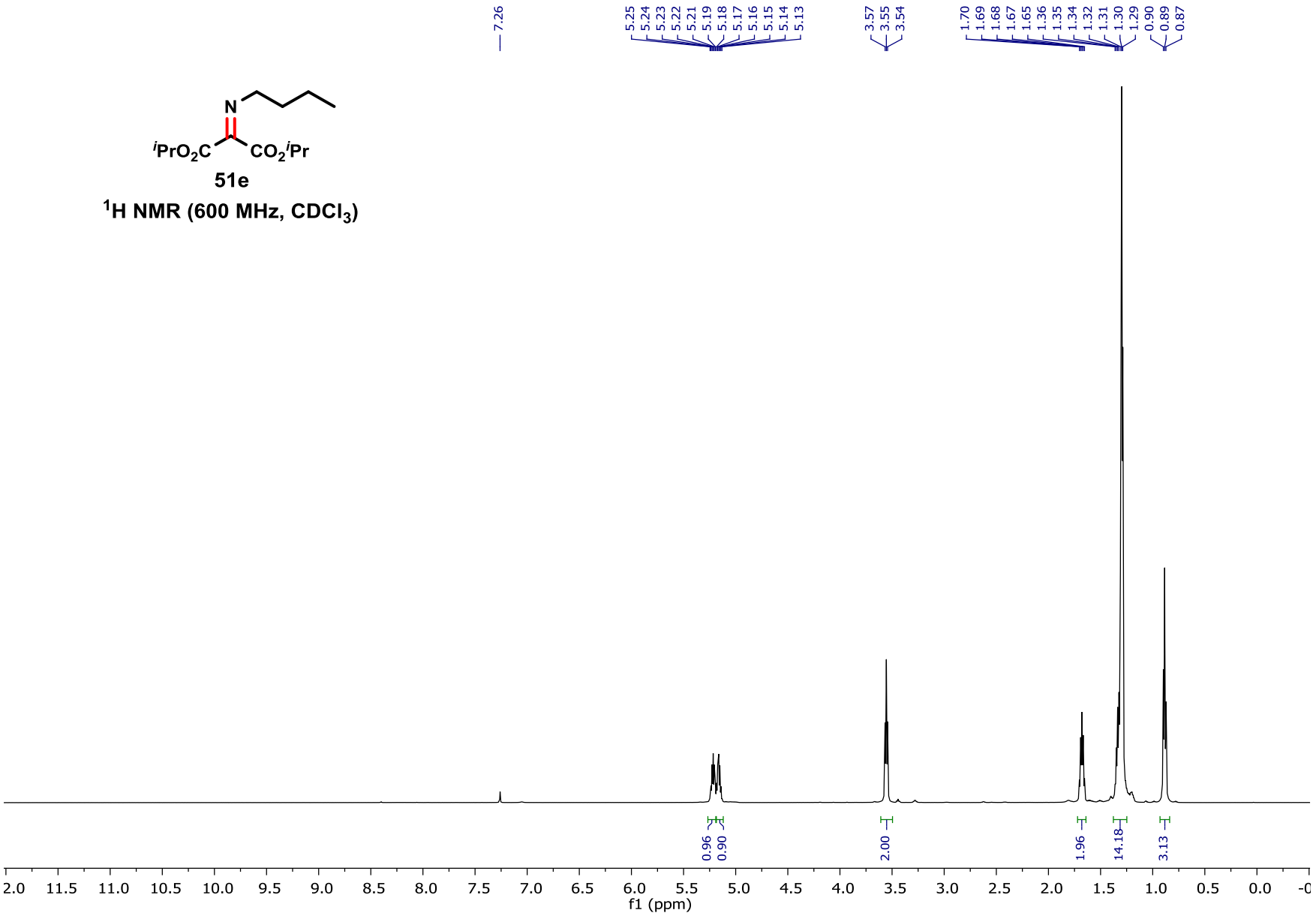

N
CF3
iPrOOC
COOiPr
51b
19F NMR (471 MHz, CDCl3)
-70.43
-70.45
-70.30 -70.35 -70.40 -70.45 -70.50 -70.55 -70.60
f1 (ppm)
55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74
f1 (ppm)

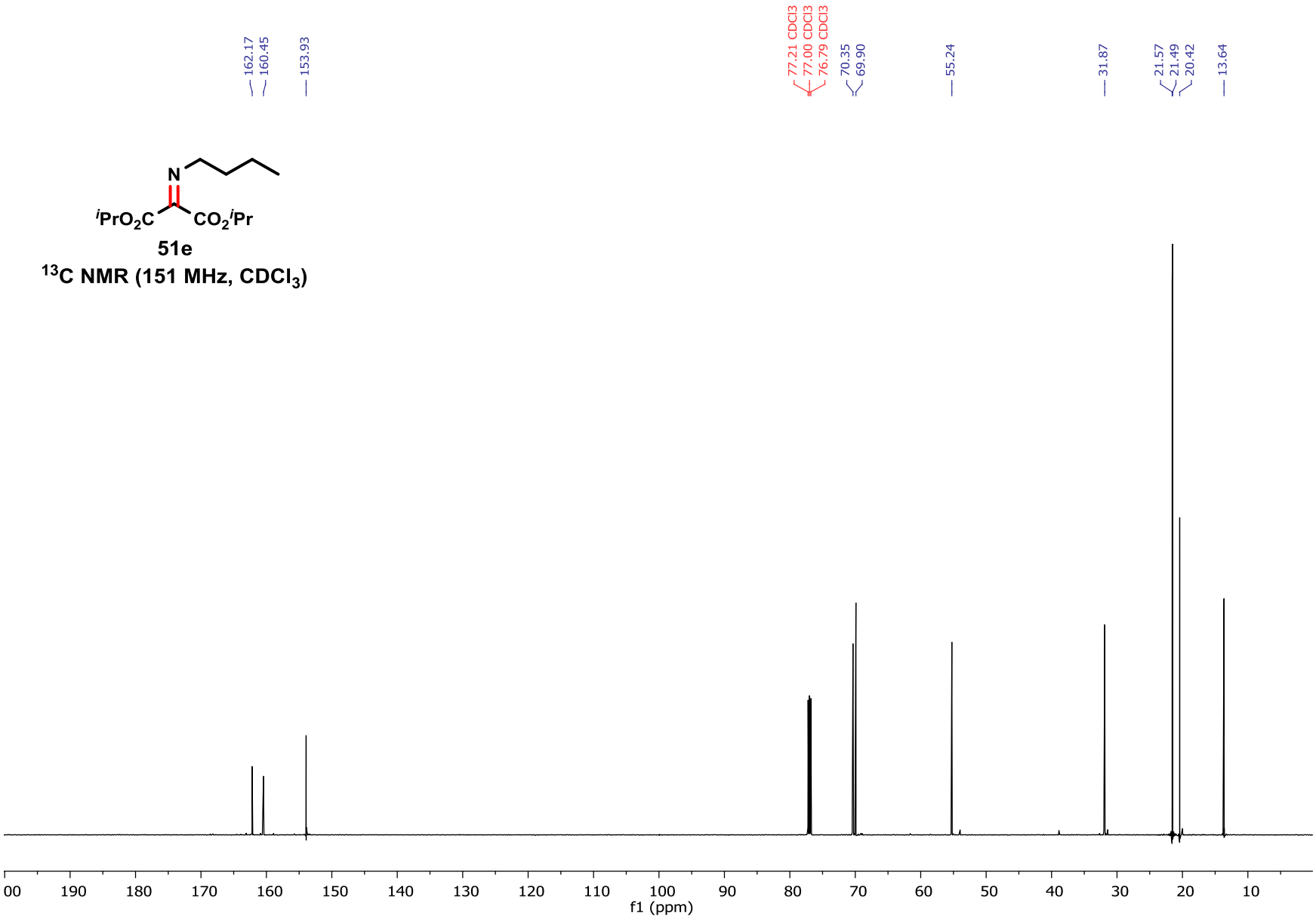

OTBS
N
iPrOOC
COOiPr
51c
1H NMR (600 MHz, CDCl3)
7.26
5.24
5.23
5.22
5.21
5.20
5.19
5.19
5.18
5.18
5.17
5.16
5.15
5.14
5.13
3.93
3.92
3.91
3.71
3.70
3.69
1.31
1.30
1.30
1.29
0.84
0.02
2.00
2.05
2.05
12.47
9.17
6.06
f1 (ppm)

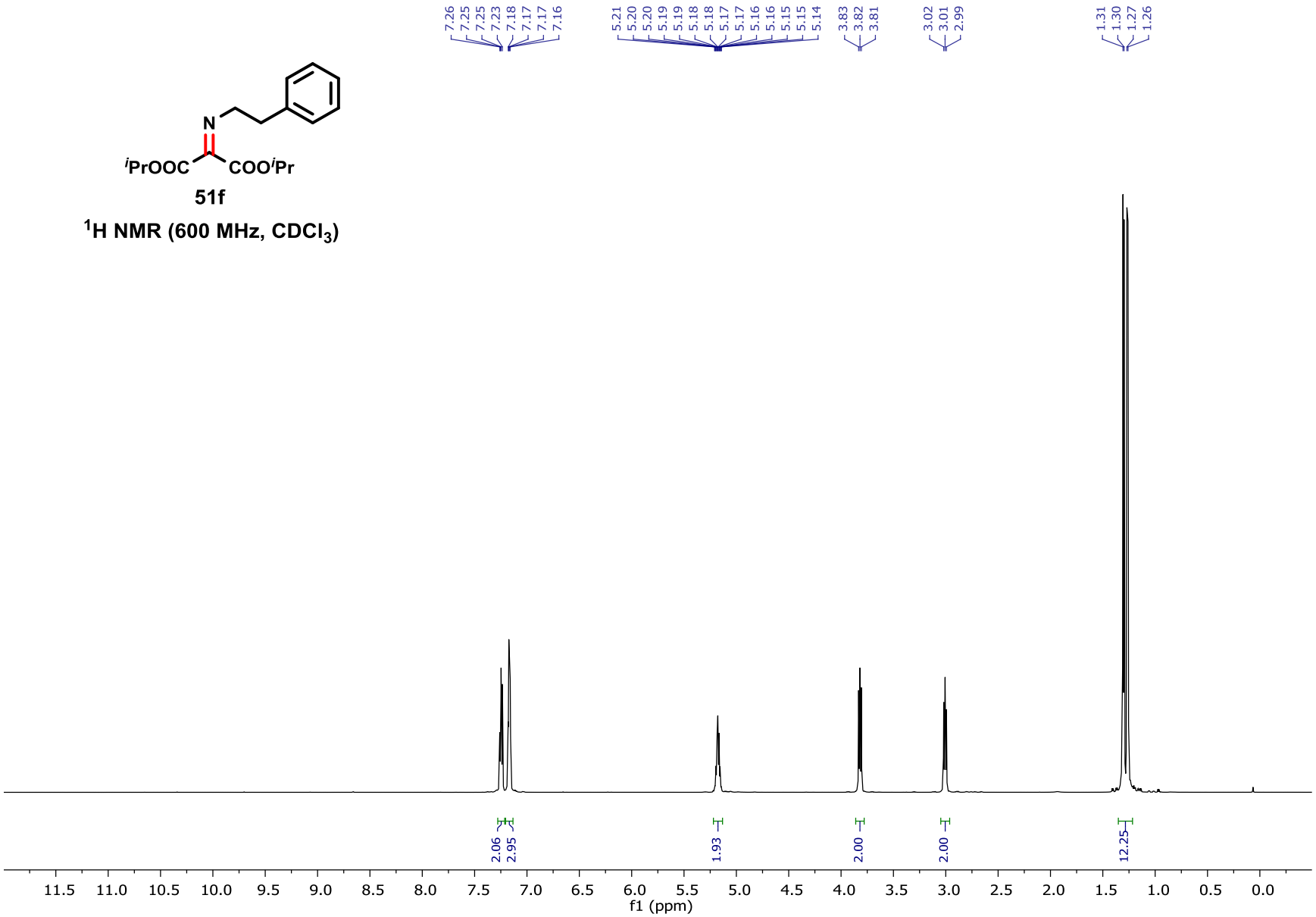

161.67
160.52
154.95
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.33
70.07
62.13
57.47
25.79
21.59
21.50
18.24
-5.36
N
OTBS
iPrOOC
COOiPr
51c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

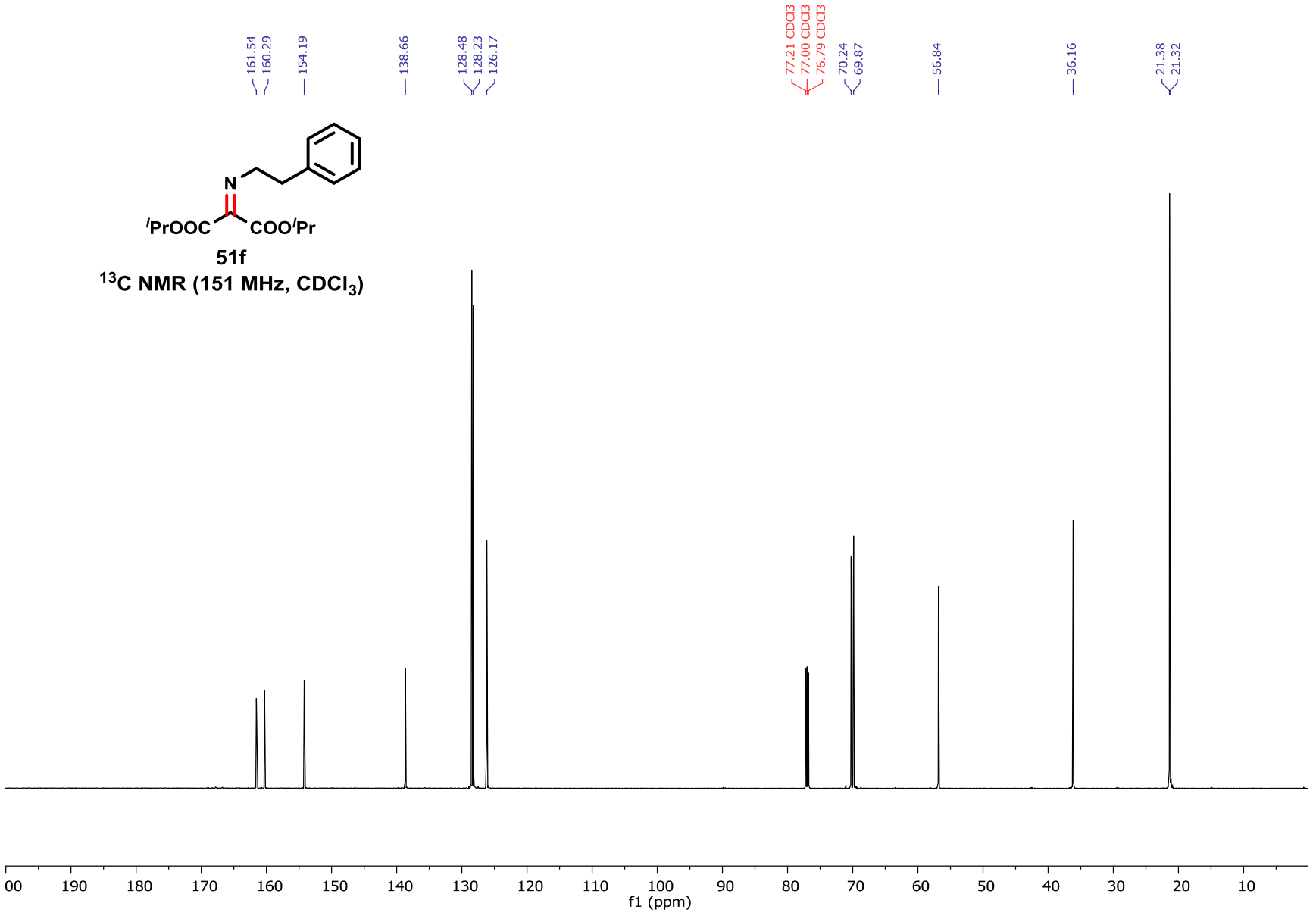

7.26
5.25
5.24
5.23
5.22
5.21
5.20
5.19
5.17
5.16
5.15
5.13
5.12
5.11
5.10
3.15
3.14
3.14
3.13
3.13
3.12
3.11
1.31
1.30
1.27
1.26
1.19
1.18
1.18
1.17
1.16
1.11
1.10
1.10
1.09
1.09
1.08
N
iPrOOC
COOiPr
51d
1H NMR (600 MHz, CDCl3)
1.00
1.00
1.01
6.41
6.46
2.05
2.00
f1 (ppm)

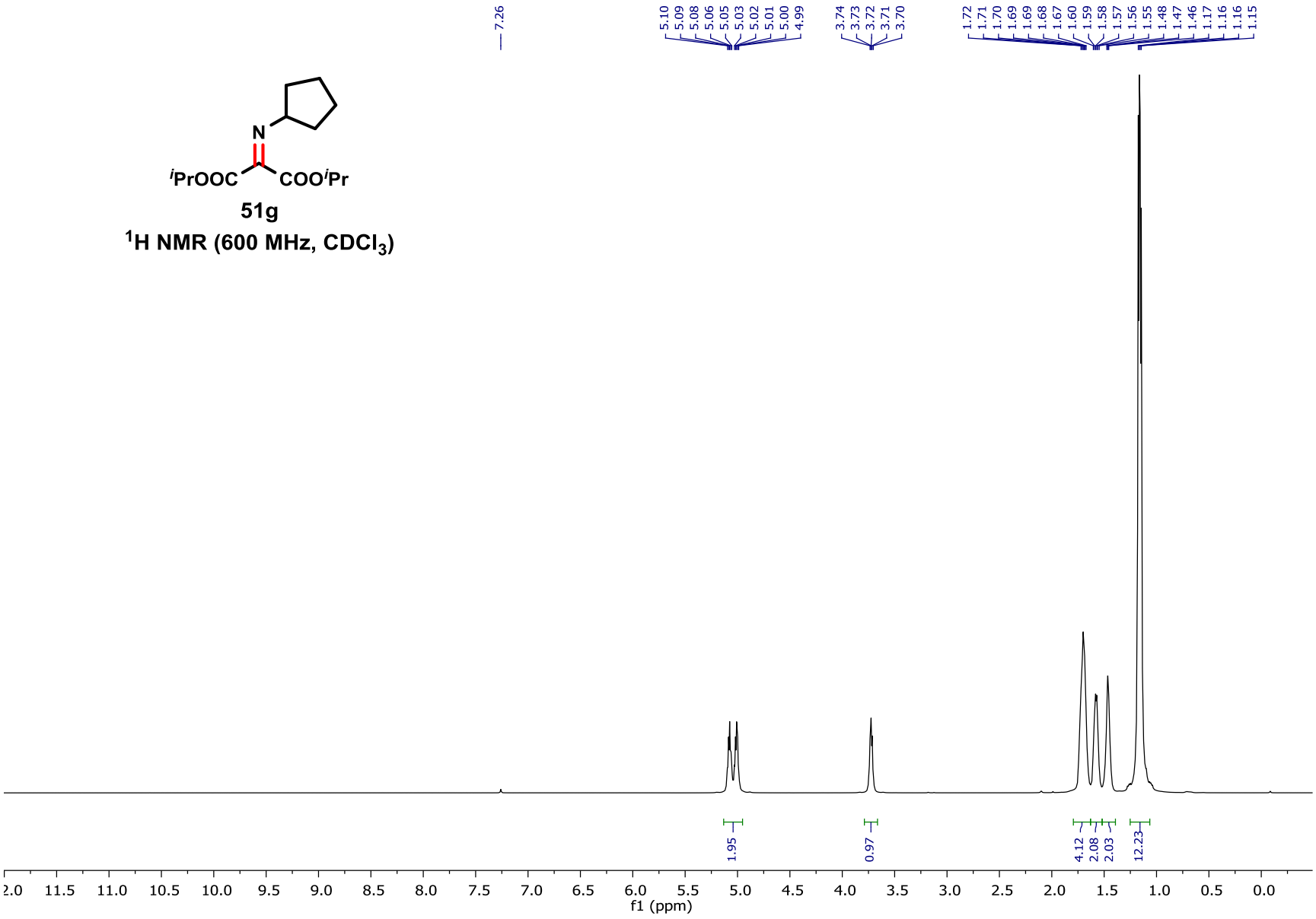

162.21
160.57
151.72
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.98
69.78
37.32
21.56
21.48
11.80
N
iPrOOC
COOiPr
51d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

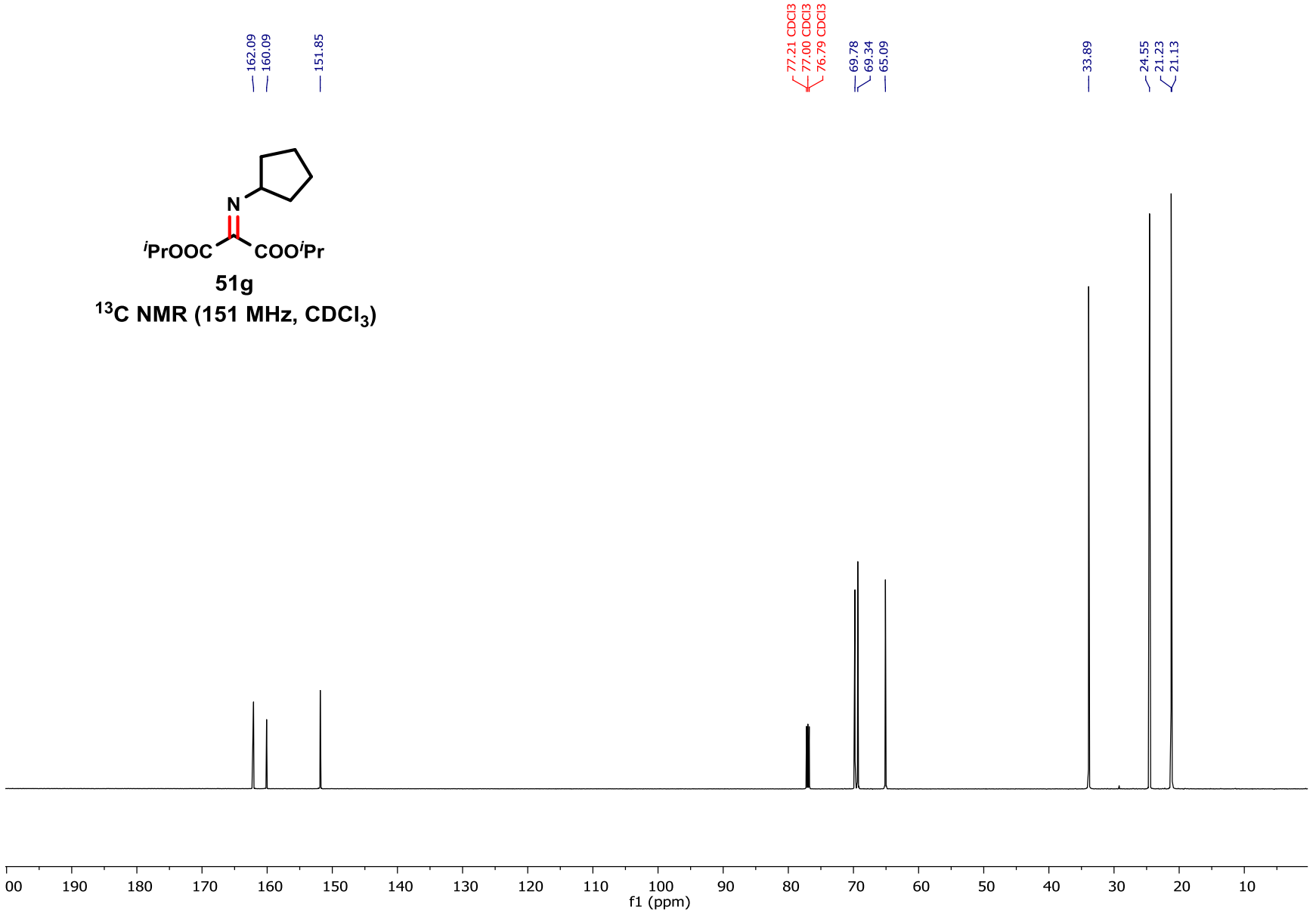

N
iPrO2C
CO2iPr
51e
1H NMR (600 MHz, CDCl3)
7.26
5.25
5.24
5.23
5.22
5.21
5.19
5.18
5.17
5.16
5.15
5.14
5.13
3.57
3.55
3.54
1.70
1.69
1.68
1.67
1.65
1.36
1.35
1.34
1.32
1.31
1.30
1.29
0.90
0.89
0.87
0.96
0.90
2.00
1.96
14.18
3.13
f1 (ppm)

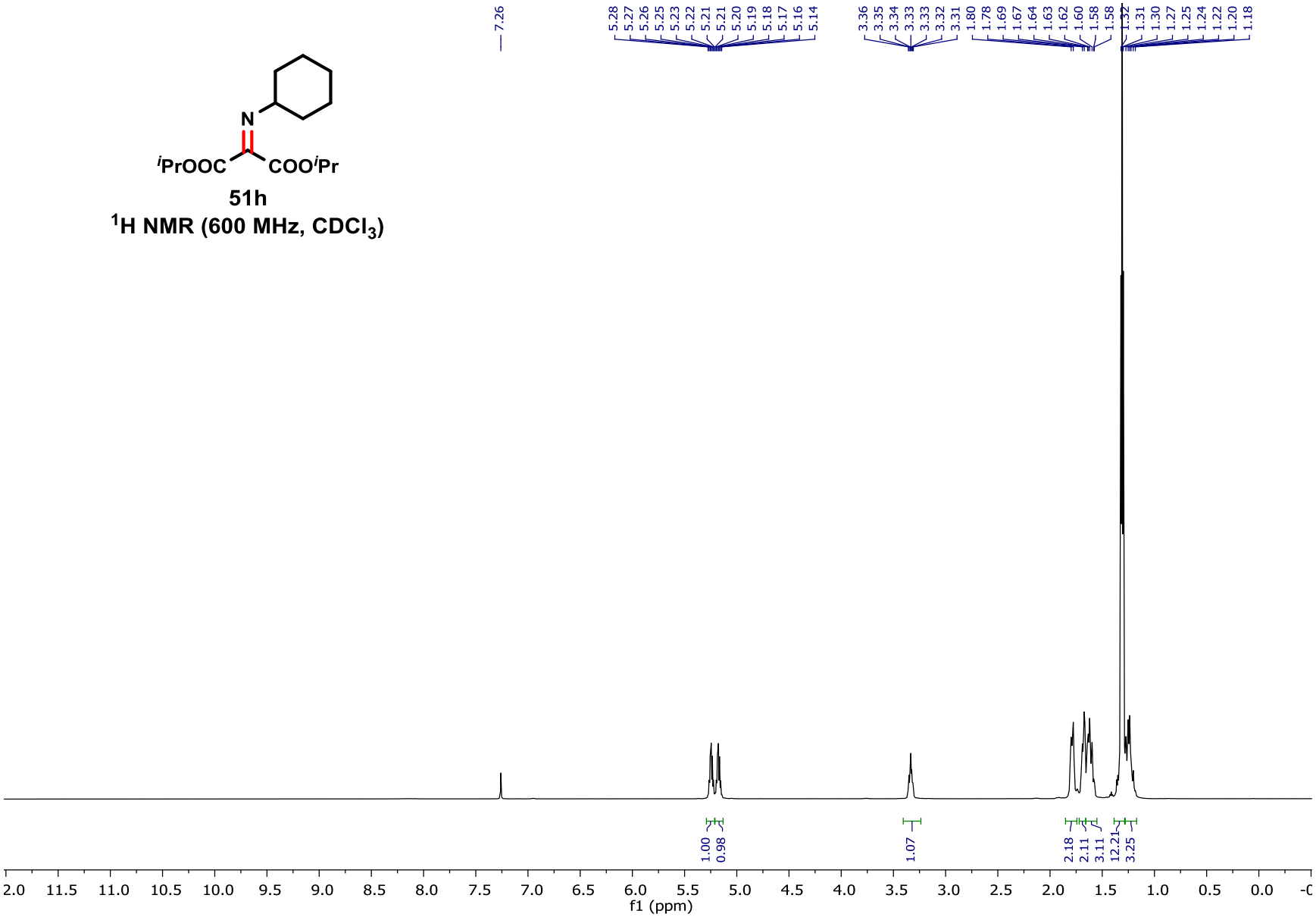

162.17
160.45
153.93
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.35
69.90
55.24
31.87
21.57
21.49
20.42
13.64
N
iPrO2C
CO2iPr
51e
13C NMR (151 MHz, CDCl3)
f1 (ppm)

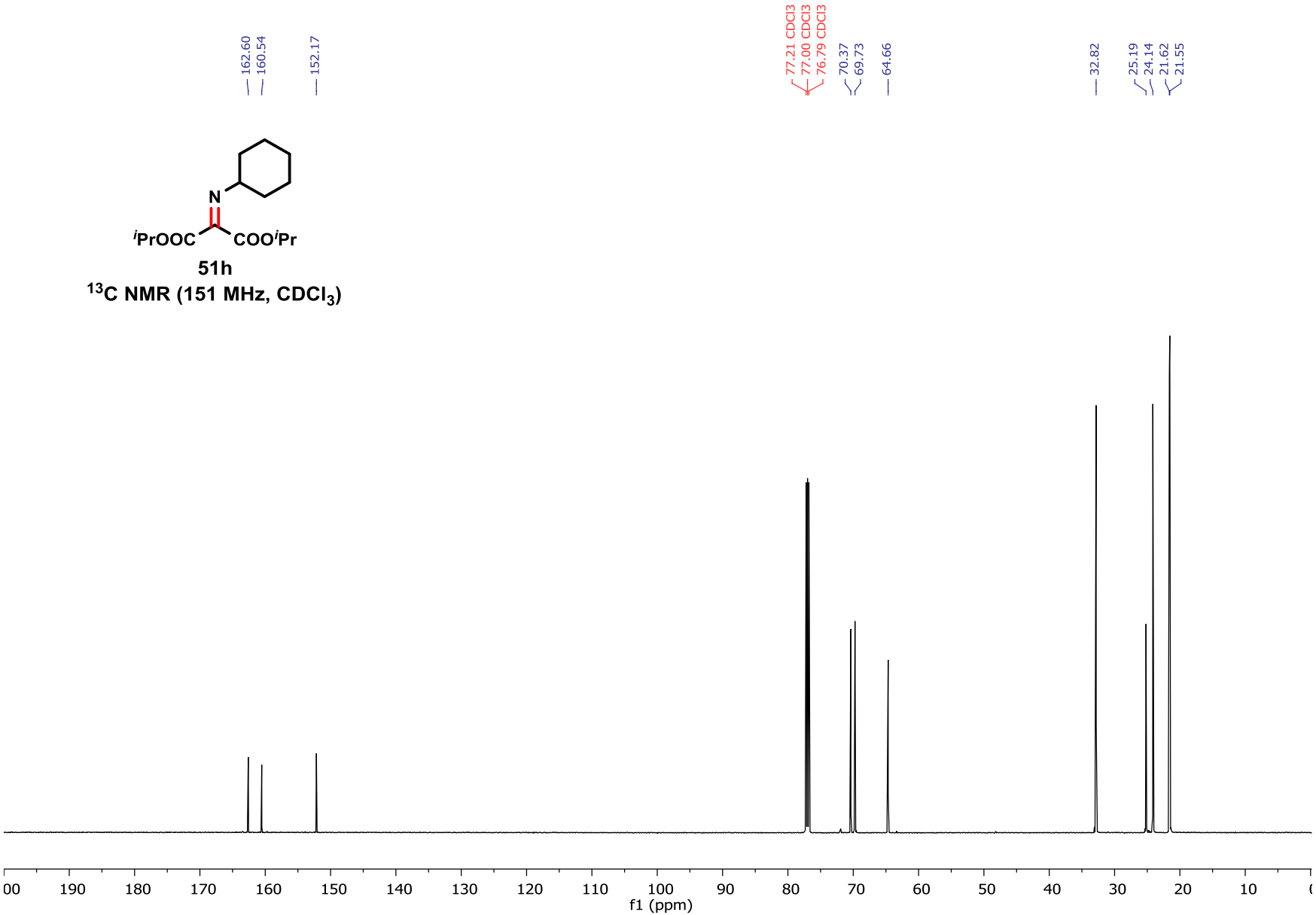

7.26
7.25
7.25
7.23
7.18
7.17
7.17
7.16
5.21
5.20
5.20
5.19
5.19
5.18
5.18
5.17
5.17
5.16
5.16
5.15
5.15
5.14
3.83
3.82
3.81
3.02
3.01
2.99
1.31
1.30
1.27
1.26
N
iPrOOC
COOiPr
51f
1H NMR (600 MHz, CDCl3)
2.06
2.95
1.93
2.00
2.00
12.25
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

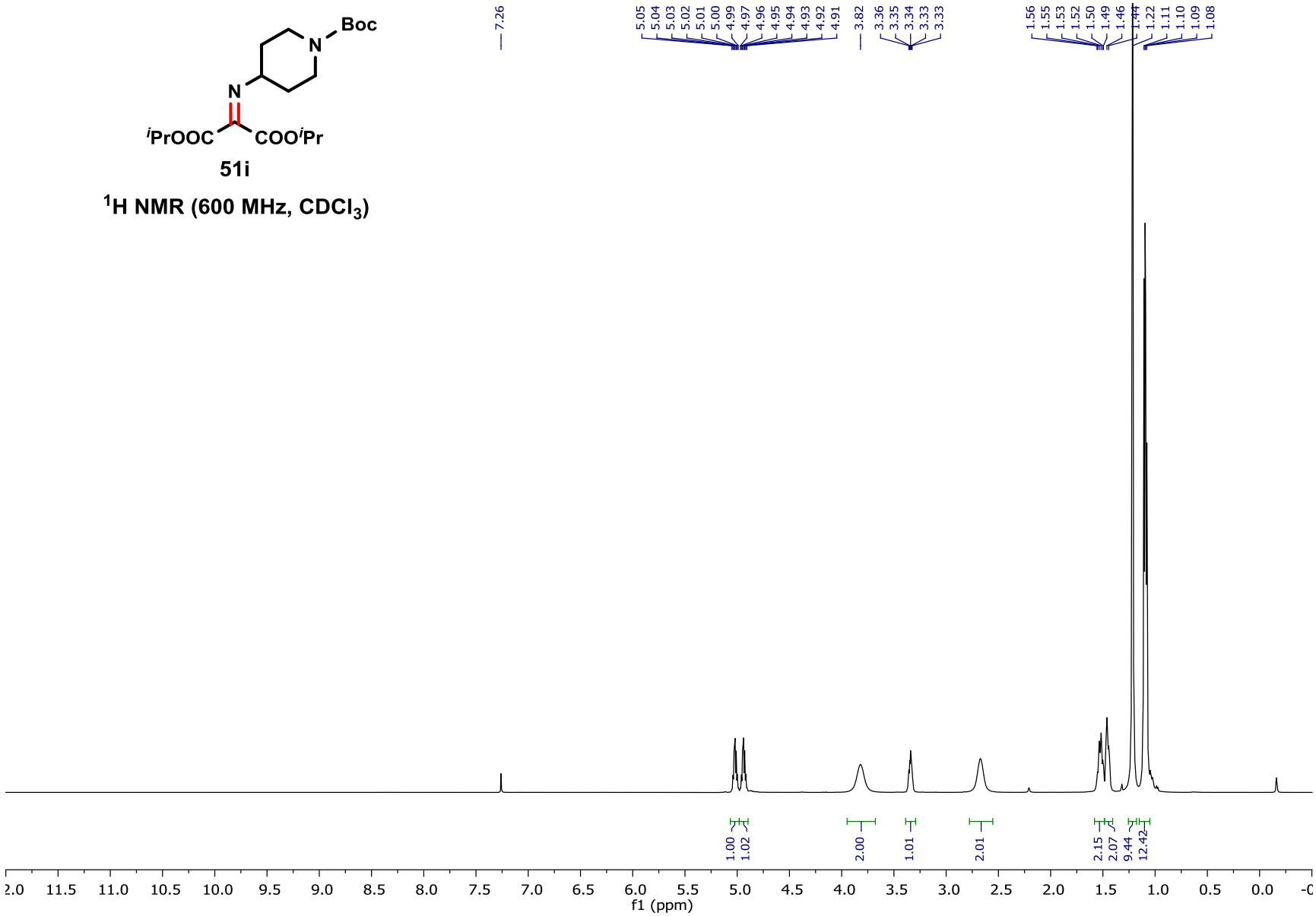

161.54
160.29
154.19
138.66
128.48
128.23
126.17
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.24
69.87
56.84
36.16
21.38
21.32
N
iPrOOC
COOiPr
51f
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

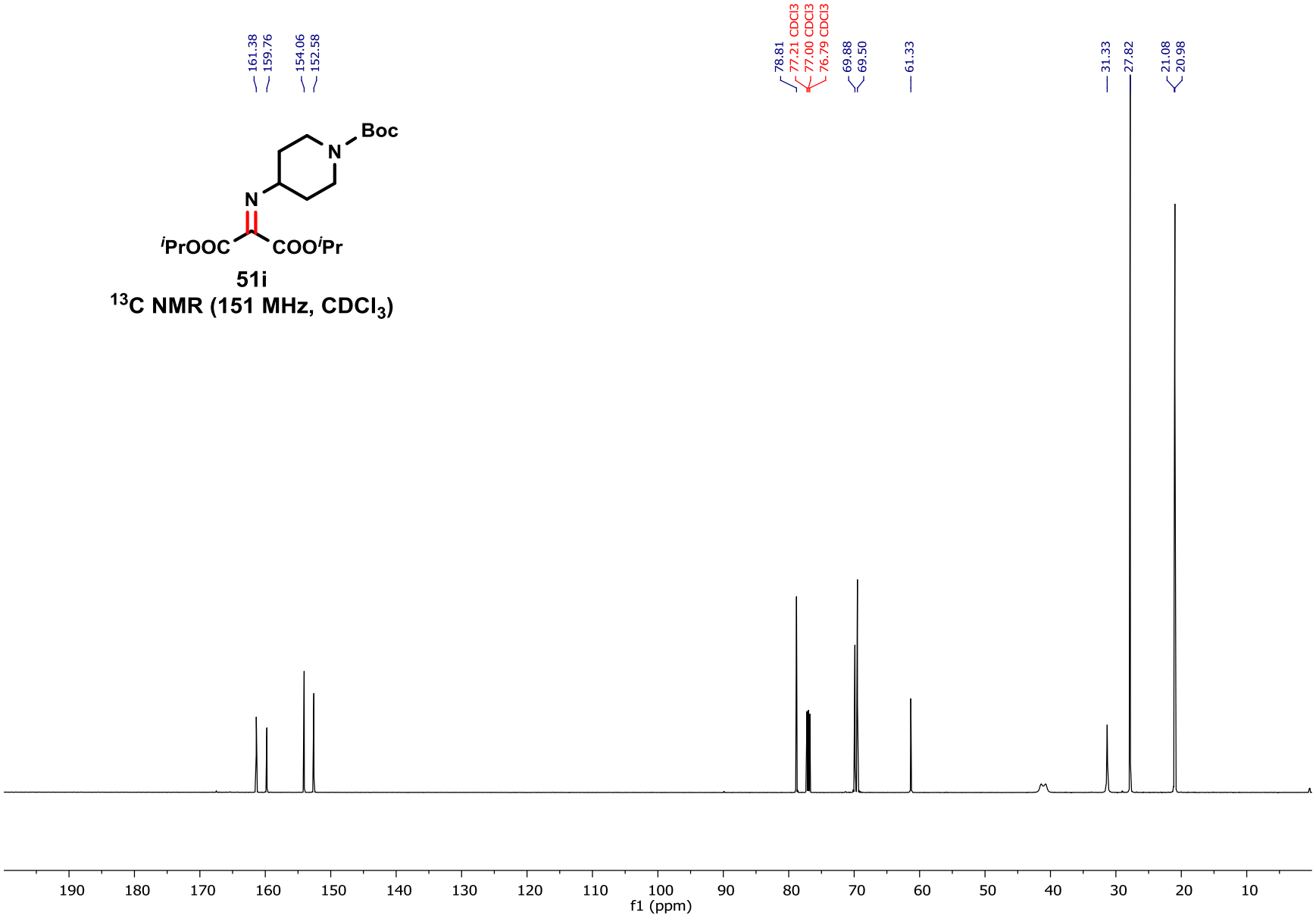

N
iPrOOC
COOiPr
51g
1H NMR (600 MHz, CDCl3)
7.26
5.10
5.09
5.08
5.06
5.05
5.03
5.02
5.01
5.00
4.99
3.74
3.73
3.72
3.71
3.70
1.72
1.71
1.70
1.69
1.69
1.68
1.67
1.60
1.59
1.58
1.57
1.56
1.55
1.48
1.47
1.46
1.17
1.16
1.16
1.15
1.95
0.97
4.12
2.08
2.03
12.23
f1 (ppm)

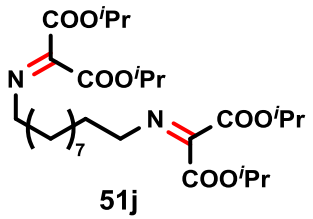

162.09
160.09
151.85
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.78
69.34
65.09
33.89
24.55
21.23
21.13
N
iPrOOC
COOiPr
51g
13C NMR (151 MHz, CDCl3)
f1 (ppm)


N
iPrOOC
COOiPr
51h
1H NMR (600 MHz, CDCl3)
7.26
5.28
5.27
5.26
5.25
5.23
5.22
5.21
5.21
5.20
5.19
5.18
5.17
5.16
5.14
3.36
3.35
3.34
3.33
3.33
3.32
3.31
1.80
1.78
1.69
1.67
1.64
1.63
1.62
1.60
1.58
1.58
1.32
1.31
1.30
1.27
1.25
1.24
1.22
1.20
1.18
1.00
0.98
1.07
2.18
2.11
3.11
12.21
3.25
f1 (ppm)


162.60
160.54
152.17
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.37
69.73
64.66
32.82
25.19
24.14
21.62
21.55
N
iPrOOC
COOiPr
51h
13C NMR (151 MHz, CDCl3)
f1 (ppm)

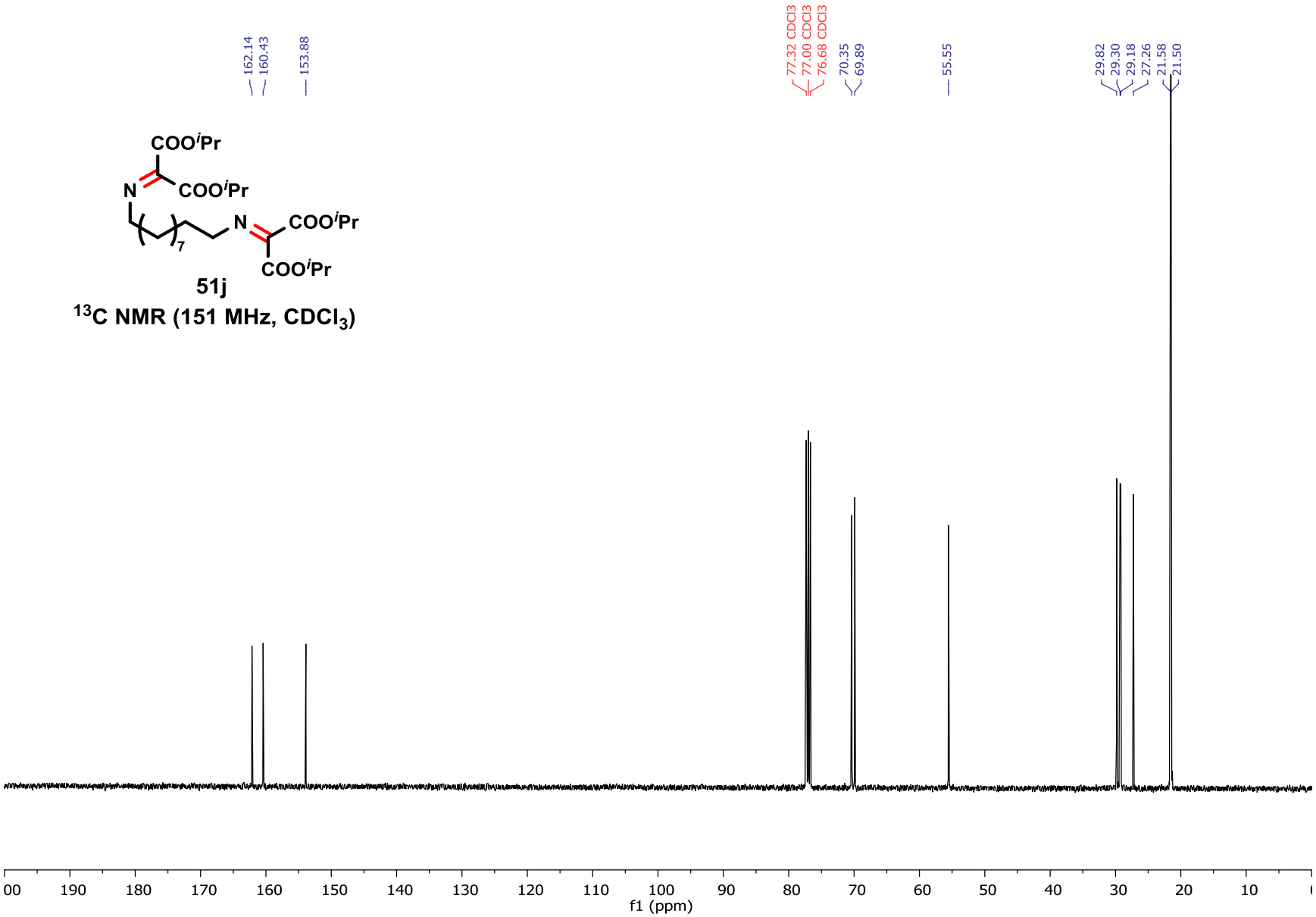

Boc
N
N
iPrOOC
COOiPr
51i
1H NMR (600 MHz, CDCl3)
7.26
5.05
5.04
5.03
5.02
5.01
5.00
4.99
4.97
4.96
4.95
4.94
4.93
4.92
4.91
3.82
3.36
3.35
3.34
3.33
3.33
1.56
1.55
1.53
1.52
1.50
1.49
1.46
1.44
1.22
1.11
1.10
1.09
1.08
1.00
1.02
2.00
1.01
2.01
2.15
2.07
9.44
12.42
f1 (ppm)


161.38
159.76
154.06
152.58
78.81
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.88
69.50
61.33
31.33
27.82
21.08
20.98
Boc
N
N
iPrOOC
COOiPr
51i
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



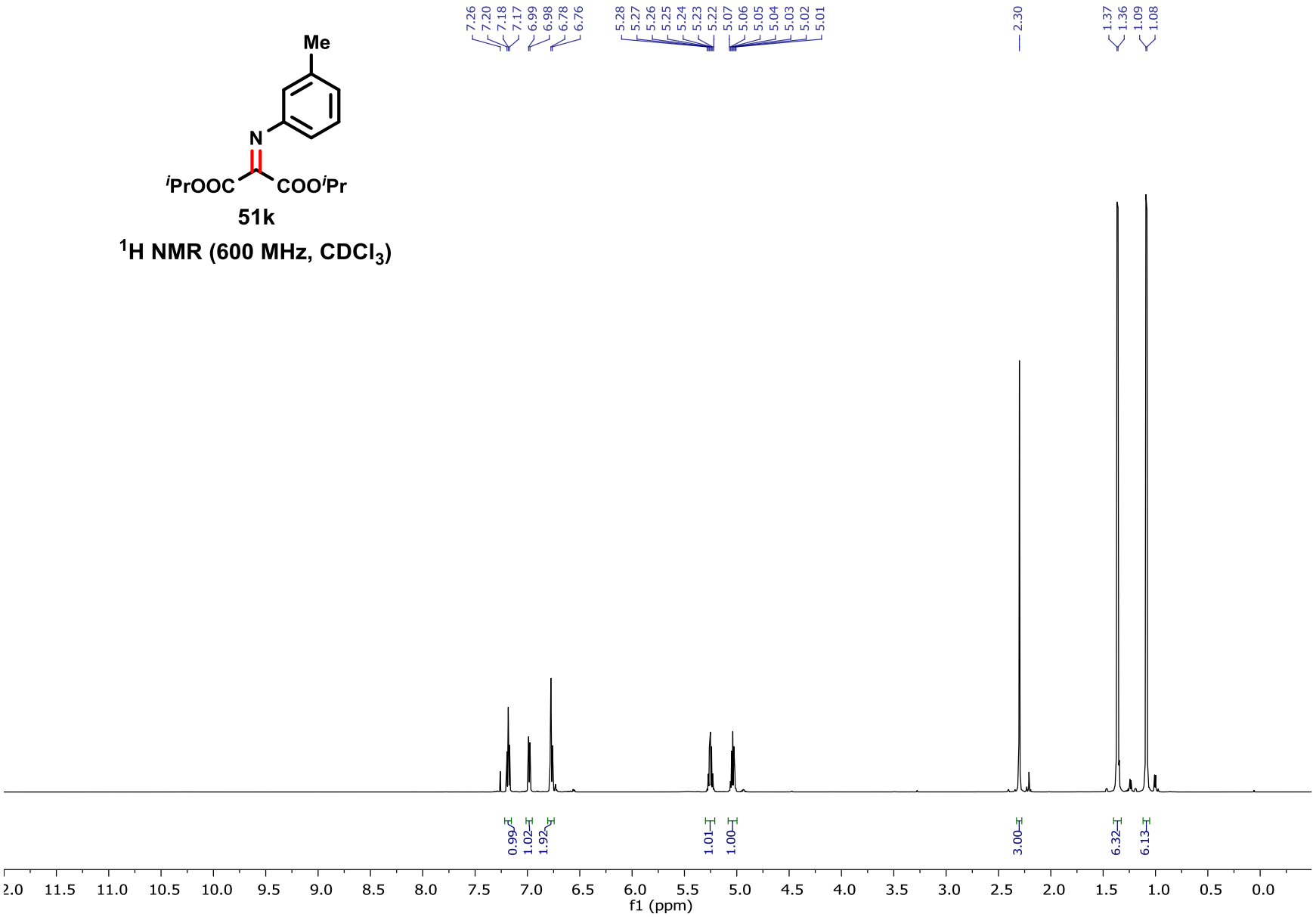
51j

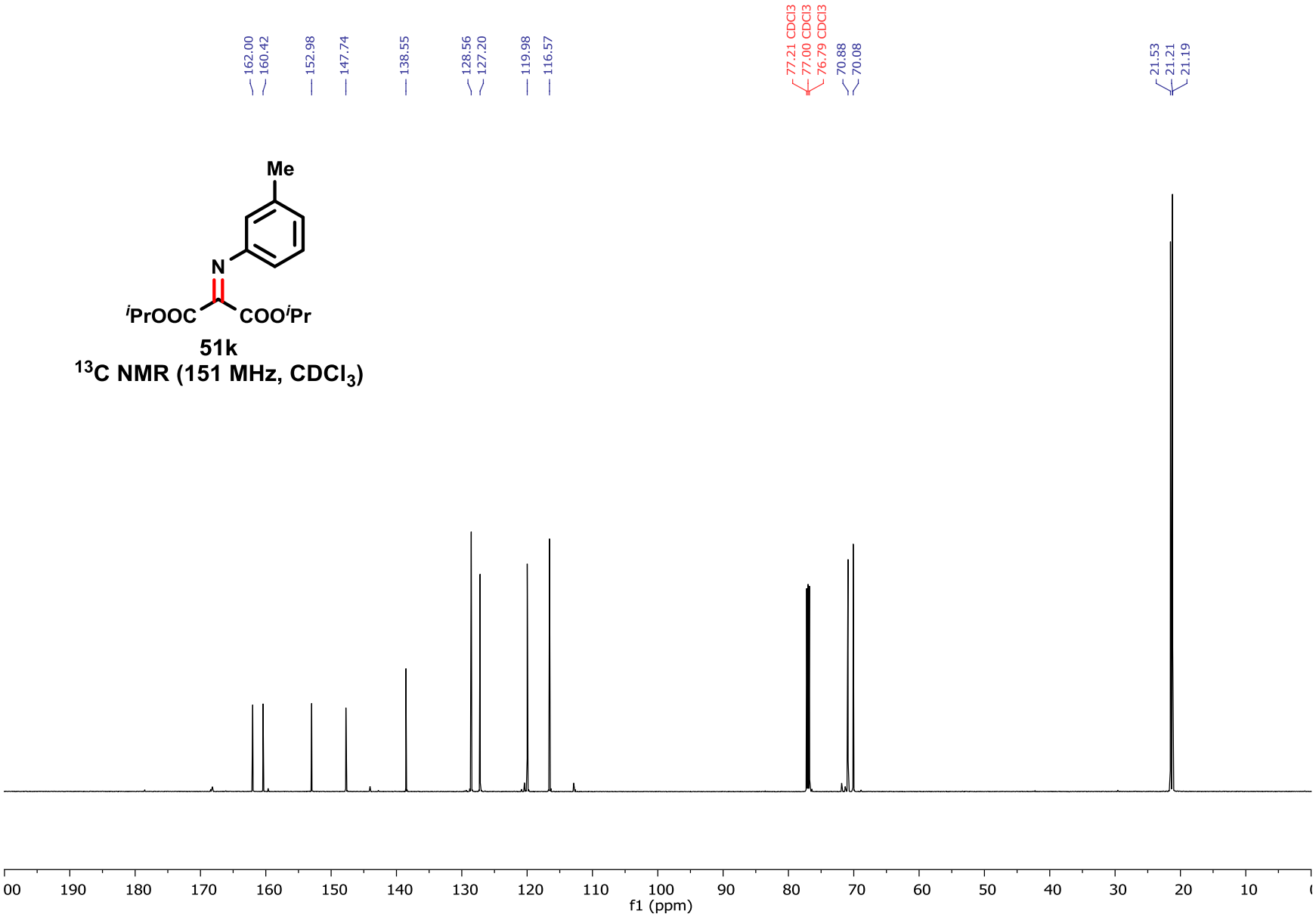
^{1}H NMR (600 MHz, $CDCl_3$)

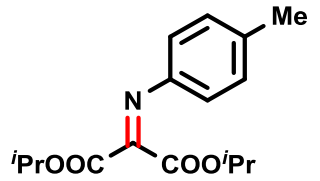


51j

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

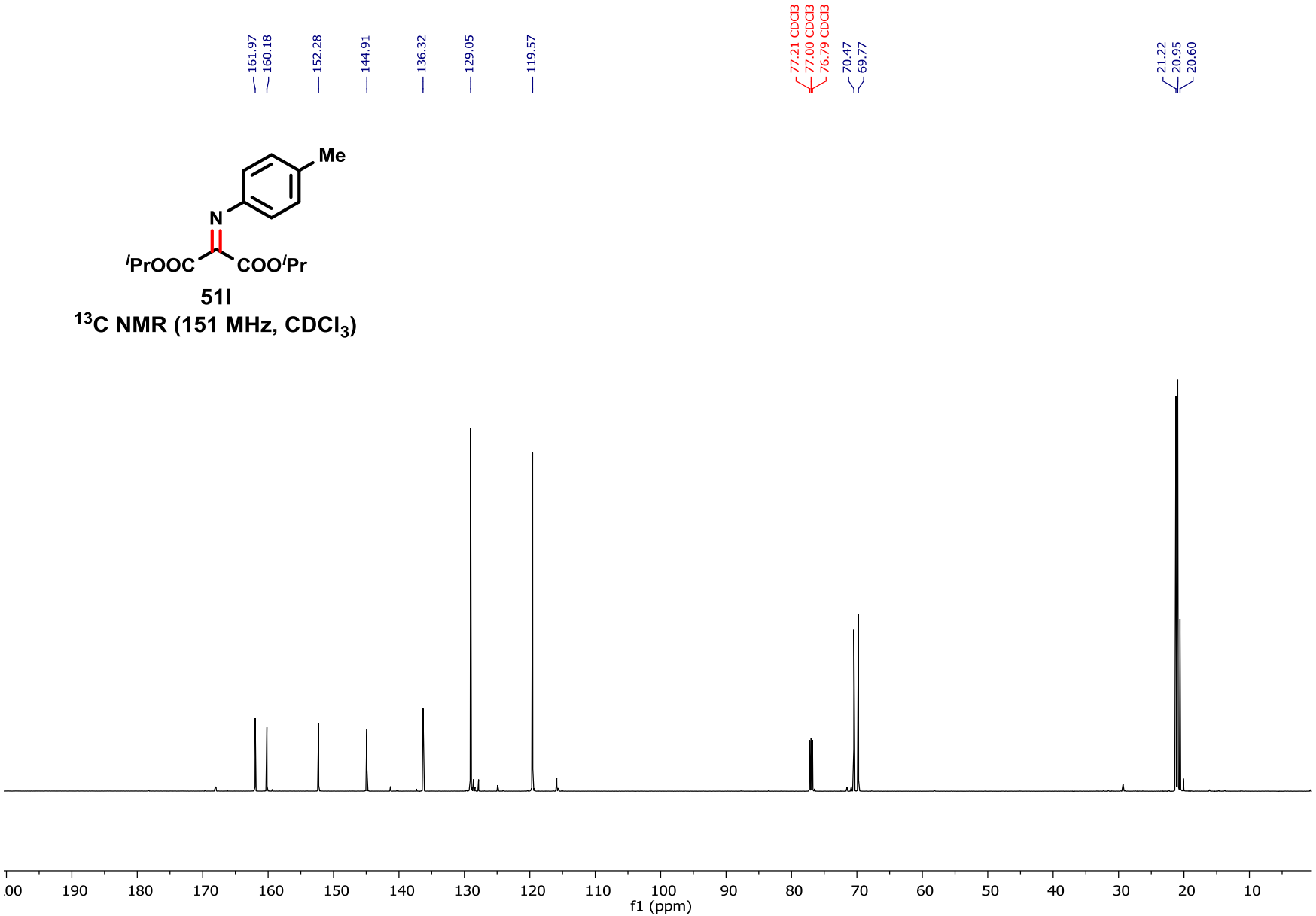

Me
N
iPrOOC
COOiPr
51k
1H NMR (600 MHz, CDCl3)
7.26
7.20
7.18
7.17
6.99
6.98
6.78
6.76
5.28
5.27
5.26
5.25
5.24
5.23
5.22
5.07
5.06
5.05
5.04
5.03
5.02
5.01
2.30
1.37
1.36
1.09
1.08
0.99
1.02
1.92
1.01
1.00
3.00
6.32
6.13
f1 (ppm)

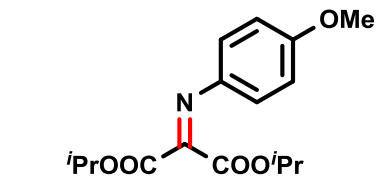

162.00
160.42
152.98
147.74
138.55
128.56
127.20
119.98
116.57
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.88
70.08
21.53
21.21
21.19
Me
N
iPrOOC
COOiPr
51k
13C NMR (151 MHz, CDCl3)
f1 (ppm)



51l

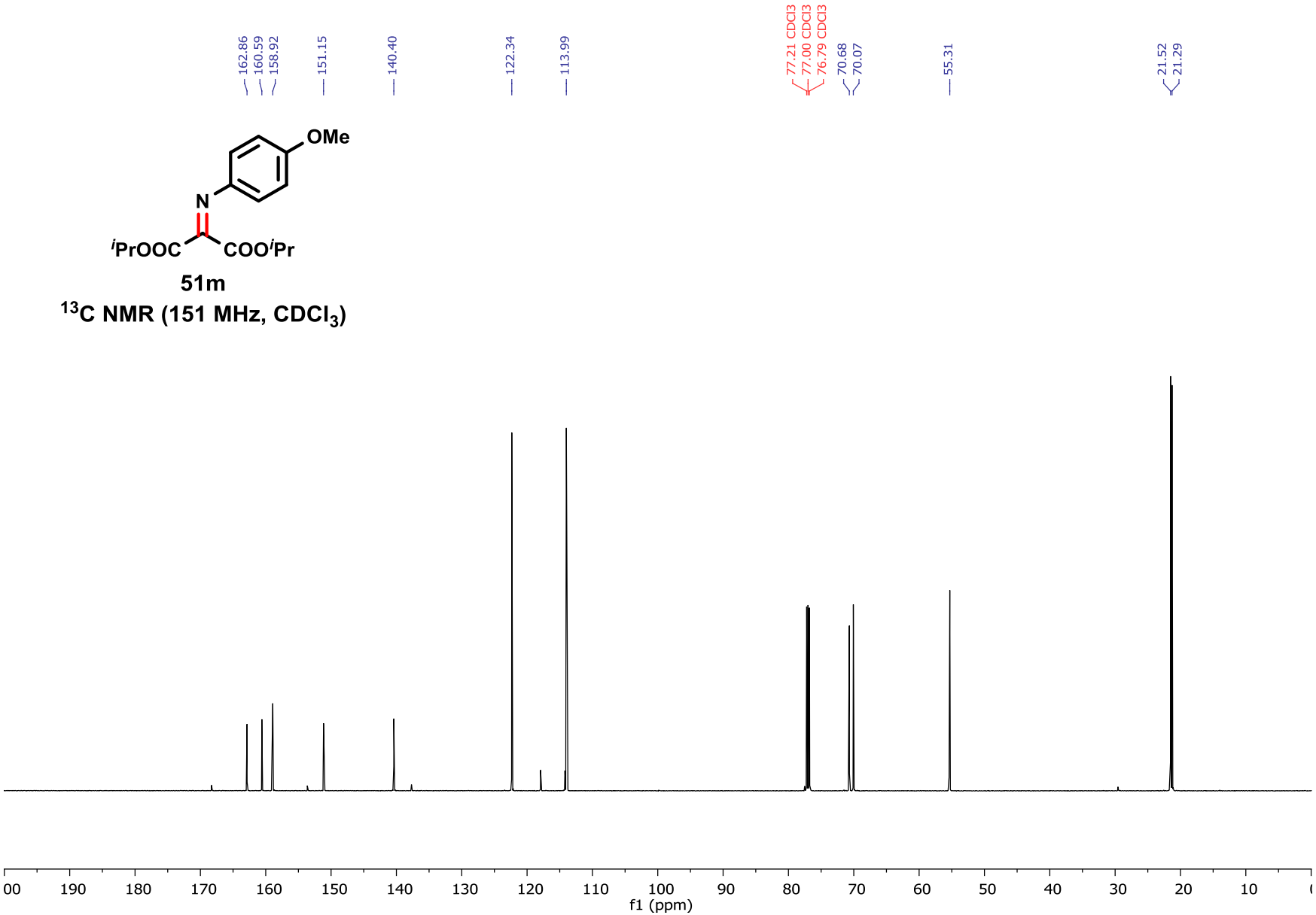
^{1}H NMR (600 MHz, $CDCl_3$)

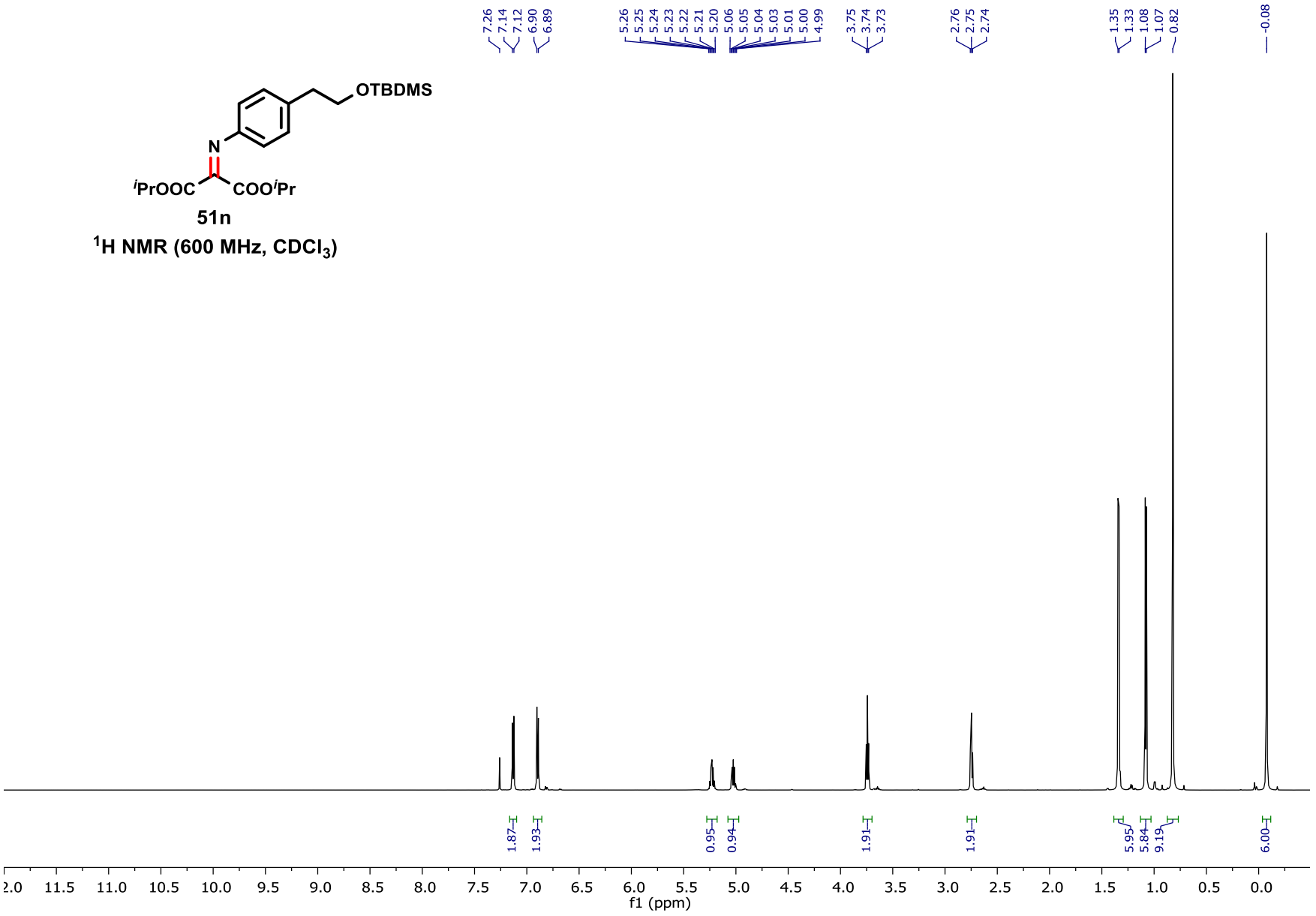

161.97
160.18
152.28
144.91
136.32
129.05
119.57
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.47
69.77
21.22
20.95
20.60
Me
N
iPrOOC
COOiPr
51l
13C NMR (151 MHz, CDCl3)
f1 (ppm)

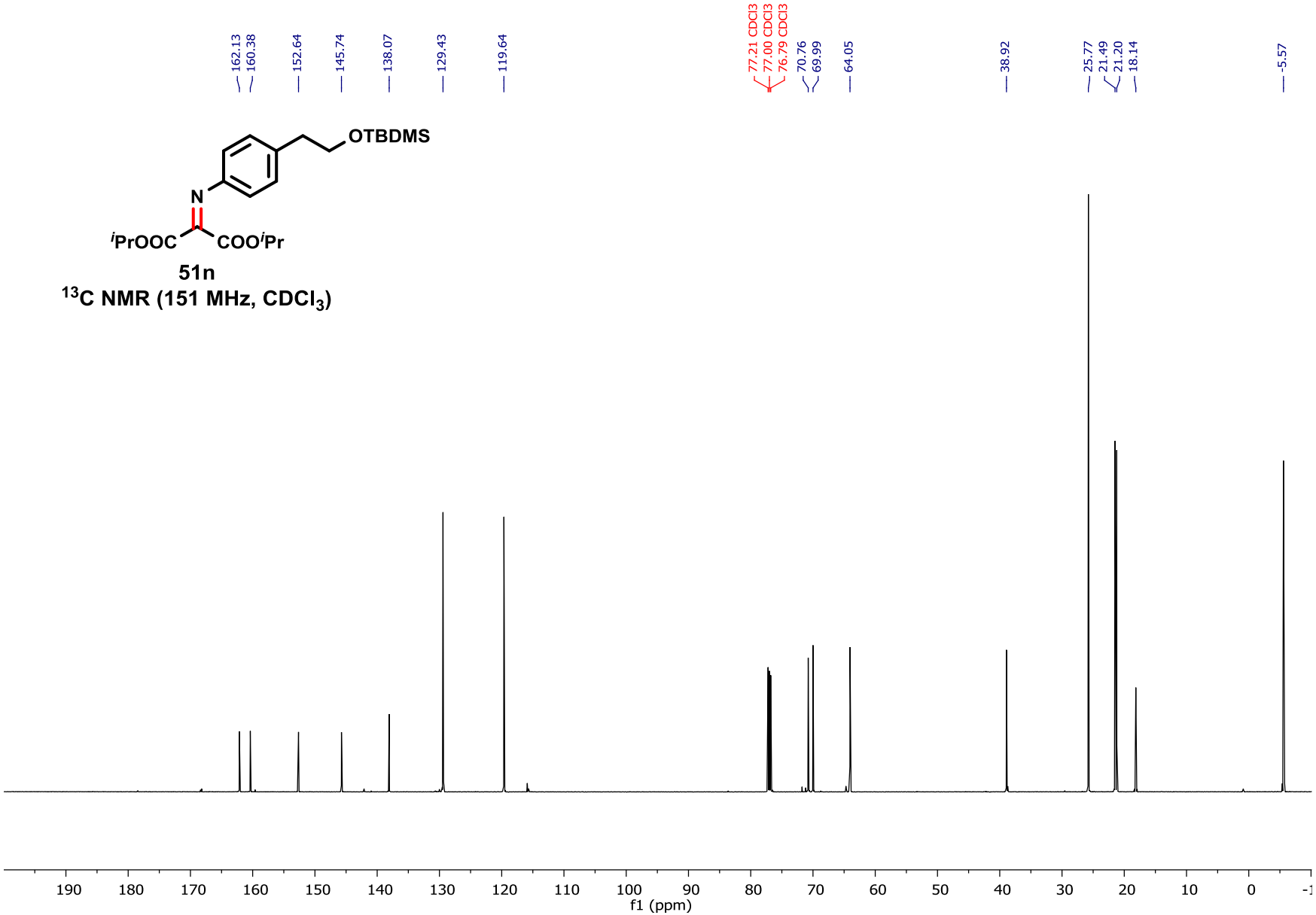


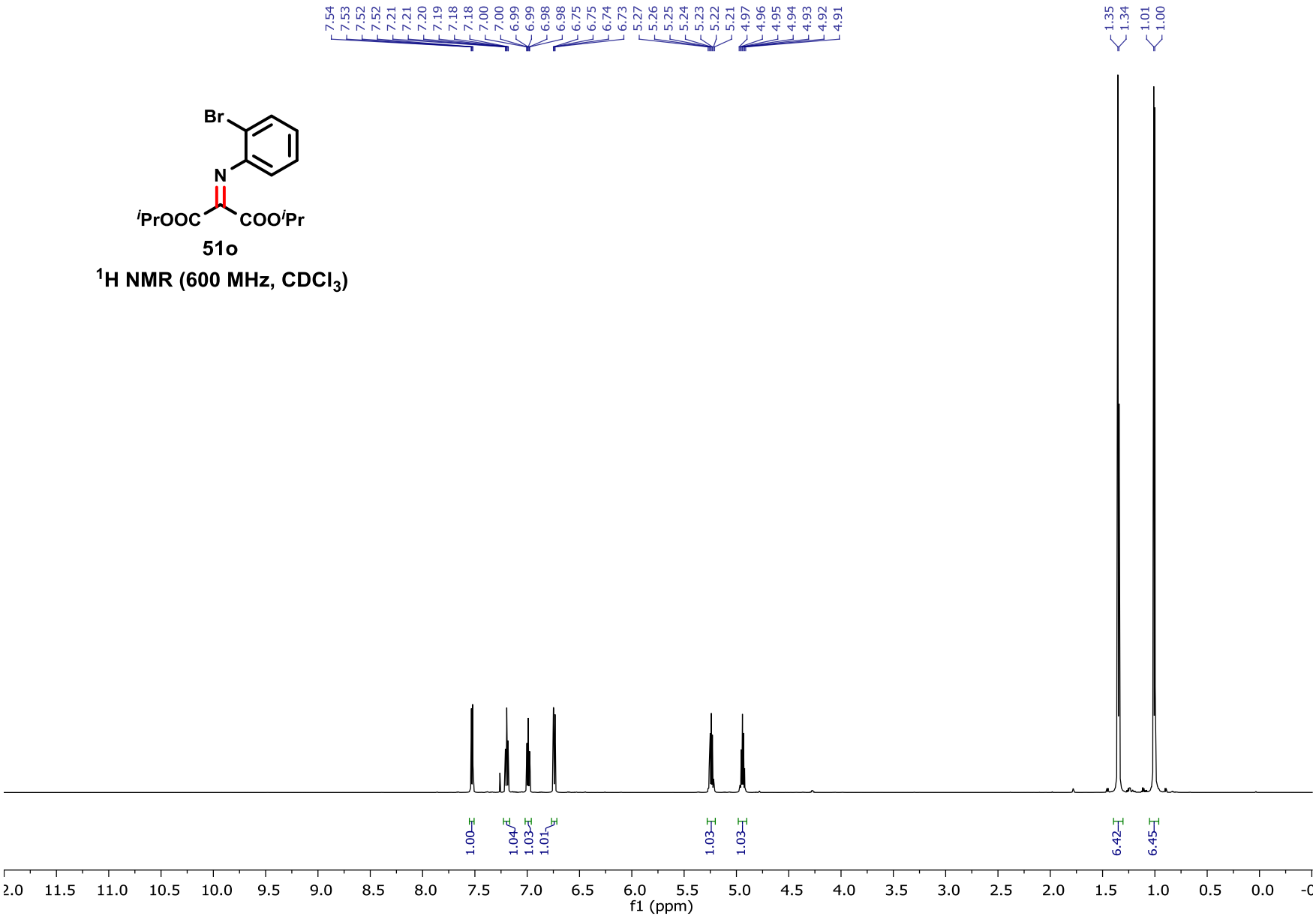
51m

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


162.86
160.59
158.92
151.15
140.40
122.34
113.99
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.68
70.07
55.31
21.52
21.29
OMe
N
iPrOOC
COOiPr
51m
13C NMR (151 MHz, CDCl3)
f1 (ppm)

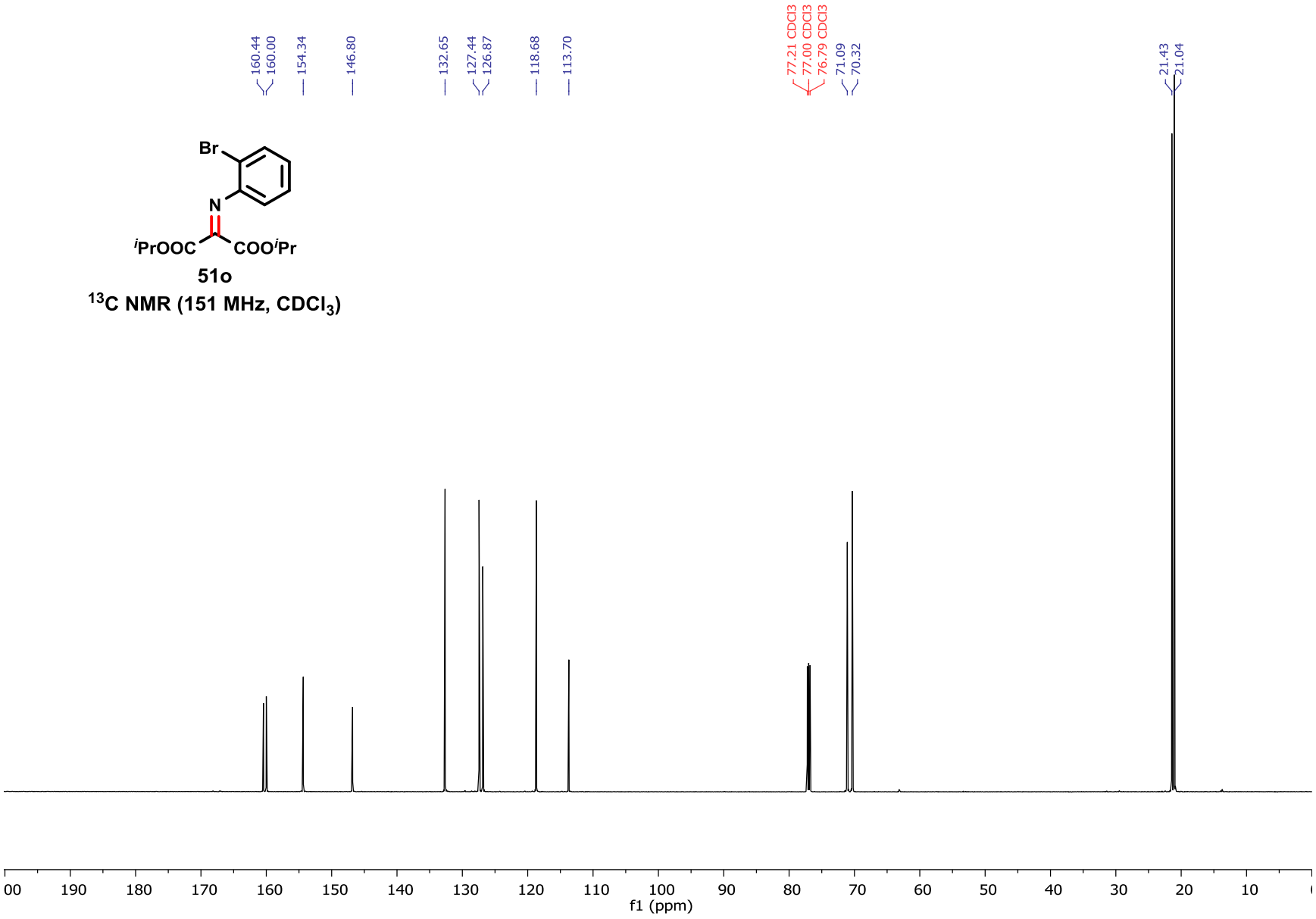

OTBDMS
N
iPrOOC
COOiPr
51n
1H NMR (600 MHz, CDCl3)
7.26
7.14
7.12
6.90
6.89
5.26
5.25
5.24
5.23
5.22
5.21
5.20
5.06
5.05
5.04
5.03
5.01
5.00
4.99
3.75
3.74
3.73
2.76
2.75
2.74
1.35
1.33
1.08
1.07
0.82
-0.08
1.87
1.93
0.95
0.94
1.91
1.91
5.95
5.84
9.19
6.00
f1 (ppm)

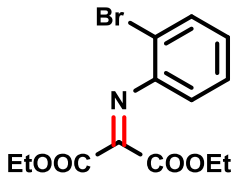

162.13
160.38
152.64
145.74
138.07
129.43
119.64
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.76
69.99
64.05
38.92
25.77
21.49
21.20
18.14
-5.57
OTBDMS
N
iPrOOC
COOiPr
51n
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



51o

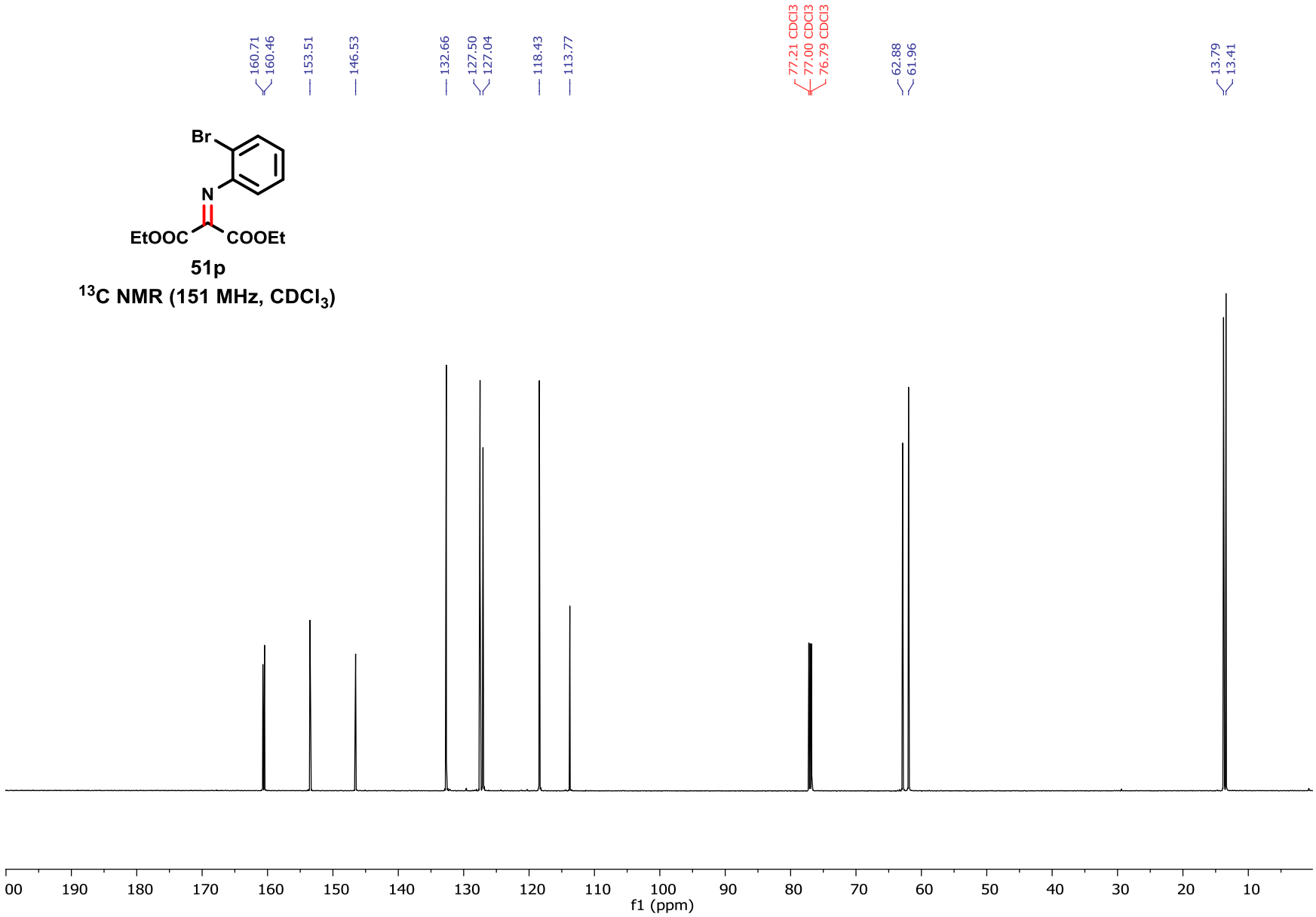
^{1}H NMR (600 MHz, $CDCl_3$)

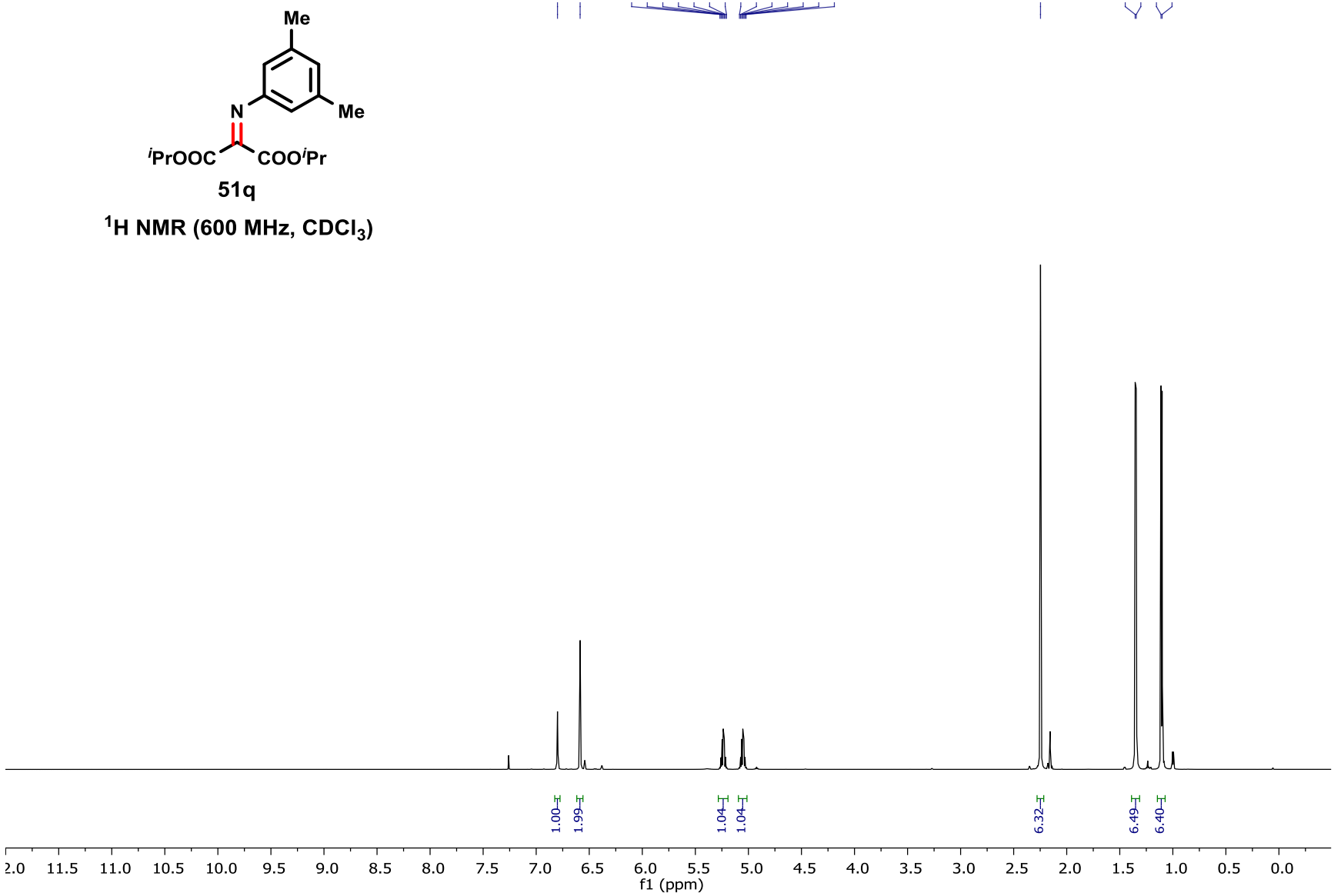

160.44
160.00
154.34
146.80
132.65
127.44
126.87
118.68
113.70
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.09
70.32
21.43
21.04
Br
N
iPrOOC
COOiPr
51o
13C NMR (151 MHz, CDCl3)
f1 (ppm)

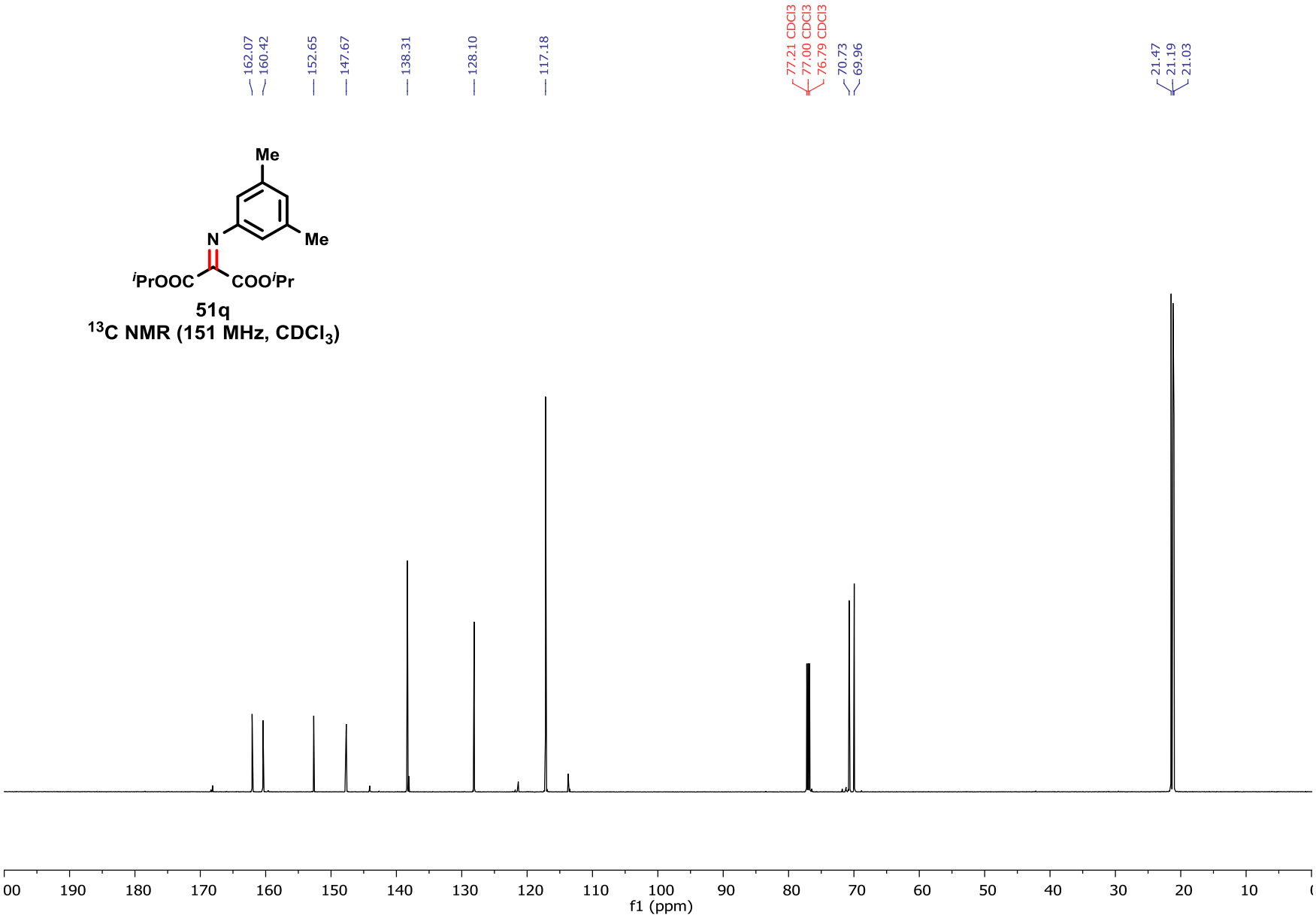


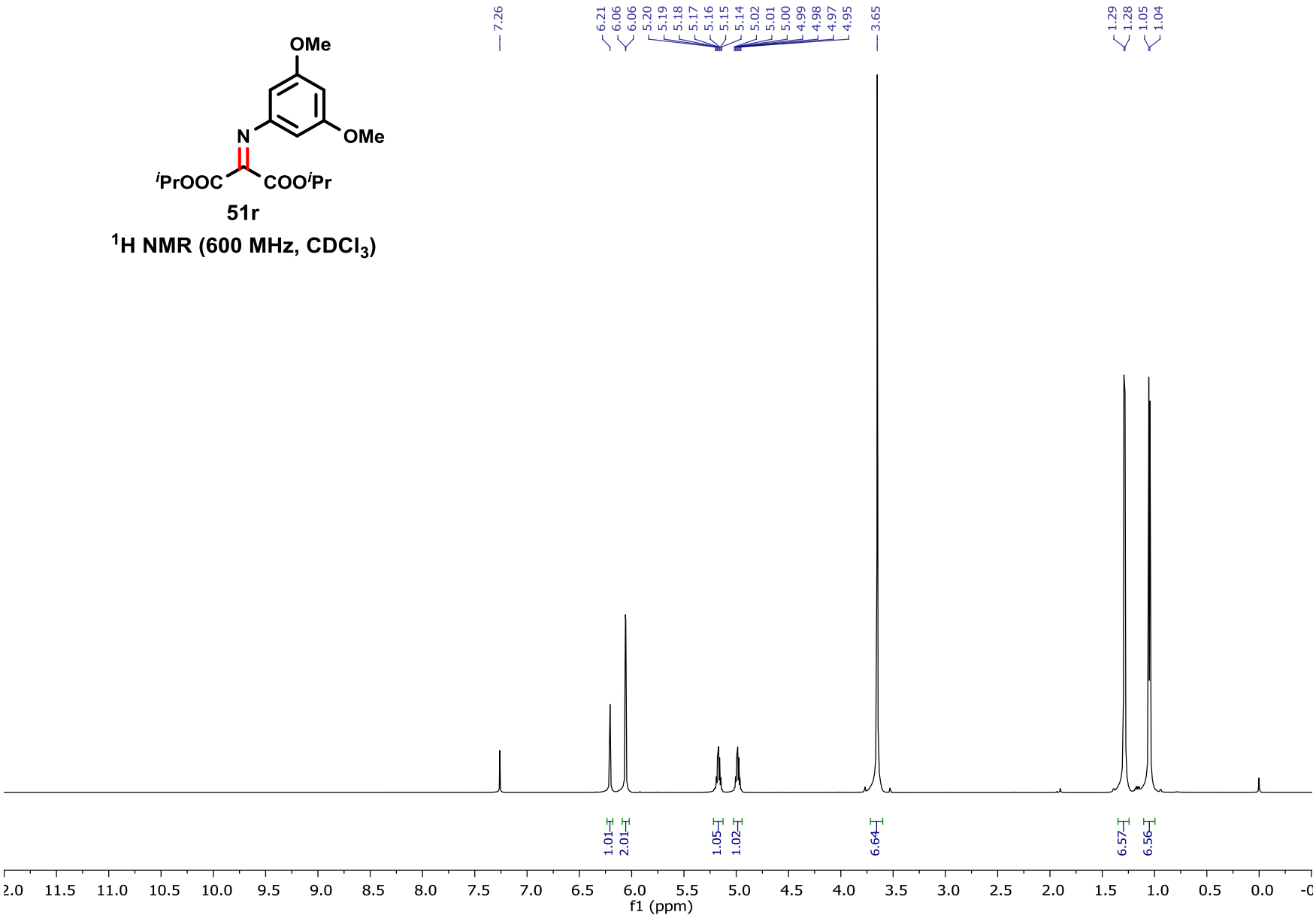
51p

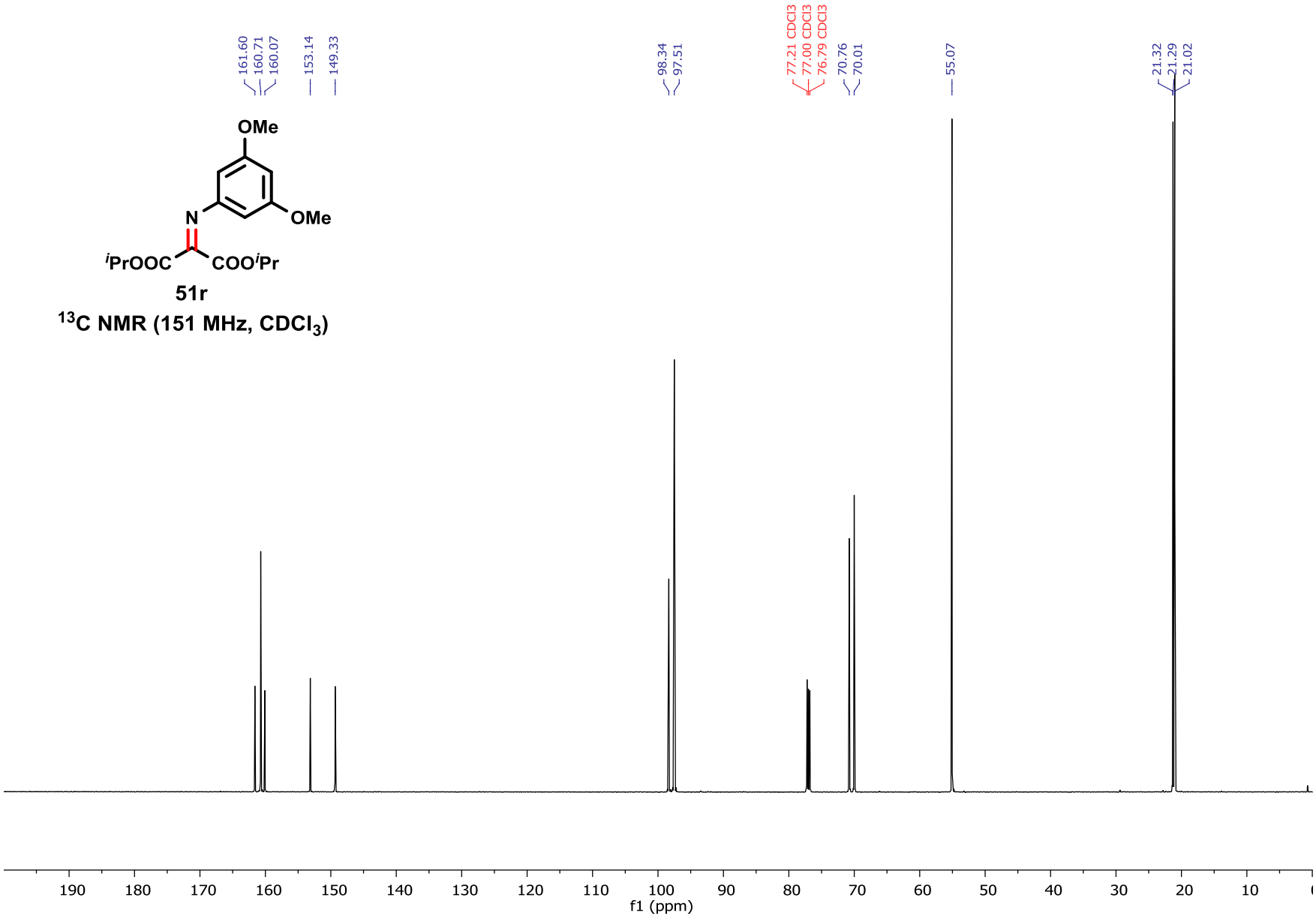
^{1}H NMR (600 MHz, $CDCl_3$)

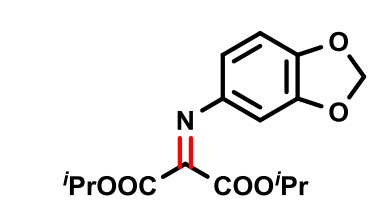

160.71
160.46
153.51
146.53
132.66
127.50
127.04
118.43
113.77
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
62.88
61.96
13.79
13.41
Br
N
EtOOC
COOEt
51p
13C NMR (151 MHz, CDCl3)
f1 (ppm)


Me
N
Me
iPrOOC
COOiPr
51q
1H NMR (600 MHz, CDCl3)
6.80
6.59
5.27
5.26
5.25
5.24
5.23
5.22
5.21
5.08
5.07
5.06
5.05
5.04
5.03
5.02
2.25
1.35
1.34
1.11
1.10
1.00
1.99
1.04
1.04
6.32
6.49
6.40
f1 (ppm)


162.07
160.42
152.65
147.67
138.31
128.10
117.18
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.73
69.96
21.47
21.19
21.03
Me
N
Me
iPrOOC
COOiPr
51q
13C NMR (151 MHz, CDCl3)
f1 (ppm)

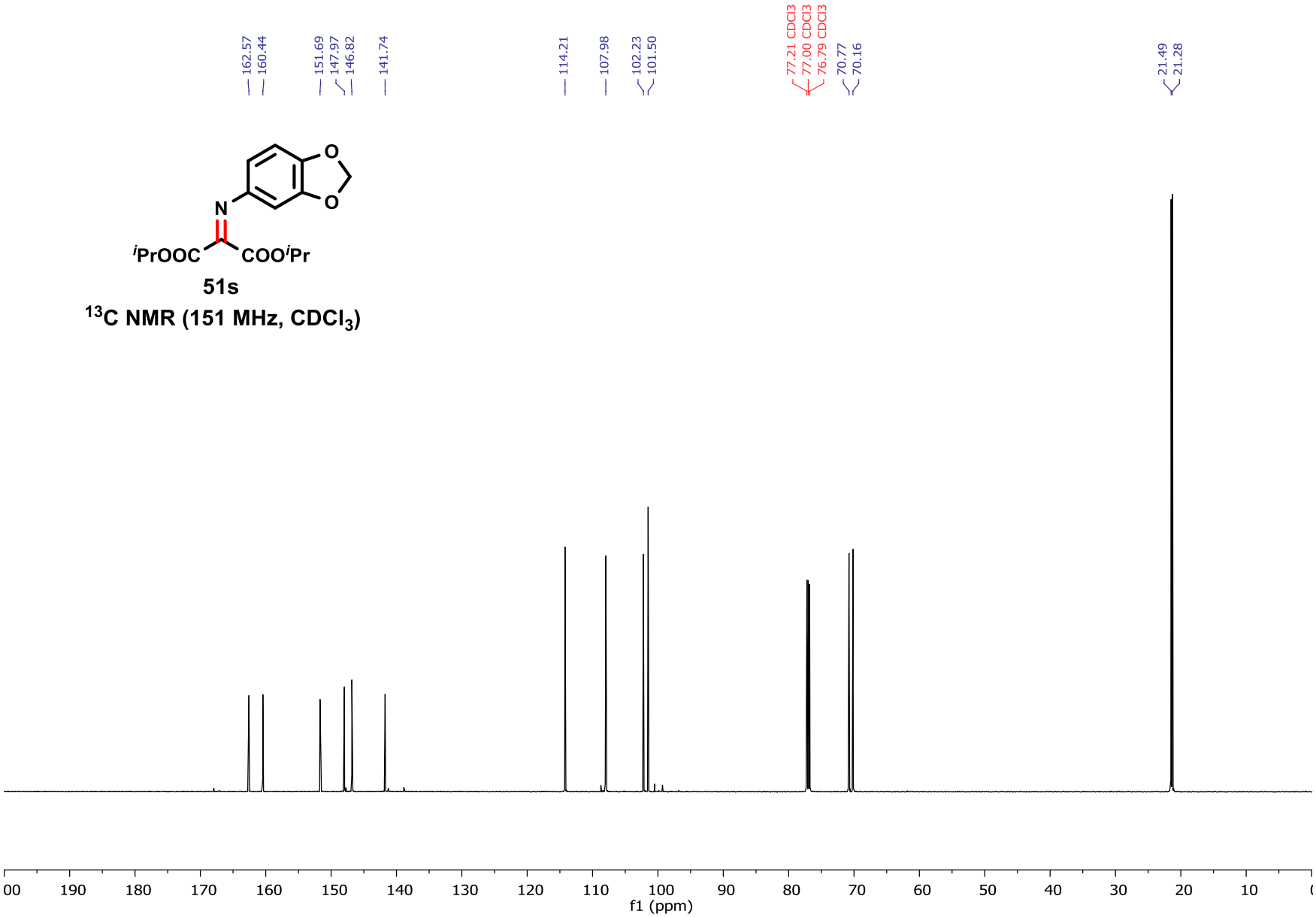

OMe
N
OMe
iPrOOC
COOiPr
51r
1H NMR (600 MHz, CDCl3)
7.26
6.21
6.06
6.06
5.20
5.19
5.18
5.17
5.16
5.15
5.14
5.02
5.01
5.00
4.99
4.98
4.97
4.95
3.65
1.29
1.28
1.05
1.04
1.01
2.01
1.05
1.02
6.64
6.57
6.56
f1 (ppm)

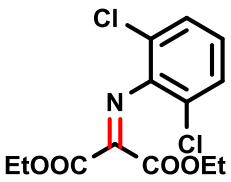

161.60
160.71
160.07
153.14
149.33
98.34
97.51
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.76
70.01
55.07
21.32
21.29
21.02
OMe
OMe
N
iPrOOC
COOiPr
51r
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



51s

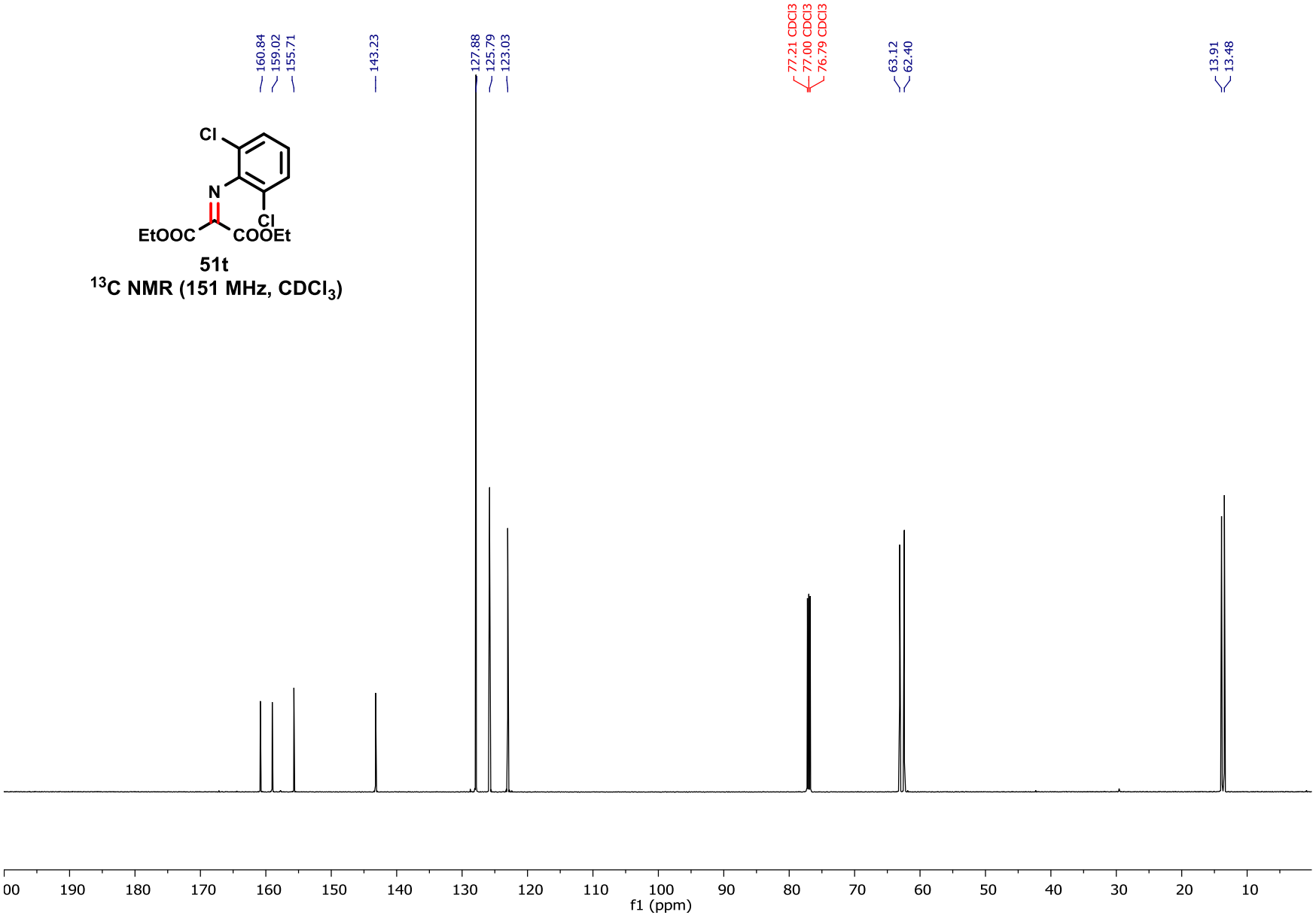
^{1}H NMR (600 MHz, $CDCl_3$)

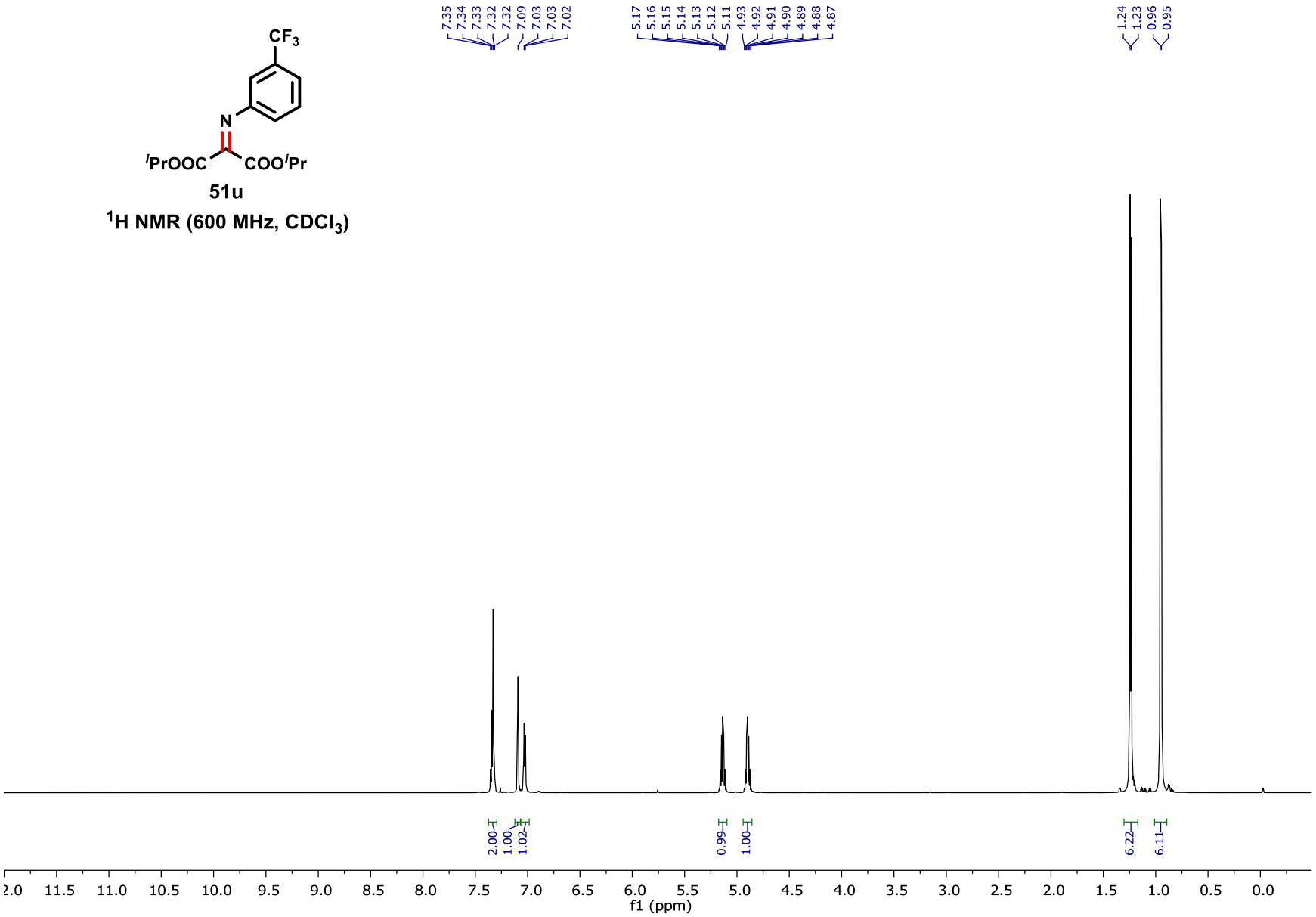

162.57
160.44
151.69
147.97
146.82
141.74
114.21
107.98
102.23
101.50
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.77
70.16
21.49
21.28
O
O
N
iPrOOC
COOiPr
51s
13C NMR (151 MHz, CDCl3)
f1 (ppm)

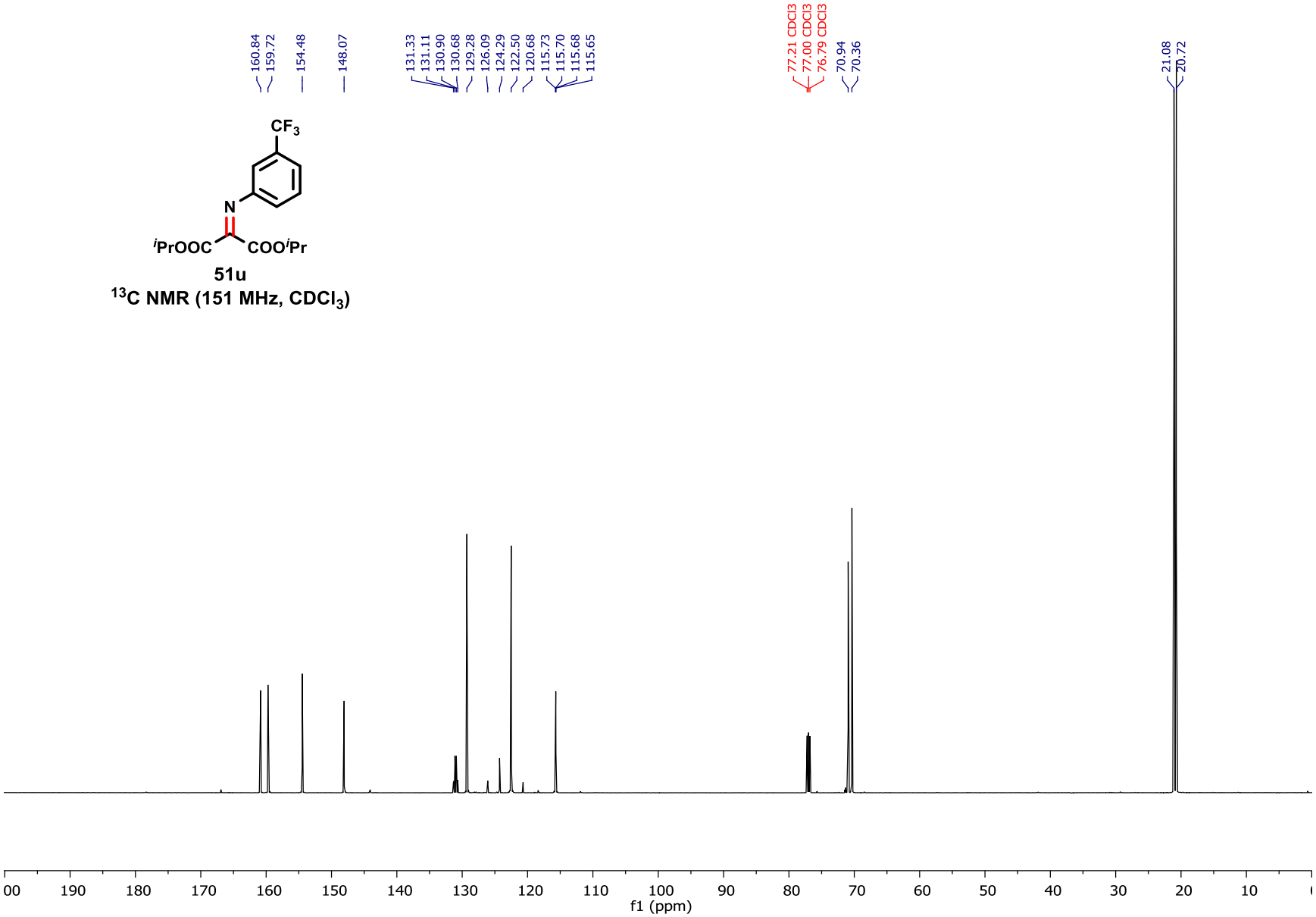


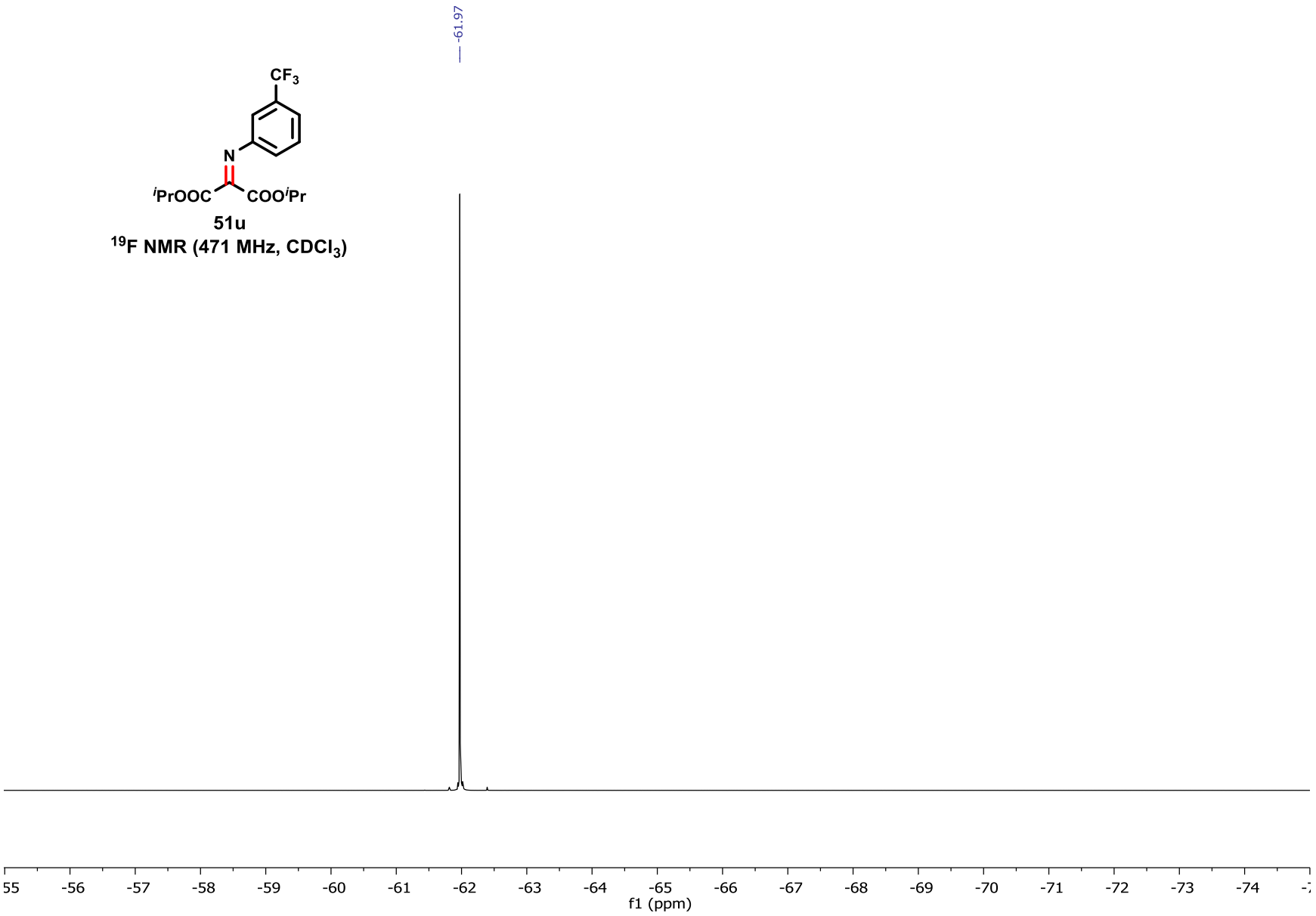
51t

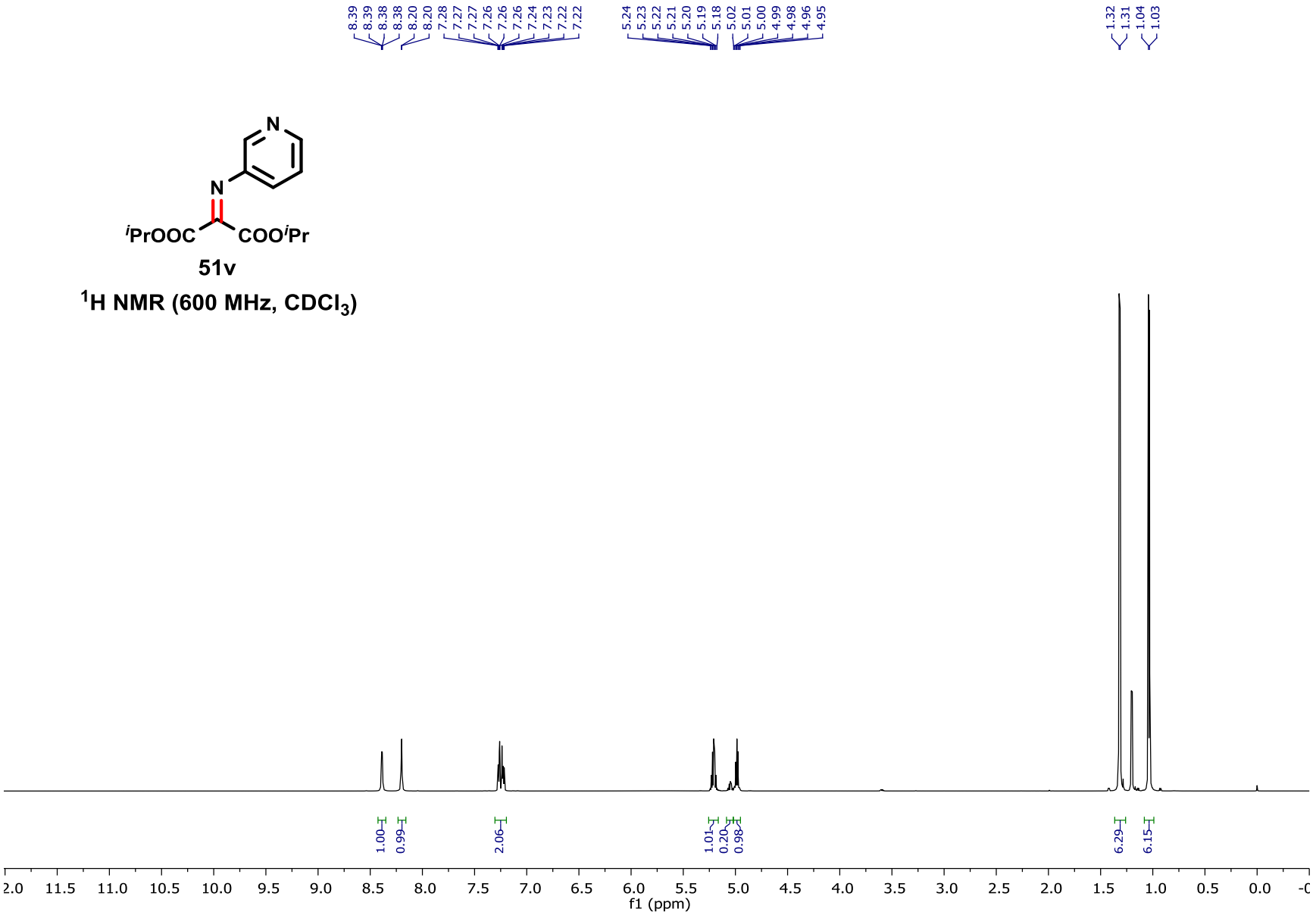
^{1}H NMR (600 MHz, $CDCl_3$)


160.84
159.02
155.71
143.23
127.88
125.79
123.03
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
63.12
62.40
13.91
13.48
Cl
N
Cl
EtOOC
COOEt
51t
13C NMR (151 MHz, CDCl3)
f1 (ppm)


CF3
N
iPrOOC
COOiPr
51u
1H NMR (600 MHz, CDCl3)
7.35
7.34
7.33
7.32
7.32
7.09
7.03
7.03
7.02
5.17
5.16
5.15
5.14
5.13
5.12
5.11
4.93
4.92
4.91
4.90
4.89
4.88
4.87
1.24
1.23
0.96
0.95
2.00
1.00
1.02
0.99
1.00
6.22
6.11
f1 (ppm)

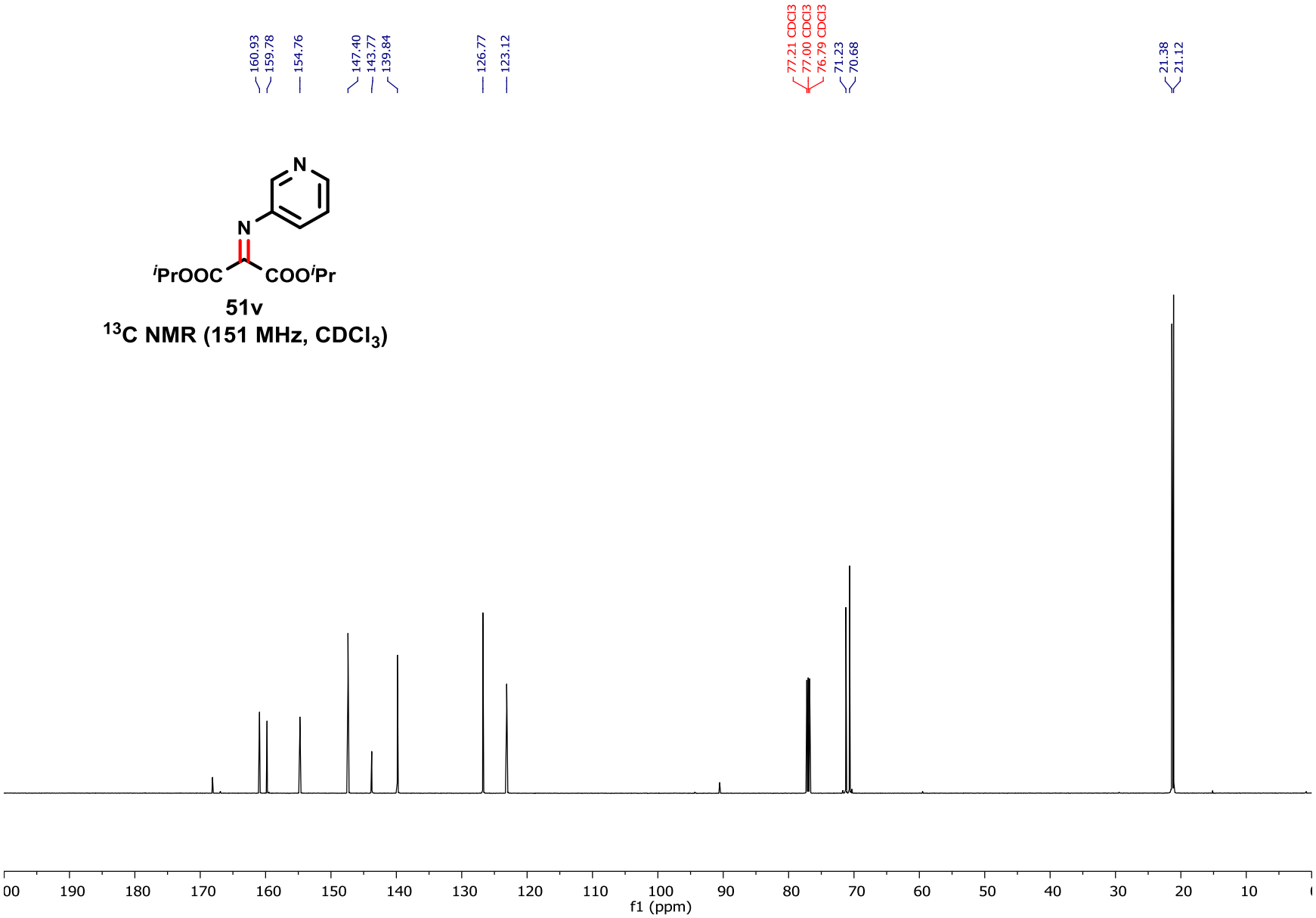

160.84
159.72
154.48
148.07
131.33
131.11
130.90
130.68
129.28
126.09
124.29
122.50
120.68
115.73
115.70
115.68
115.65
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.94
70.36
21.08
20.72
CF3
N
iPrOOC
COOiPr
51u
13C NMR (151 MHz, CDCl3)
f1 (ppm)

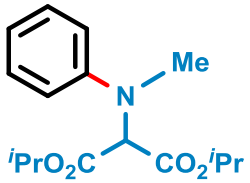

CF3
N
iPrOOC
COOiPr
51u
19F NMR (471 MHz, CDCl3)
-61.97
55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
f1 (ppm)



51v

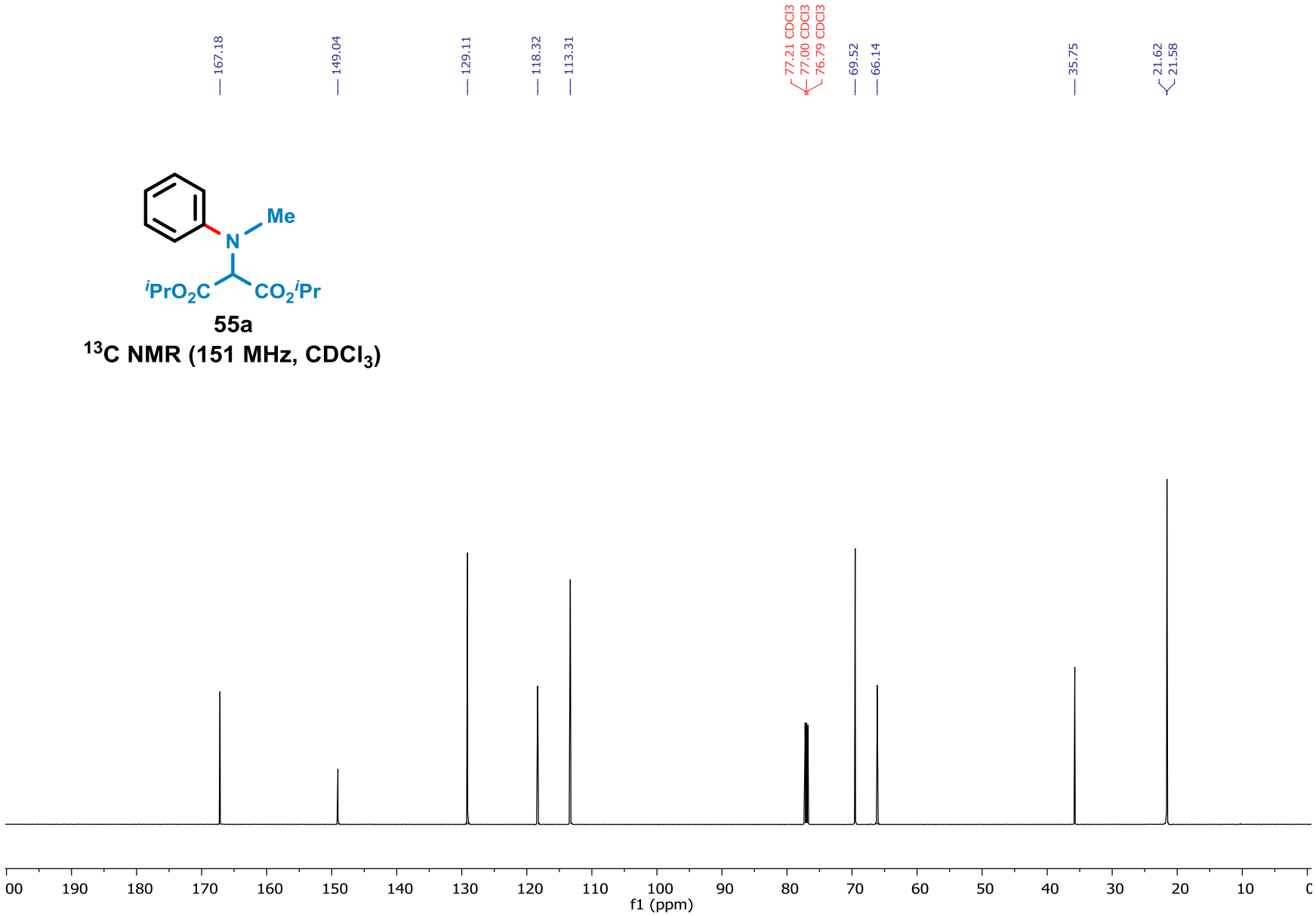
^{1}H NMR (600 MHz, $CDCl_3$)

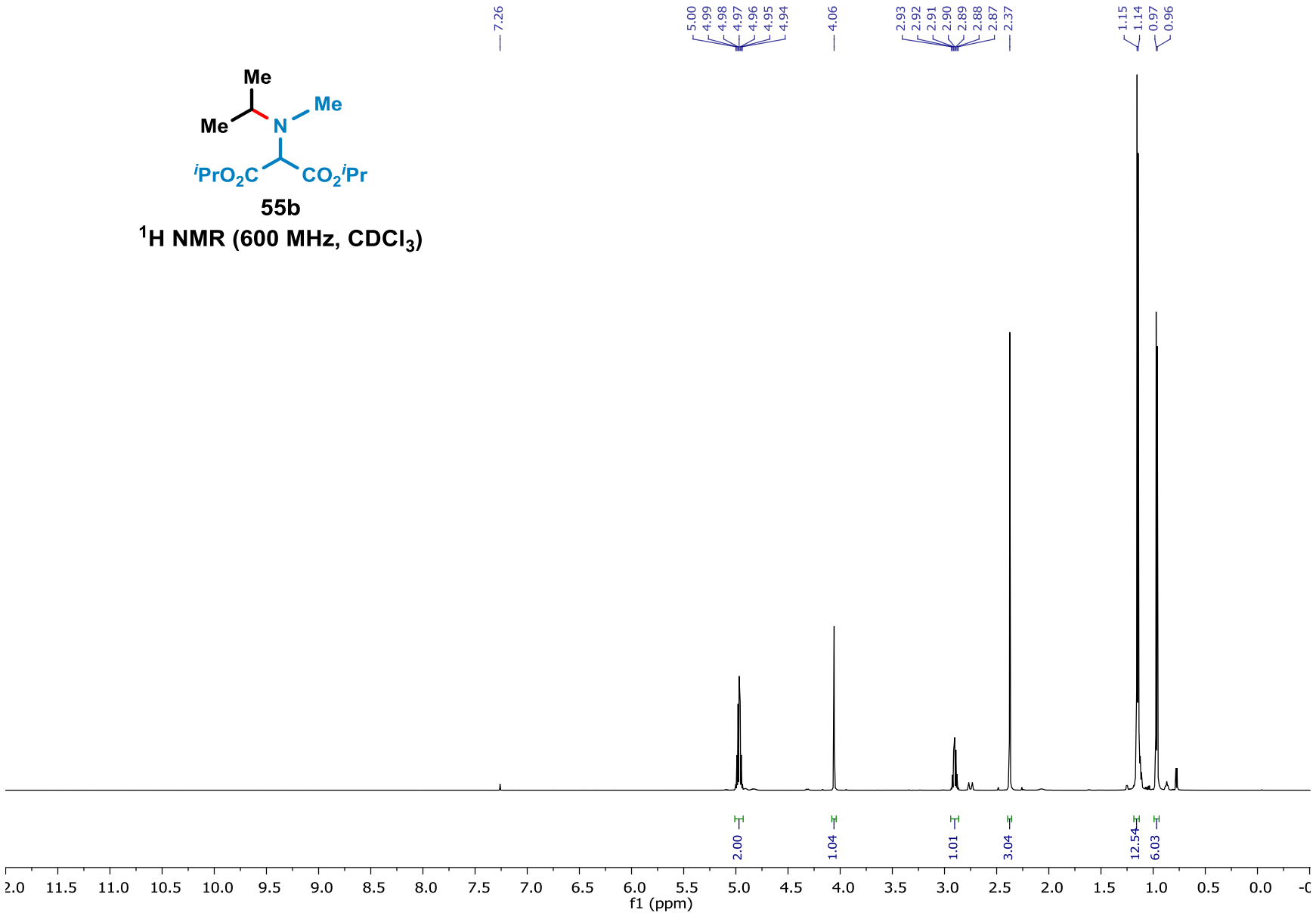

160.93
159.78
154.76
147.40
143.77
139.84
126.77
123.12
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.23
70.68
21.38
21.12
N
N
iPrOOC
COOiPr
51v
13C NMR (151 MHz, CDCl3)
f1 (ppm)

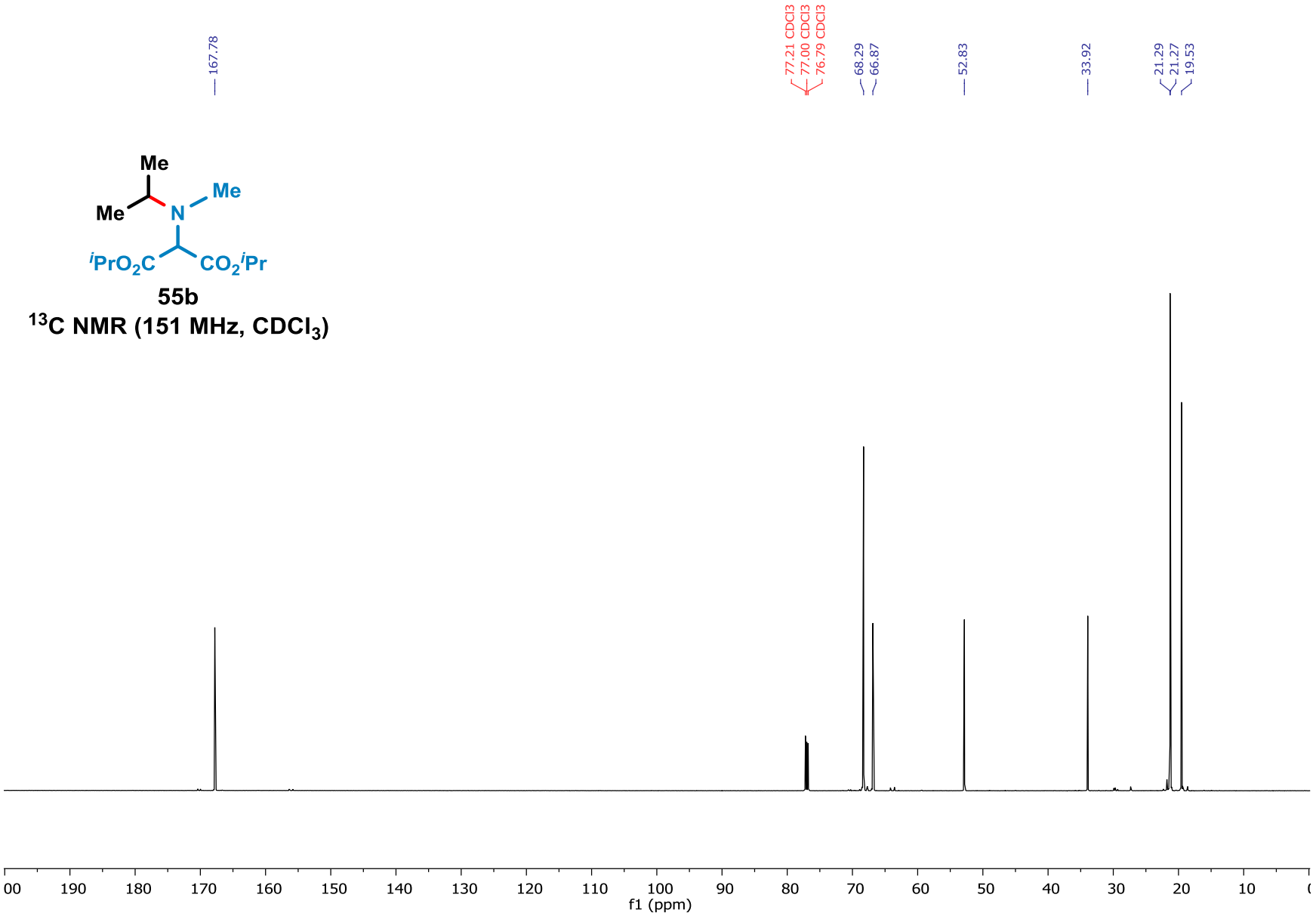


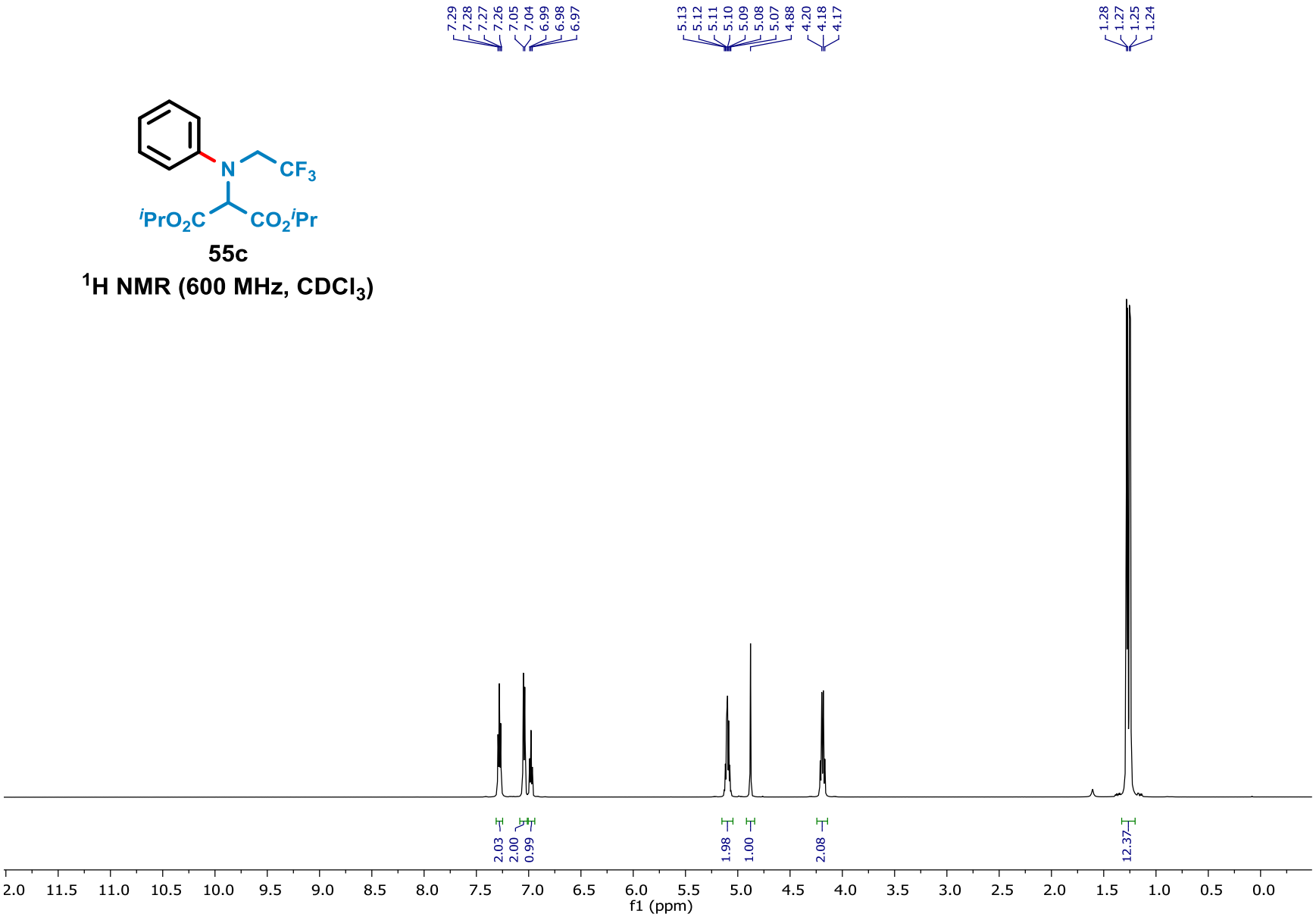
55a

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


167.18
149.04
129.11
118.32
113.31
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.52
66.14
35.75
21.62
21.58
Me
N
iPrO2C
CO2iPr
55a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

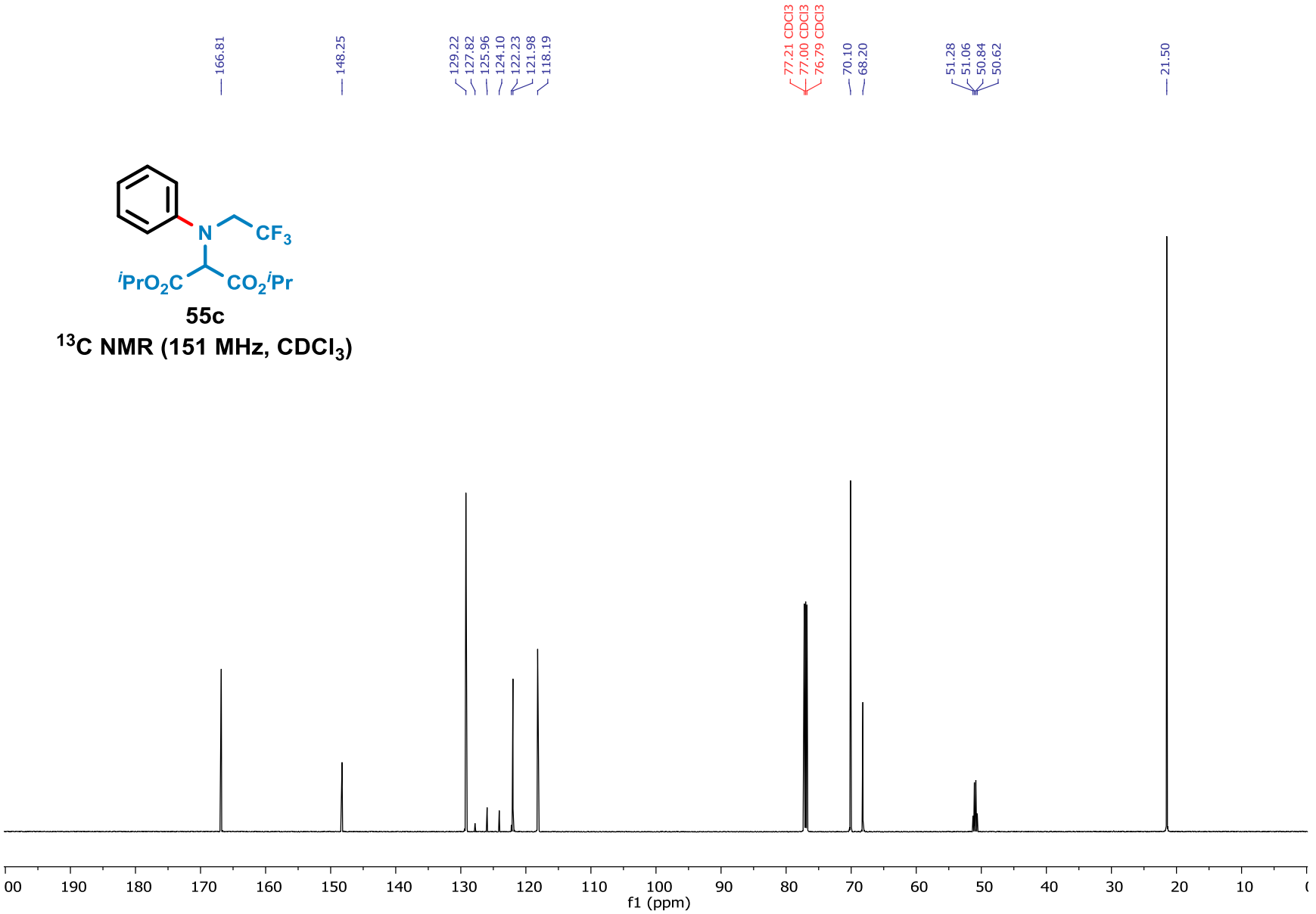

Me
Me
N
Me
iPrO2C
CO2iPr
55b
1H NMR (600 MHz, CDCl3)
7.26
5.00
4.99
4.98
4.97
4.96
4.95
4.94
4.06
2.93
2.92
2.91
2.90
2.89
2.88
2.87
2.37
1.15
1.14
0.97
0.96
2.00
1.04
1.01
3.04
12.54
6.03
f1 (ppm)


167.78
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.29
66.87
52.83
33.92
21.29
21.27
19.53
Me
Me
Me
N
iPrO2C
CO2iPr
55b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



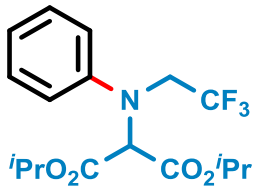
55c

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



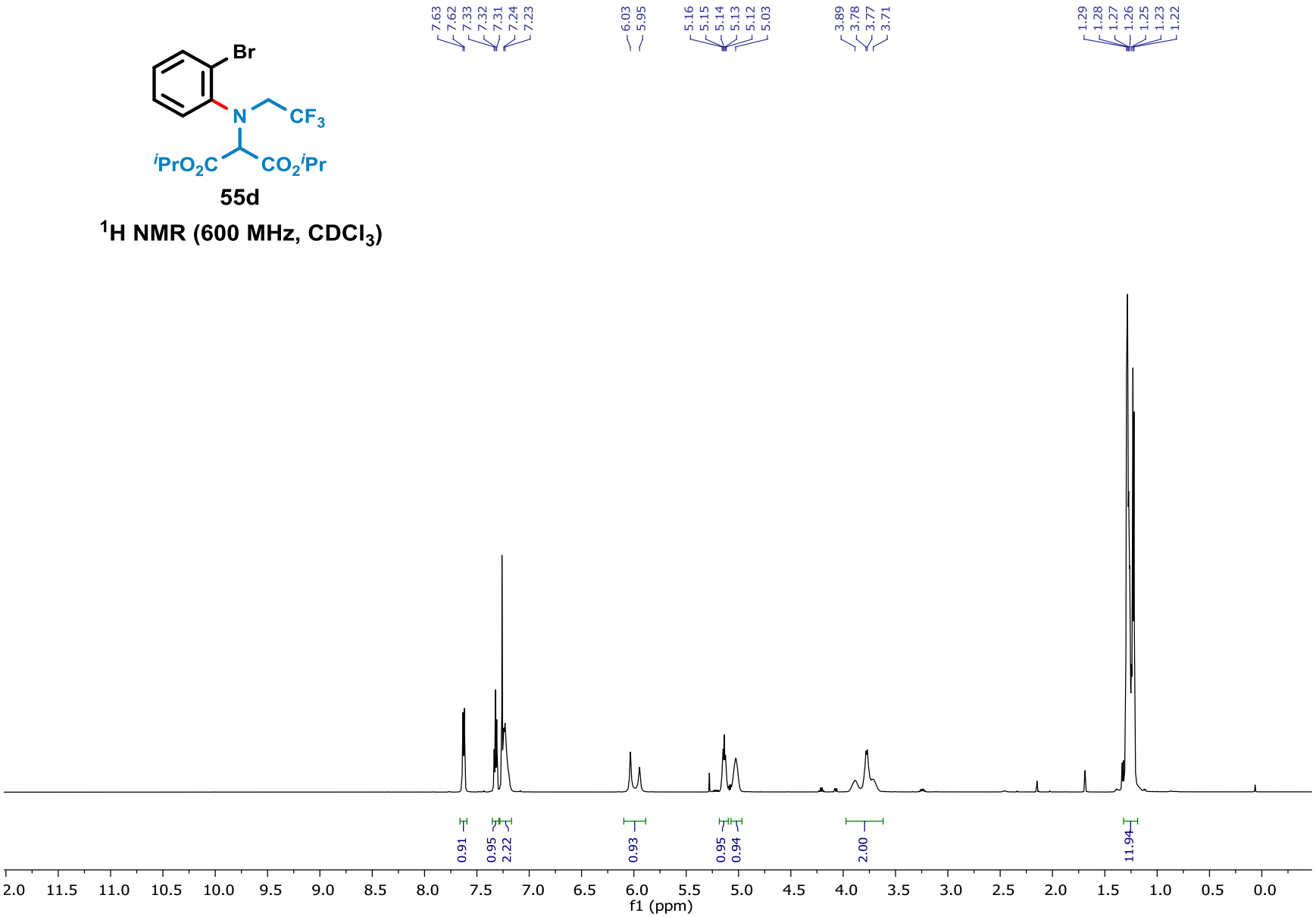
55c

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



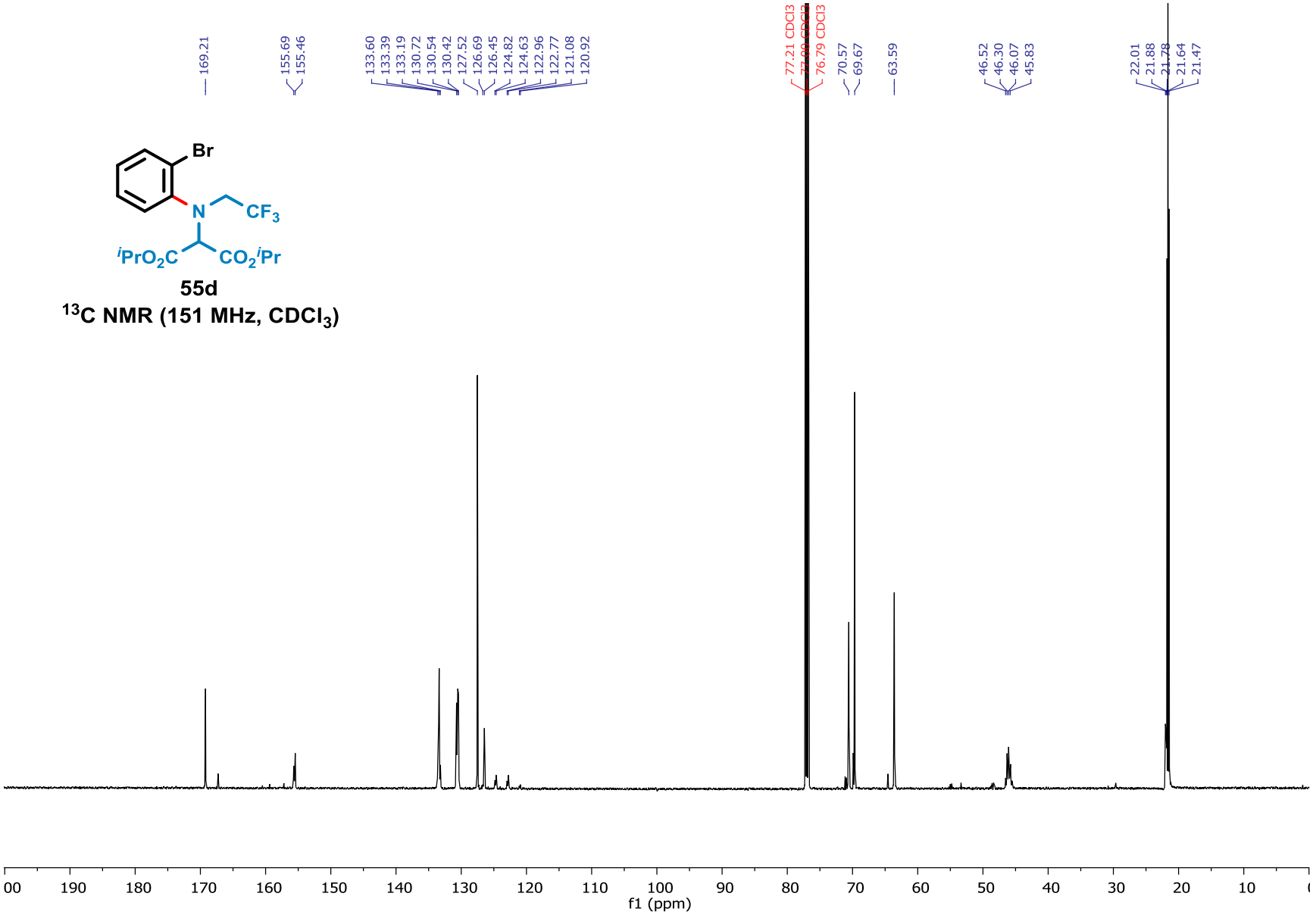
55c

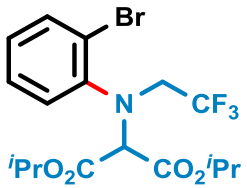
^{19}F NMR (471 MHz, $CDCl_3$)



55d

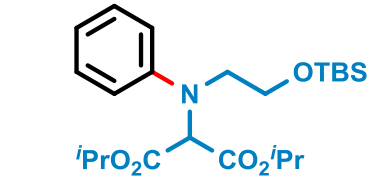
^{1}H NMR (600 MHz, $CDCl_3$)


169.21
155.69
155.46
133.60
133.39
133.19
130.72
130.54
130.42
127.52
126.69
126.45
124.82
124.63
122.96
122.77
121.08
120.92
77.21 CDCl3
76.79 CDCl3
70.57
69.67
63.59
46.52
46.30
46.07
45.83
22.01
21.88
21.78
21.64
21.47
Br
N
CF3
iPrO2C
CO2iPr
55d
13C NMR (151 MHz, CDCl3)
f1 (ppm)



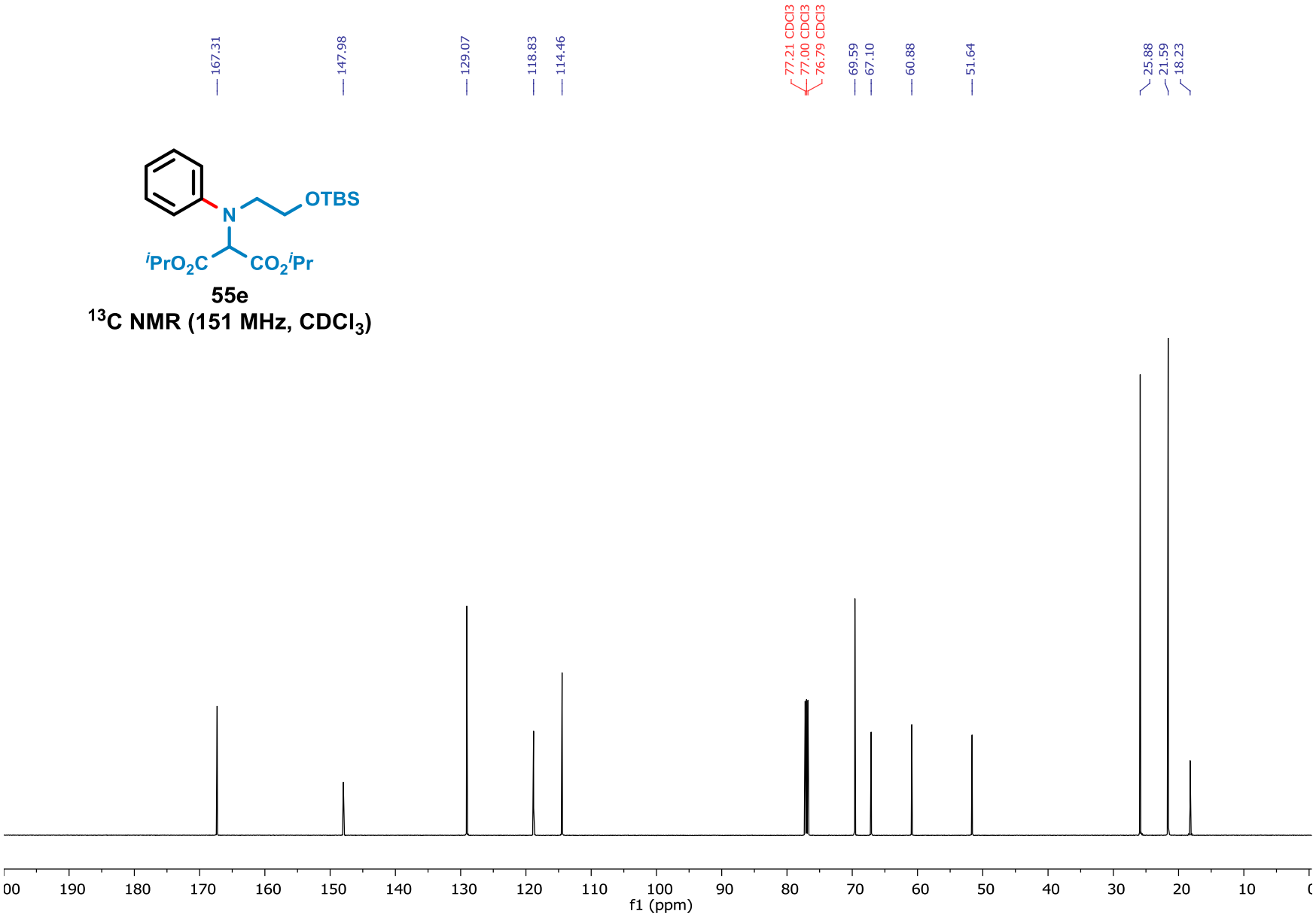
55d

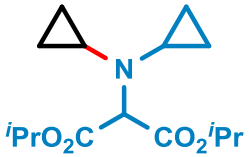
^{19}F NMR (471 MHz, $CDCl_3$)



55e

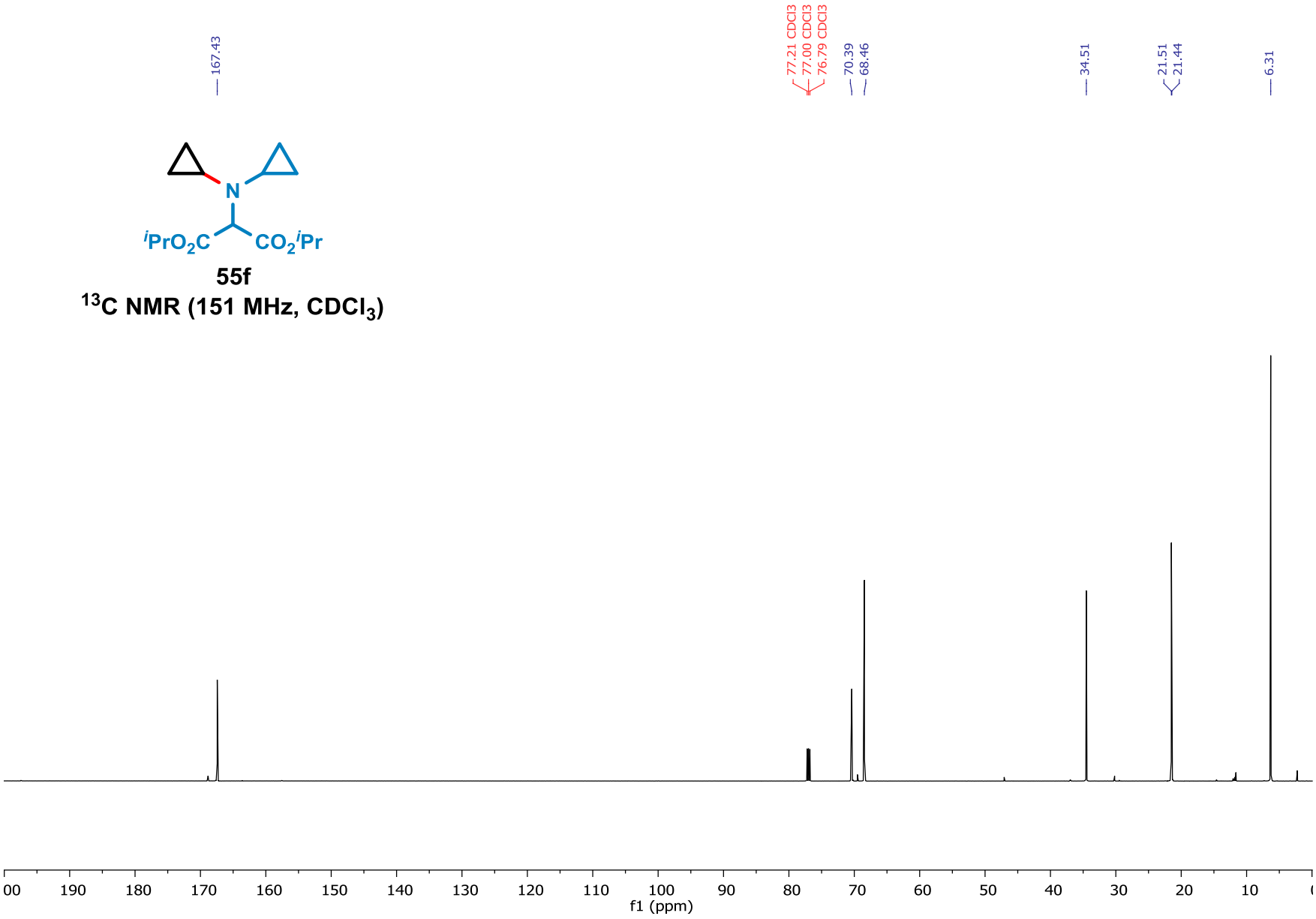
^{1}H NMR (600 MHz, $CDCl_3$)


167.31
147.98
129.07
118.83
114.46
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.59
67.10
60.88
51.64
25.88
21.59
18.23
OTBS
N
iPrO2C
CO2iPr
55e
13C NMR (151 MHz, CDCl3)
f1 (ppm)



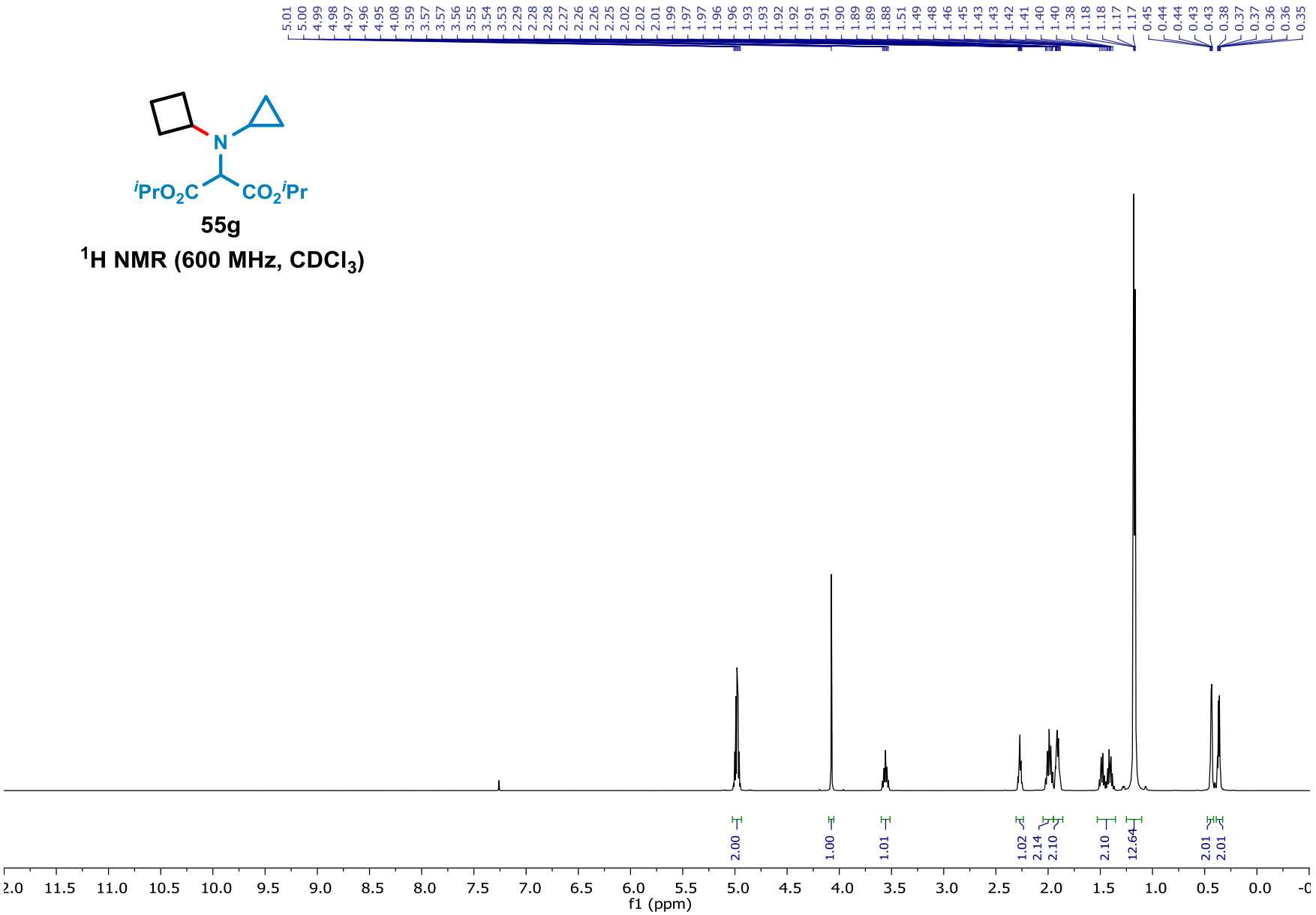
55f

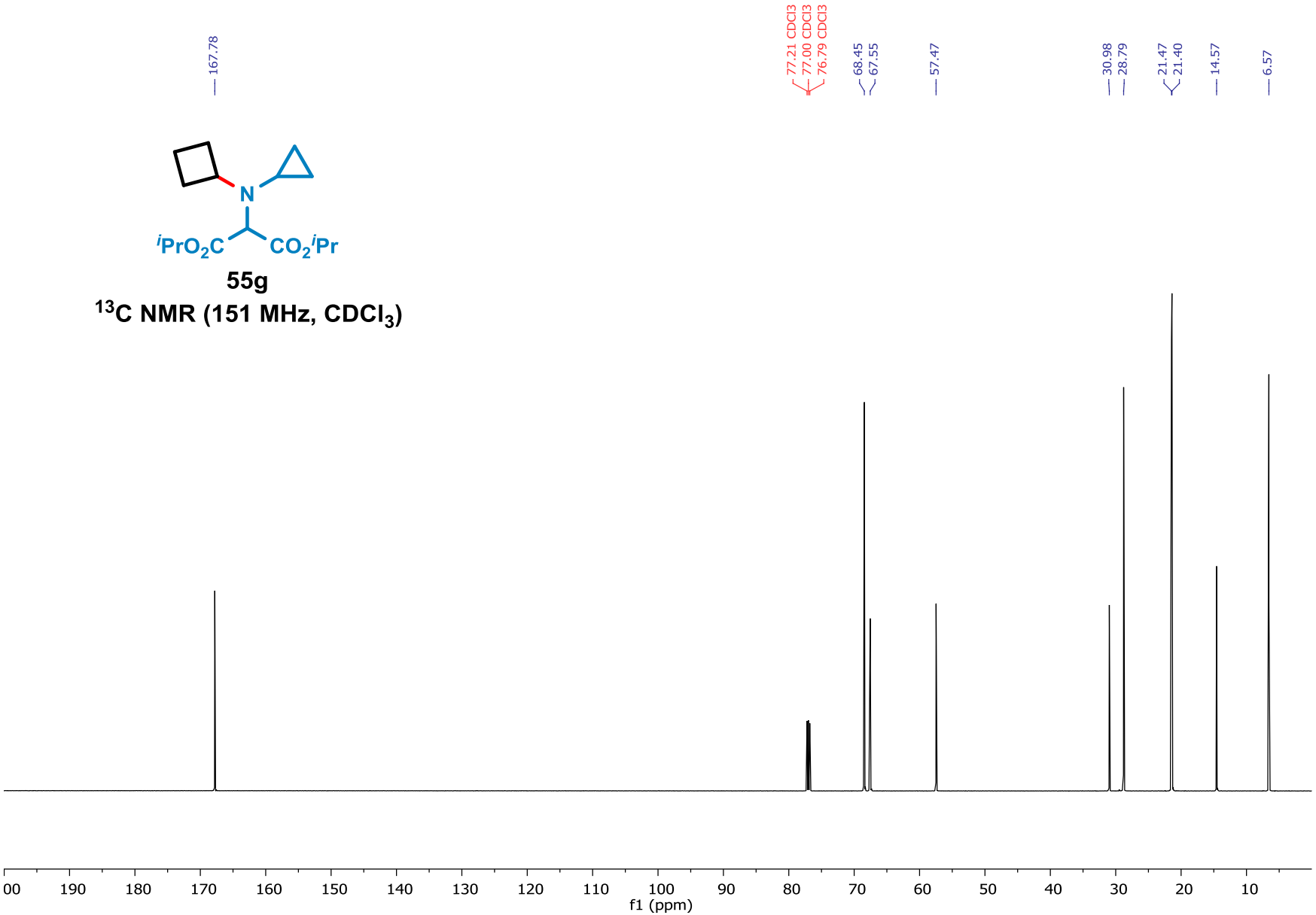
^{1}H NMR (600 MHz, $CDCl_3$)

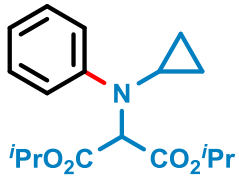


55f

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

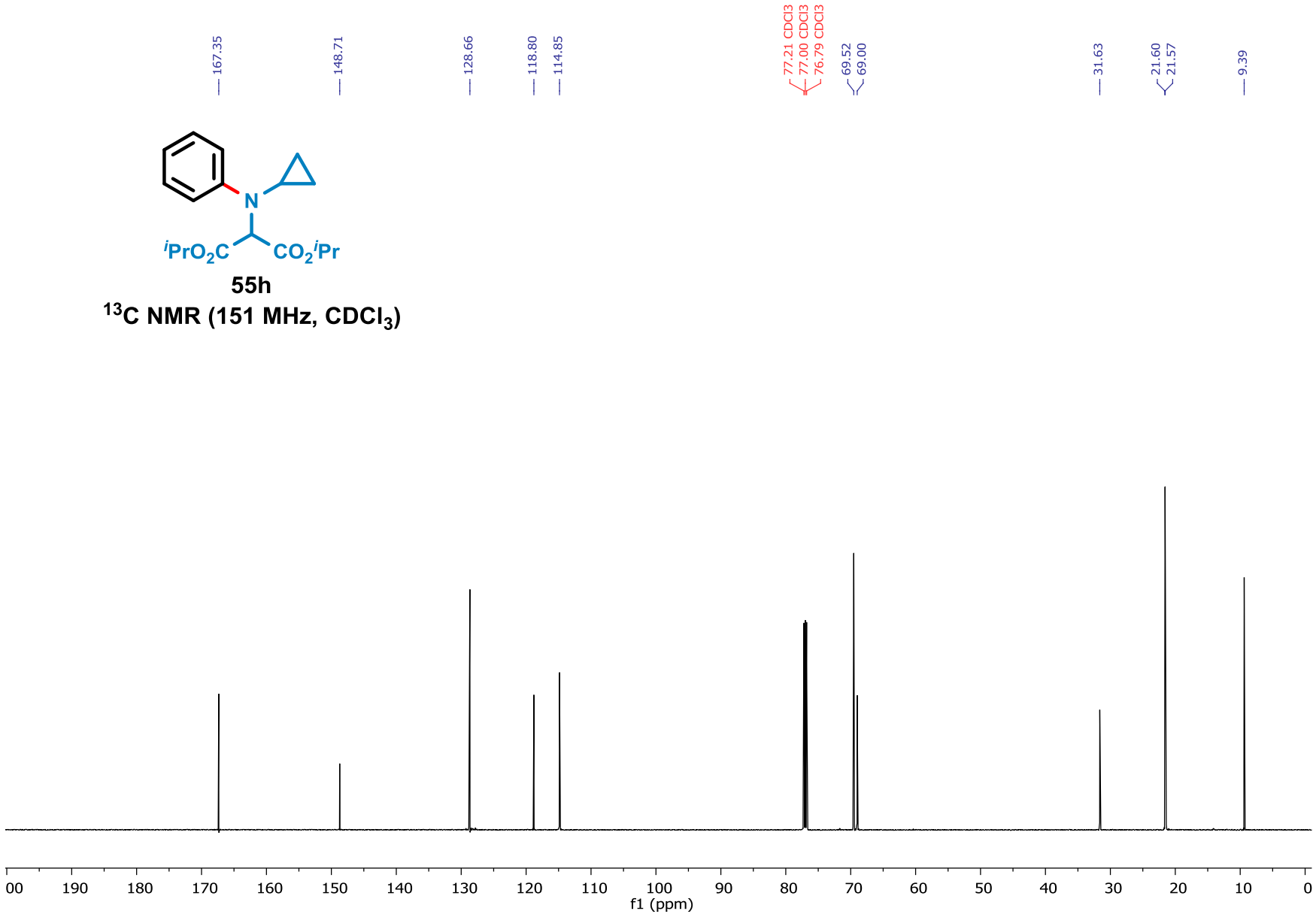

N
iPrO2C
CO2iPr
55g
1H NMR (600 MHz, CDCl3)
f1 (ppm)


167.78
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.45
67.55
57.47
30.98
28.79
21.47
21.40
14.57
6.57
N
iPrO2C
CO2iPr
55g
13C NMR (151 MHz, CDCl3)
f1 (ppm)



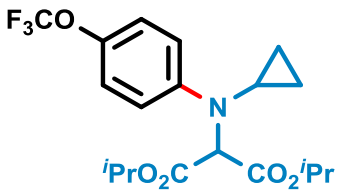
55h

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



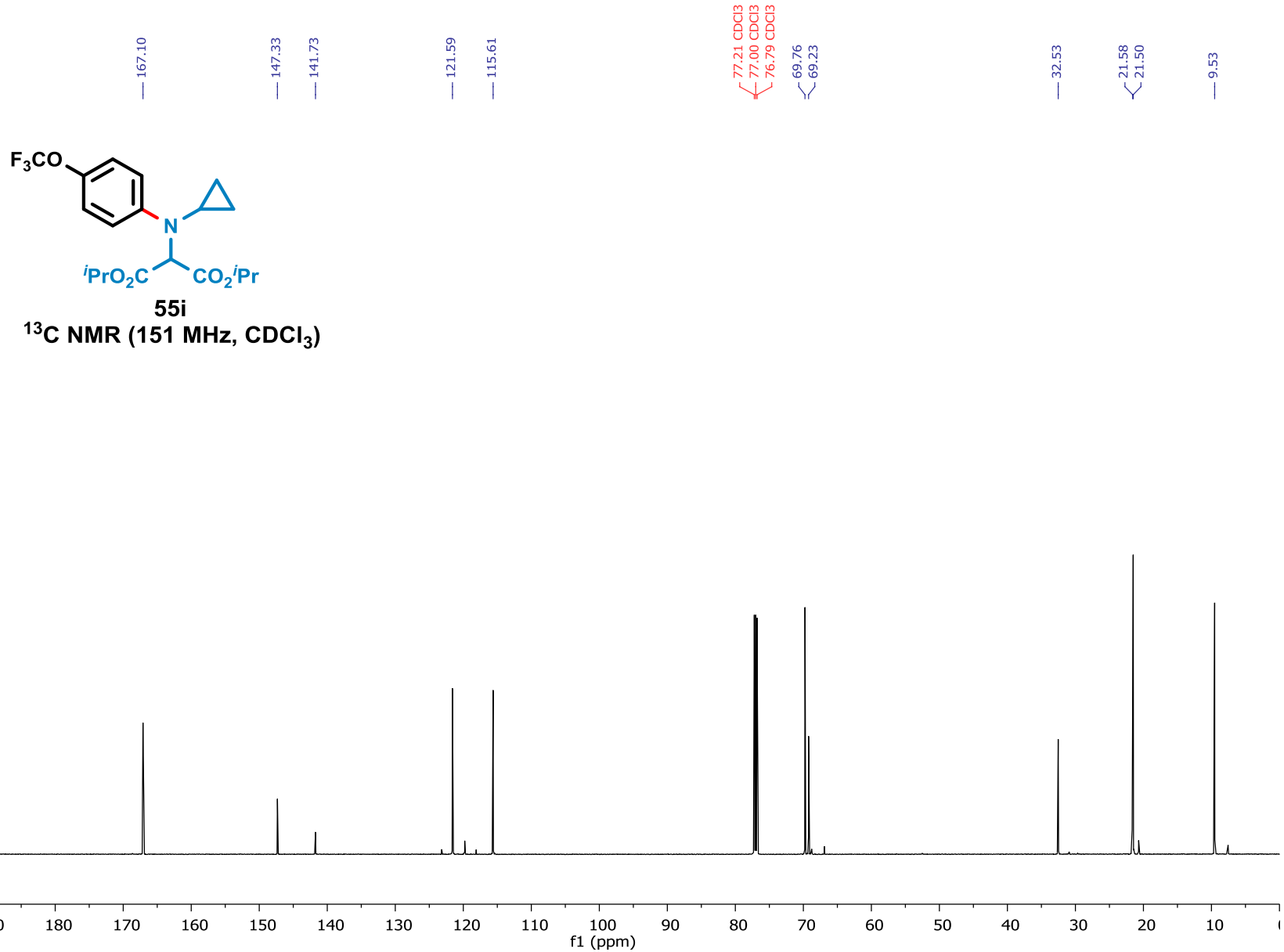
55h

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



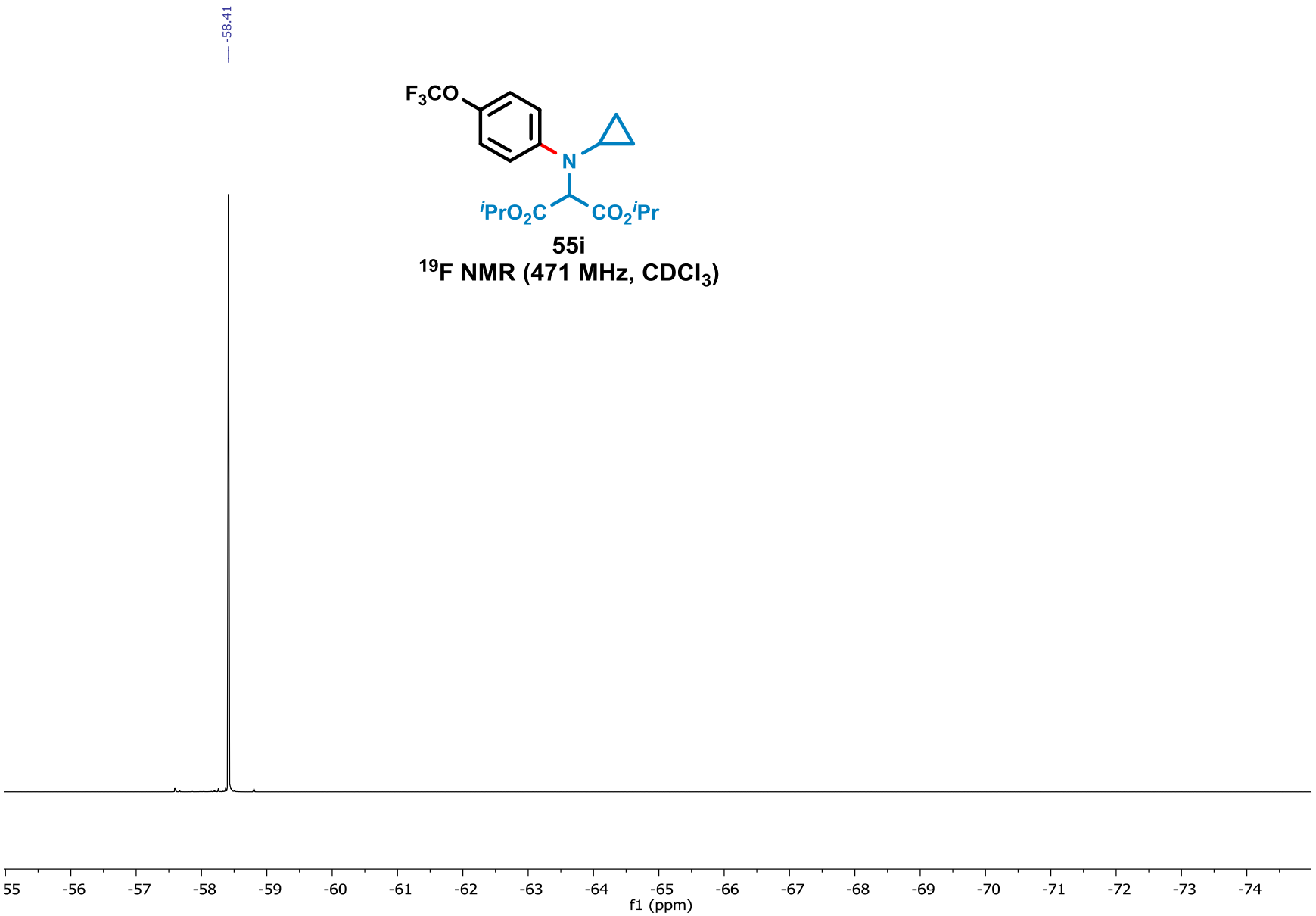
55i

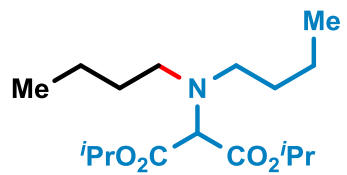
^{1}H NMR (600 MHz, $CDCl_3$)



55i

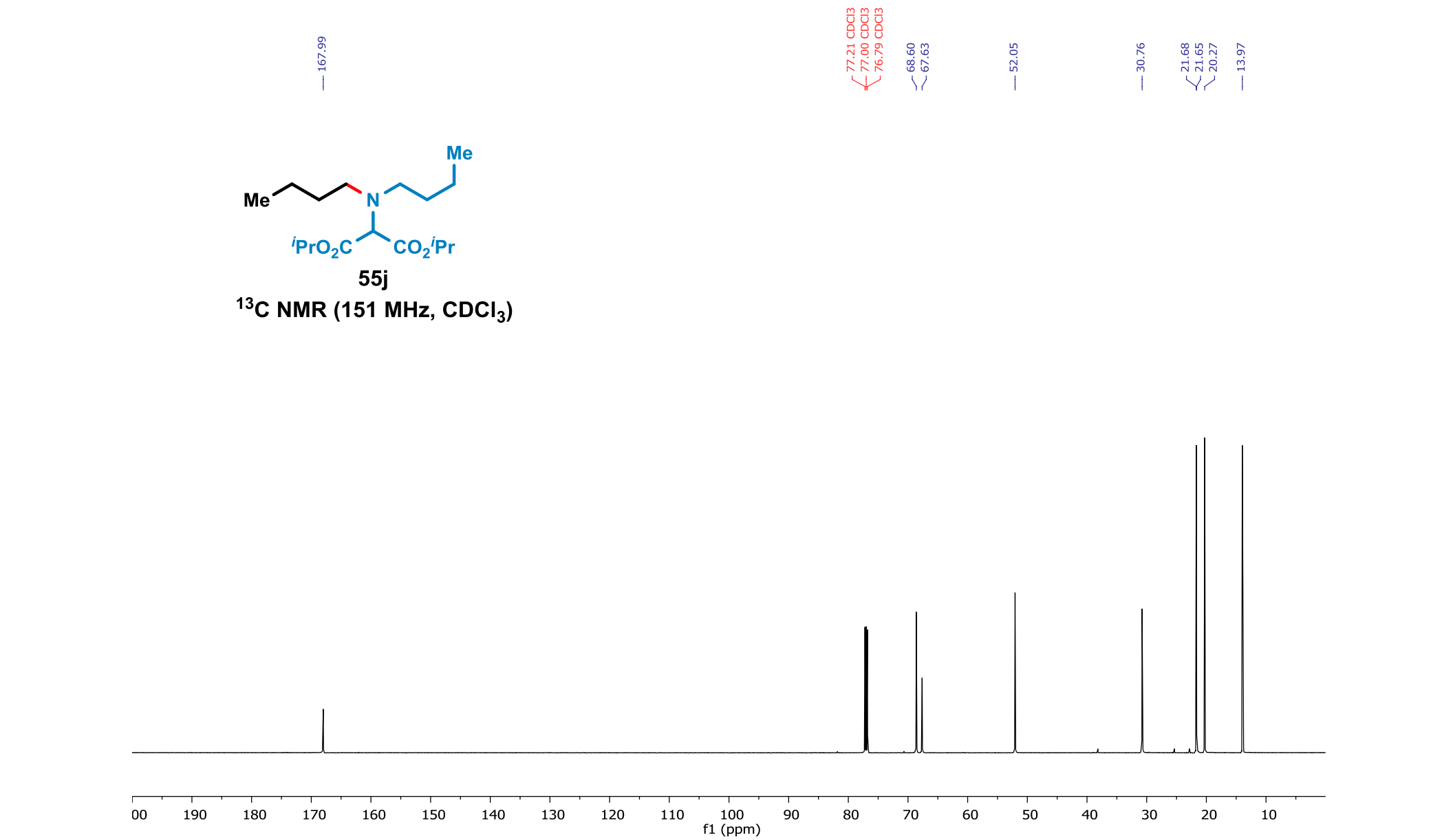
^{13}C NMR (151 MHz, $CDCl_3$)


-58.41
F3CO
N
iPrO2C
CO2iPr
55
19F NMR (471 MHz, CDCl3)
55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
f1 (ppm)



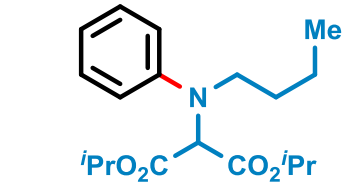
55j

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



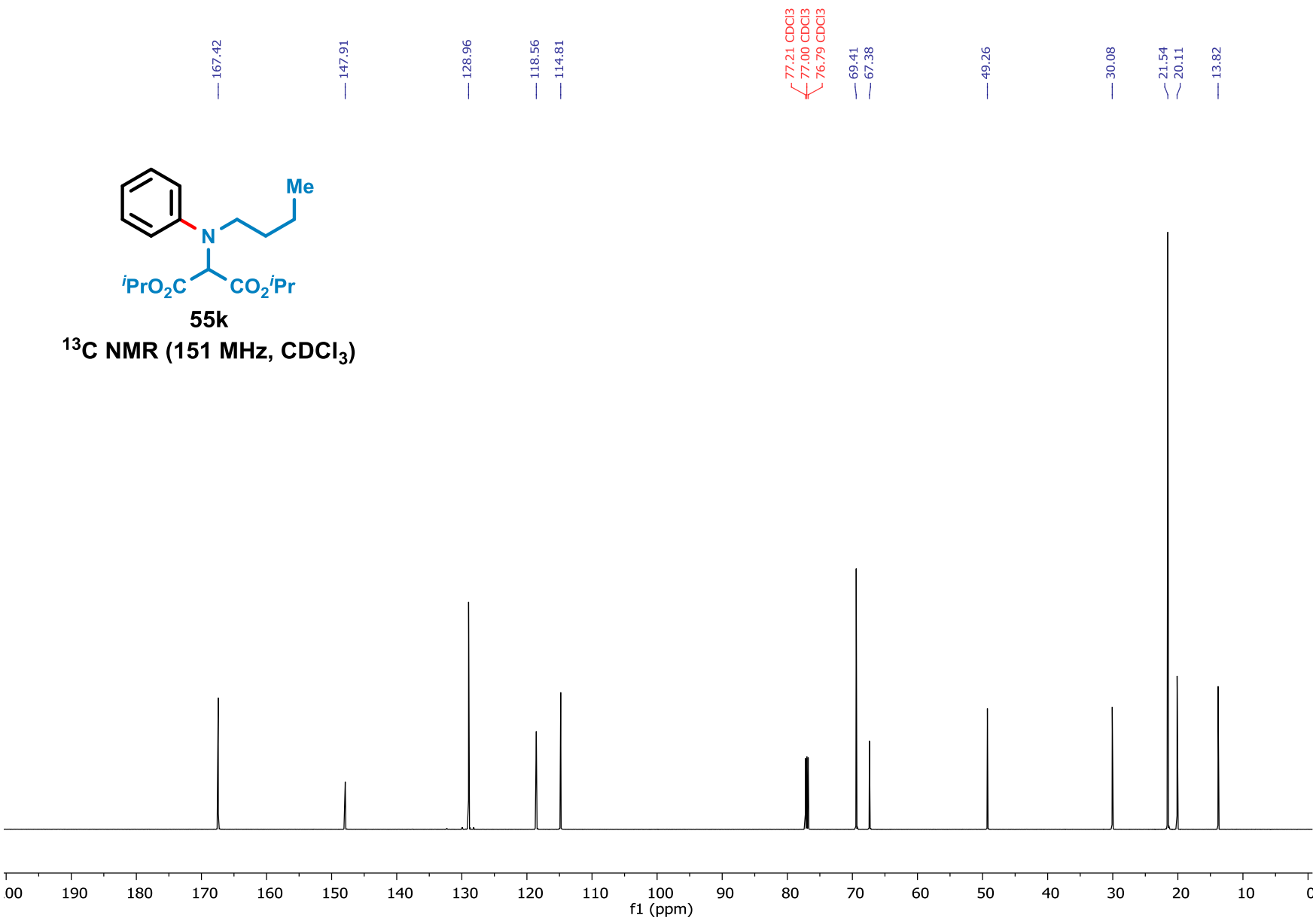
55j

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



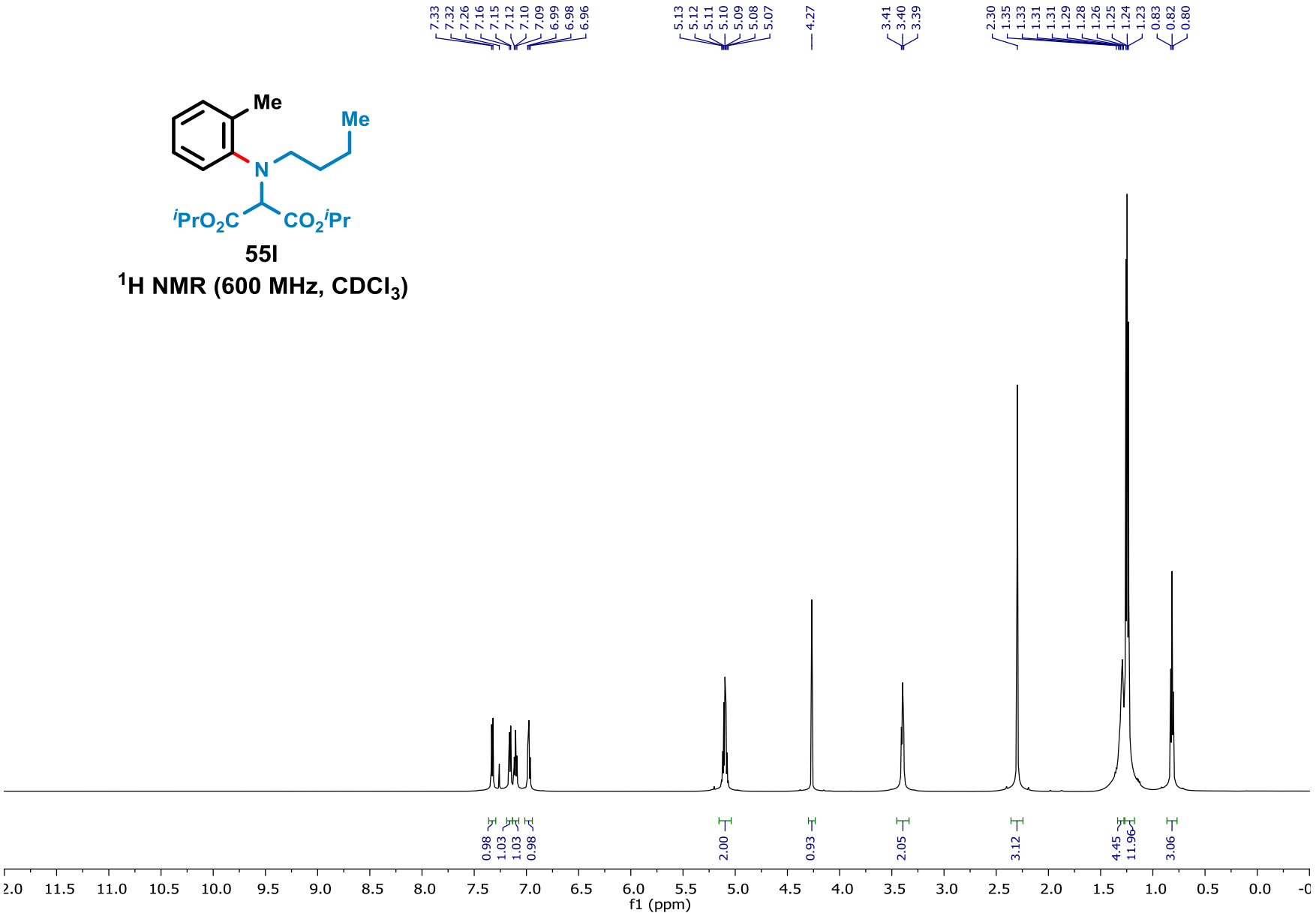
55k

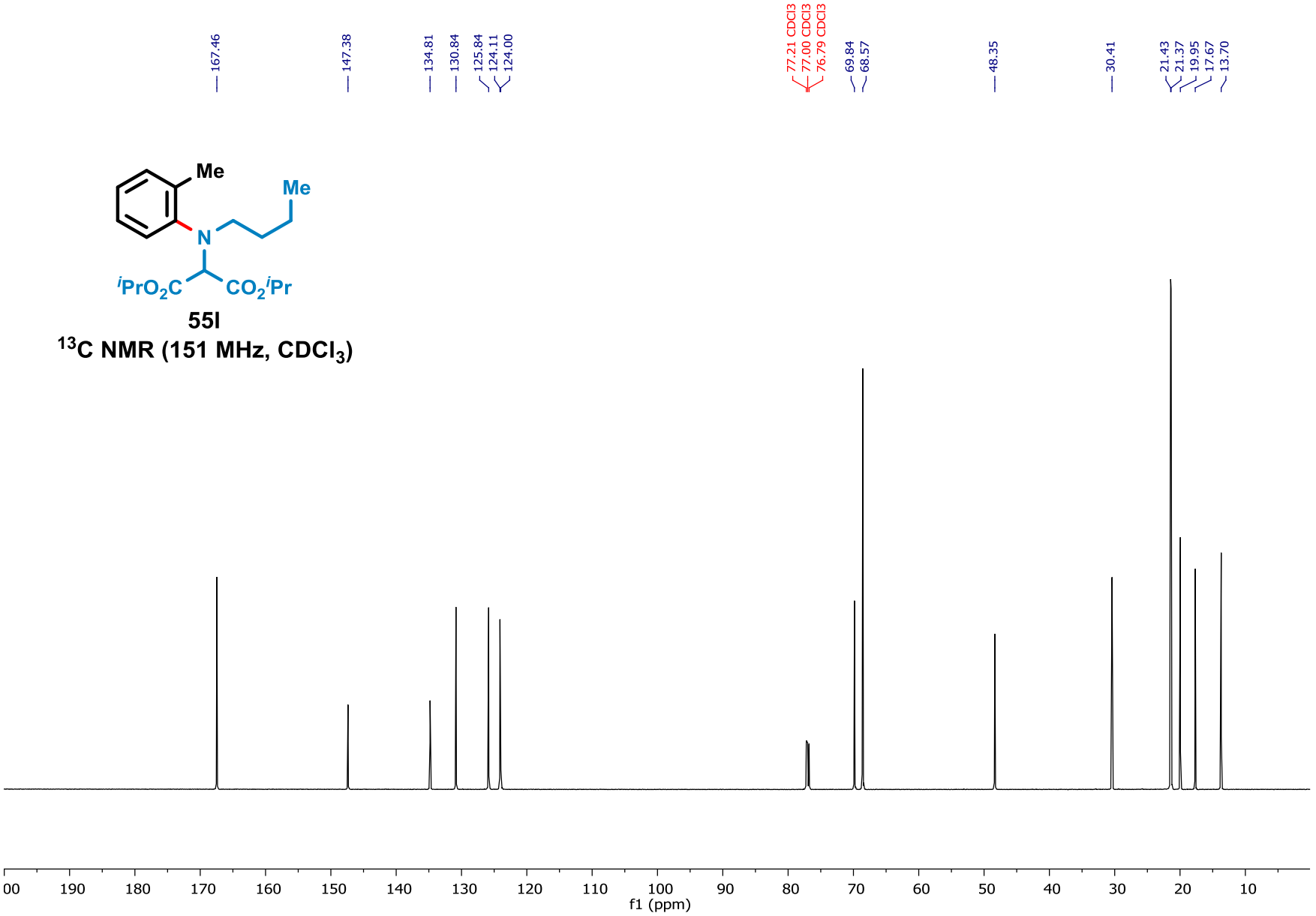
^{1}H NMR (600 MHz, $CDCl_3$)



55k

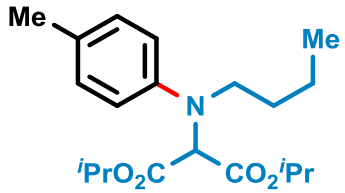
^{13}C NMR (151 MHz, $CDCl_3$)


Me
Me
N
iPrO2C
CO2iPr
55l
1H NMR (600 MHz, CDCl3)
7.33
7.32
7.26
7.16
7.15
7.12
7.10
7.09
6.99
6.98
6.96
5.13
5.12
5.11
5.10
5.09
5.08
5.07
4.27
3.41
3.40
3.39
2.30
1.35
1.33
1.31
1.31
1.29
1.28
1.26
1.25
1.24
1.23
0.83
0.82
0.80
0.98
1.03
1.03
0.98
2.00
0.93
2.05
3.12
4.45
11.96
3.06
f1 (ppm)



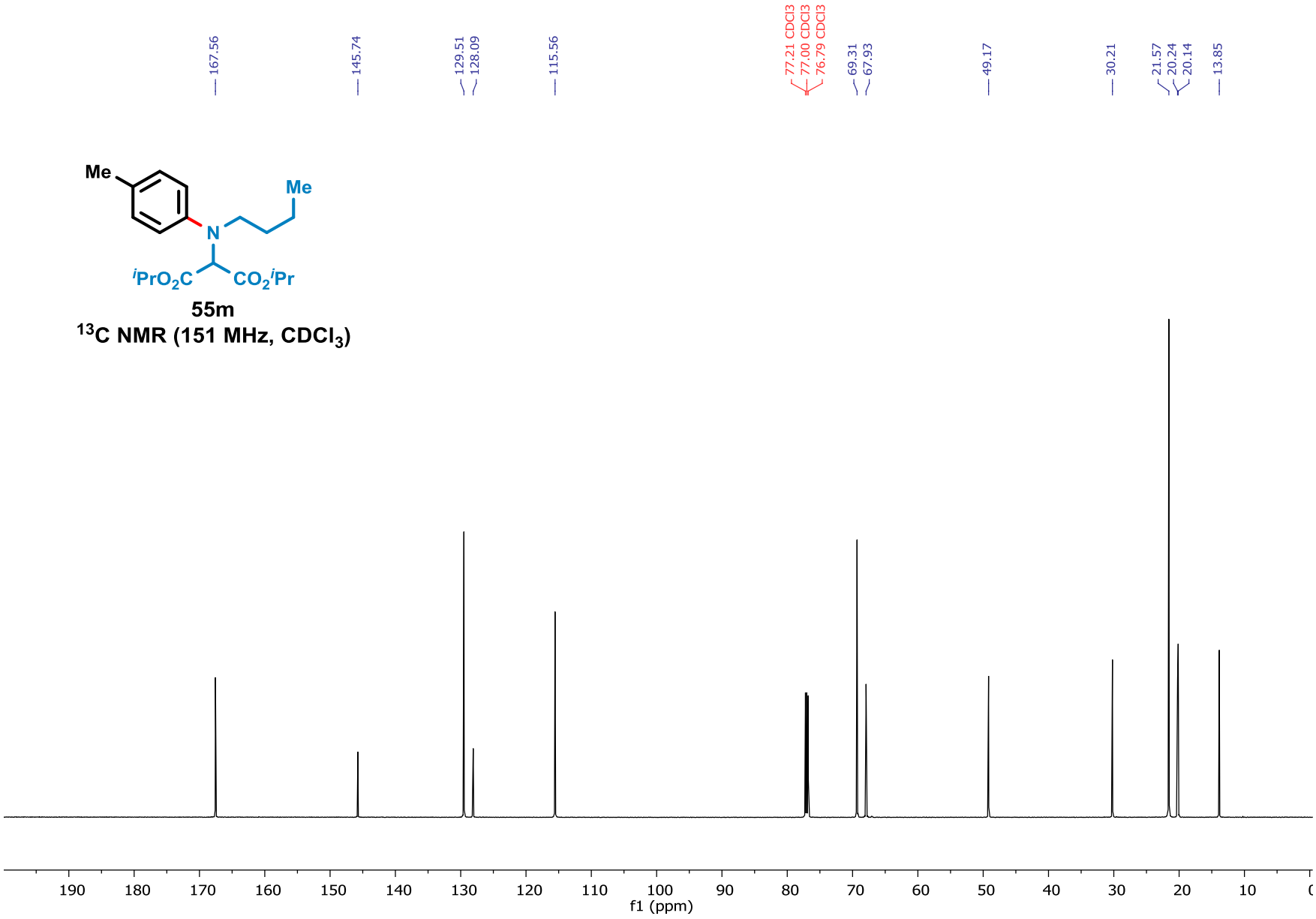
55l

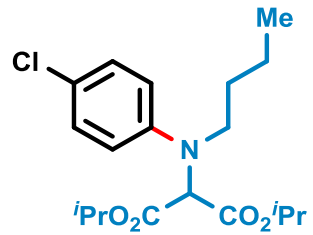
^{13}C NMR (151 MHz, $CDCl_3$)



55m

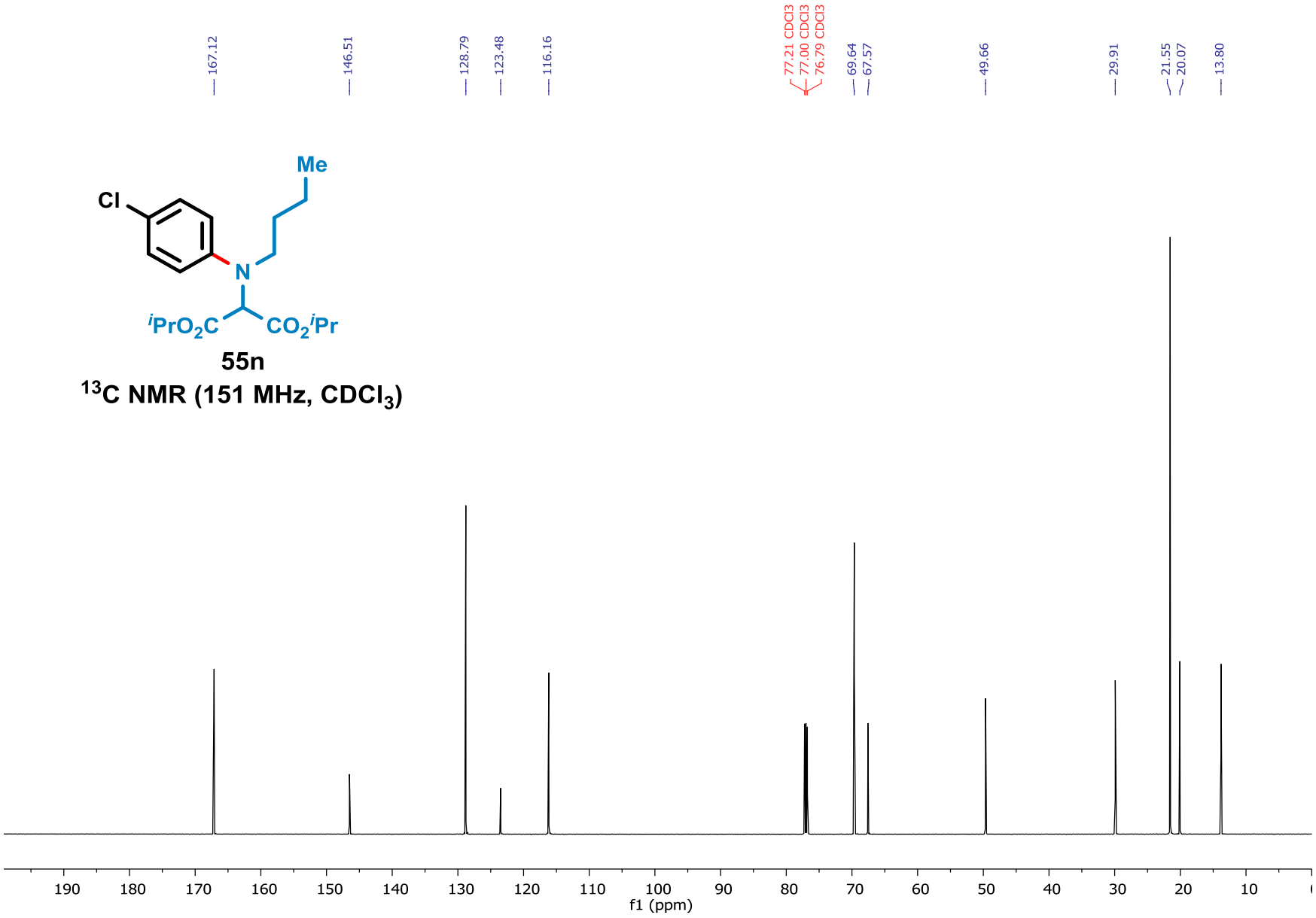
^{1}H NMR (600 MHz, $CDCl_3$)

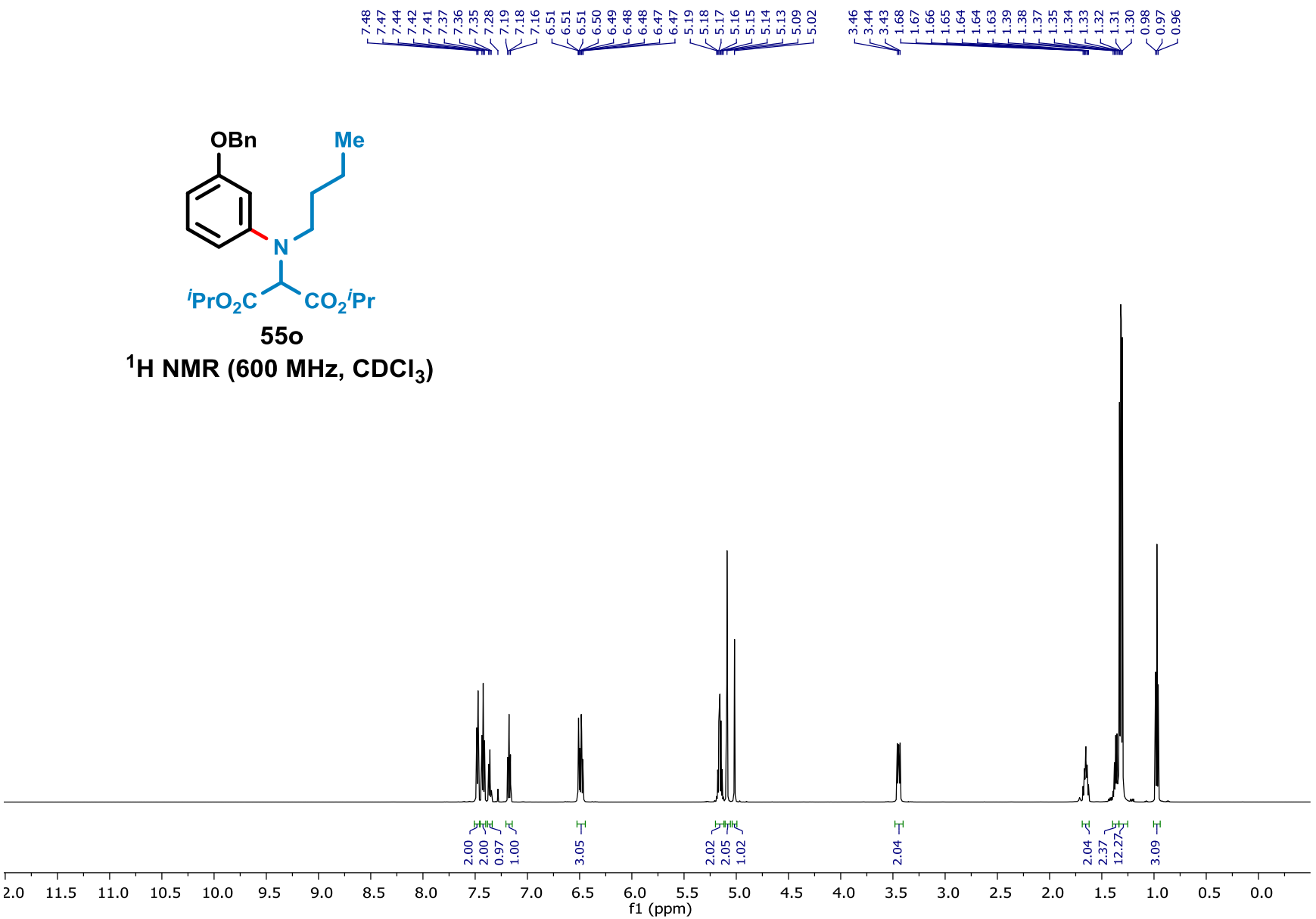

167.56
145.74
129.51
128.09
115.56
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.31
67.93
49.17
30.21
21.57
20.24
20.14
13.85
Me
Me
N
iPrO2C
CO2iPr
55m
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

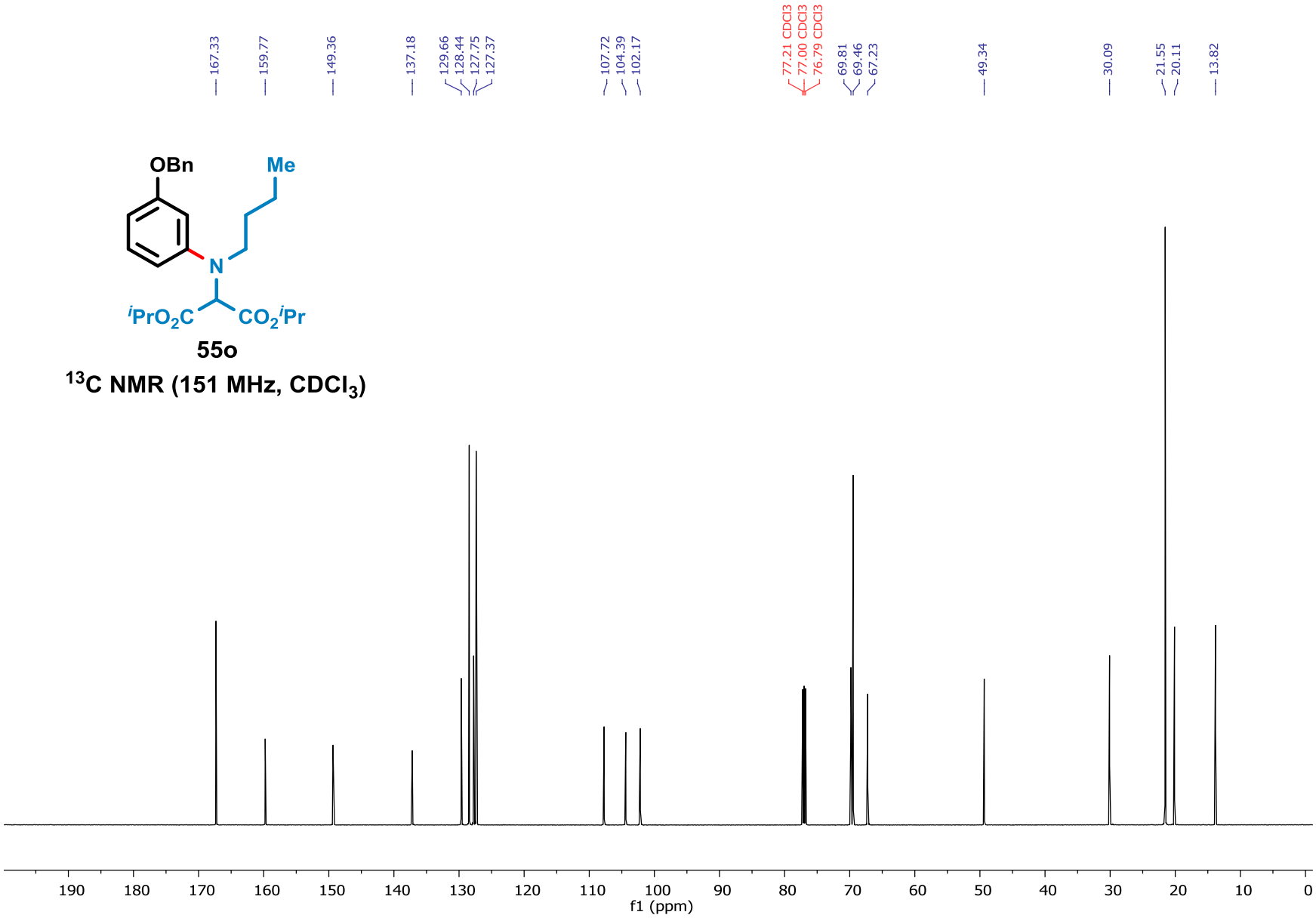


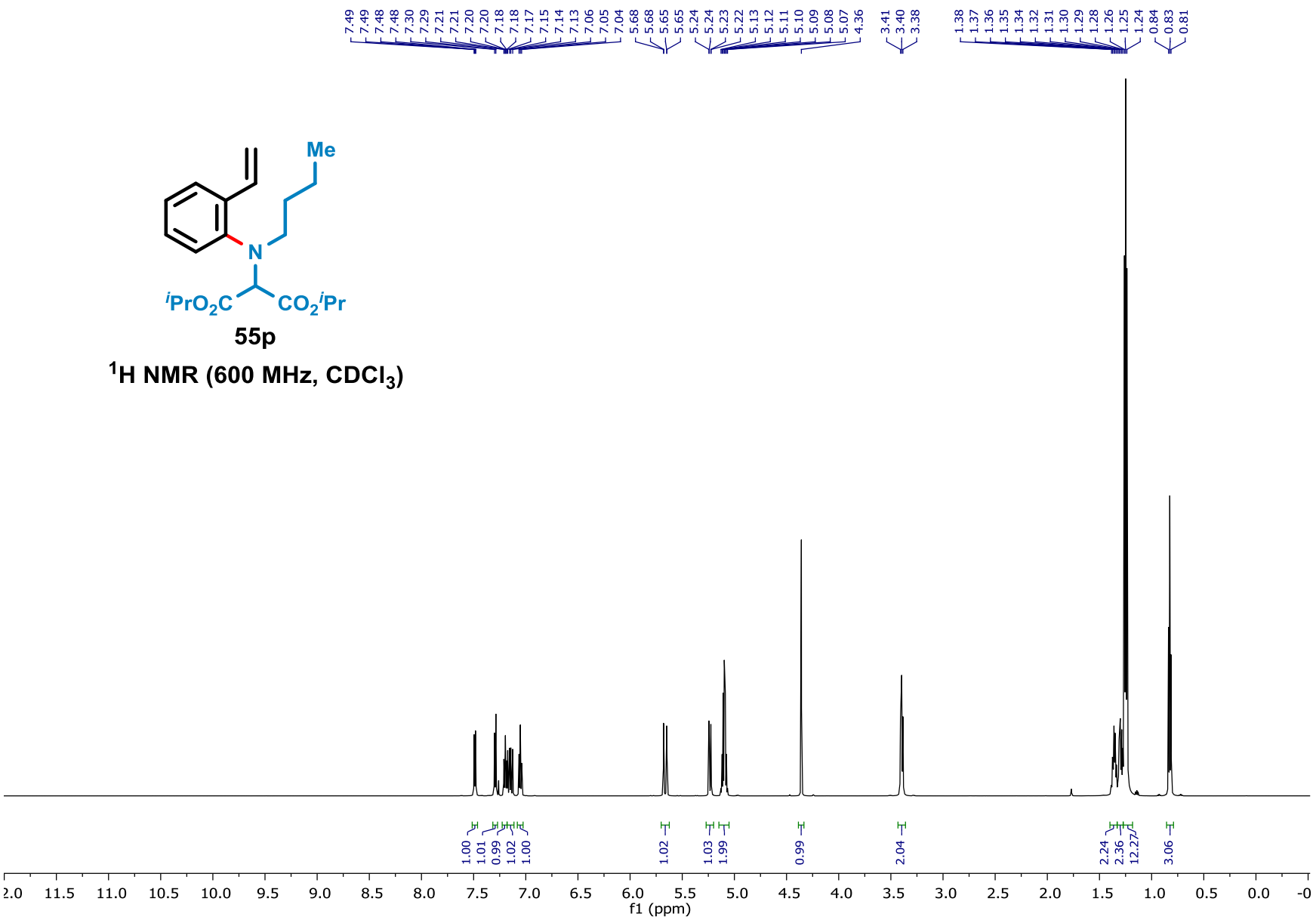
55n

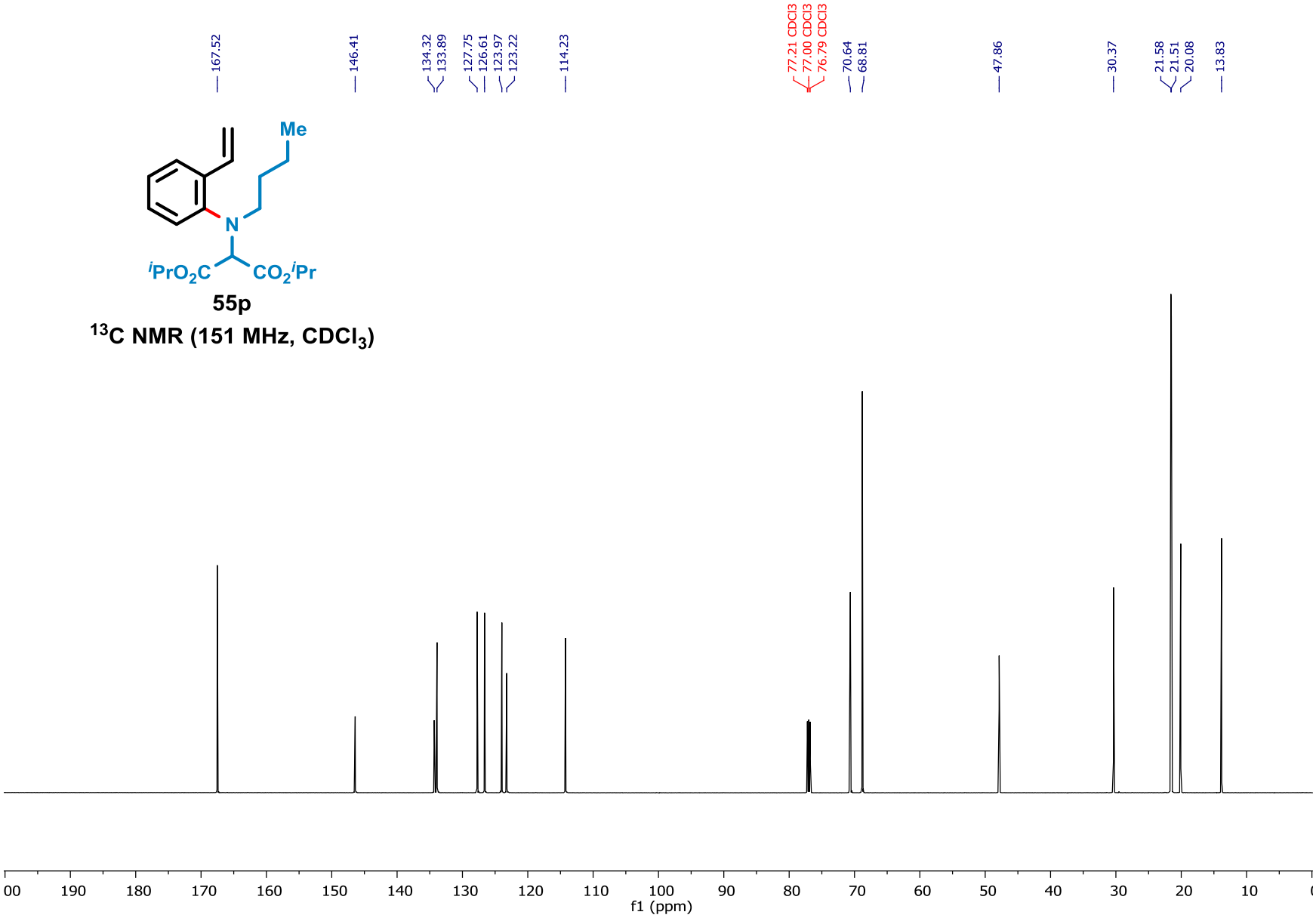
^{1}H NMR (600 MHz, $CDCl_3$)


167.12
146.51
128.79
123.48
116.16
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.64
67.57
49.66
29.91
21.55
20.07
13.80
Me
Cl
N
iPrO2C
CO2iPr
55n
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.48
7.47
7.44
7.42
7.41
7.37
7.36
7.35
7.28
7.19
7.18
7.16
6.51
6.51
6.51
6.50
6.49
6.48
6.48
6.47
6.47
5.19
5.18
5.17
5.16
5.15
5.14
5.13
5.09
5.02
3.46
3.44
3.43
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.39
1.38
1.37
1.35
1.34
1.33
1.32
1.31
1.30
0.98
0.97
0.96
OBn
Me
N
iPrO2C
CO2iPr
55o
1H NMR (600 MHz, CDCl3)
2.00
2.00
0.97
1.00
3.05
2.02
2.05
1.02
2.04
2.04
2.37
12.27
3.09
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

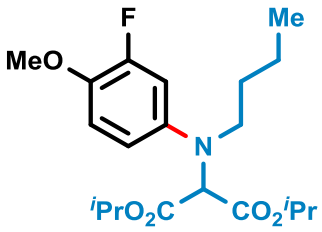

167.33
159.77
149.36
137.18
129.66
128.44
127.75
127.37
107.72
104.39
102.17
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.81
69.46
67.23
49.34
30.09
21.55
20.11
13.82
OBn
Me
N
iPrO2C
CO2iPr
55o
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
N
iPrO2C
CO2iPr
55p
1H NMR (600 MHz, CDCl3)
f1 (ppm)



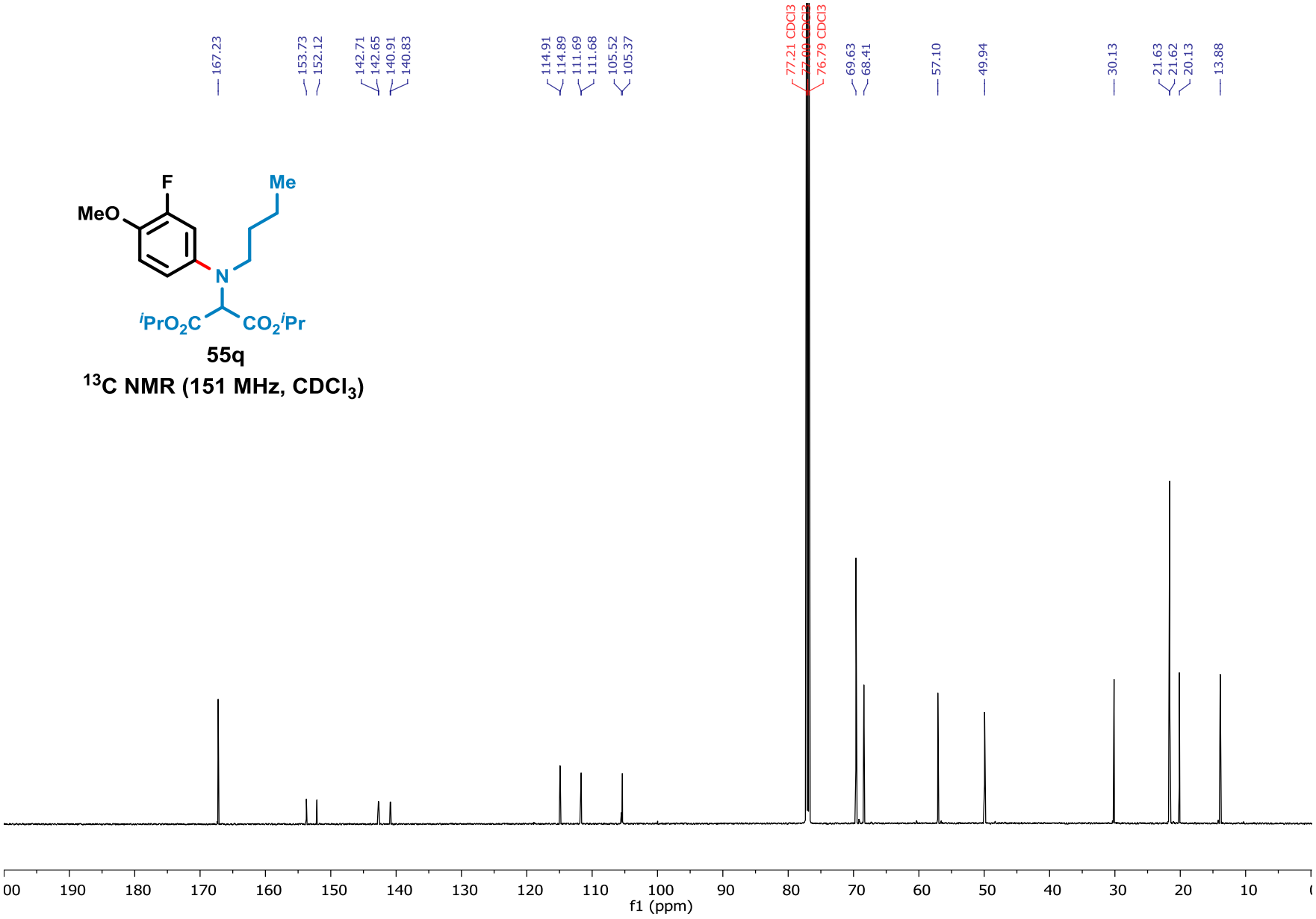
55p

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



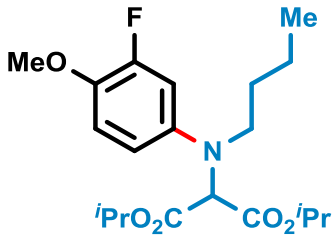
55q

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



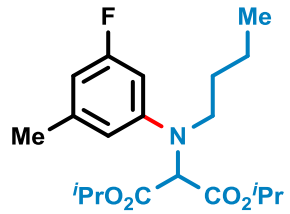
55q

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



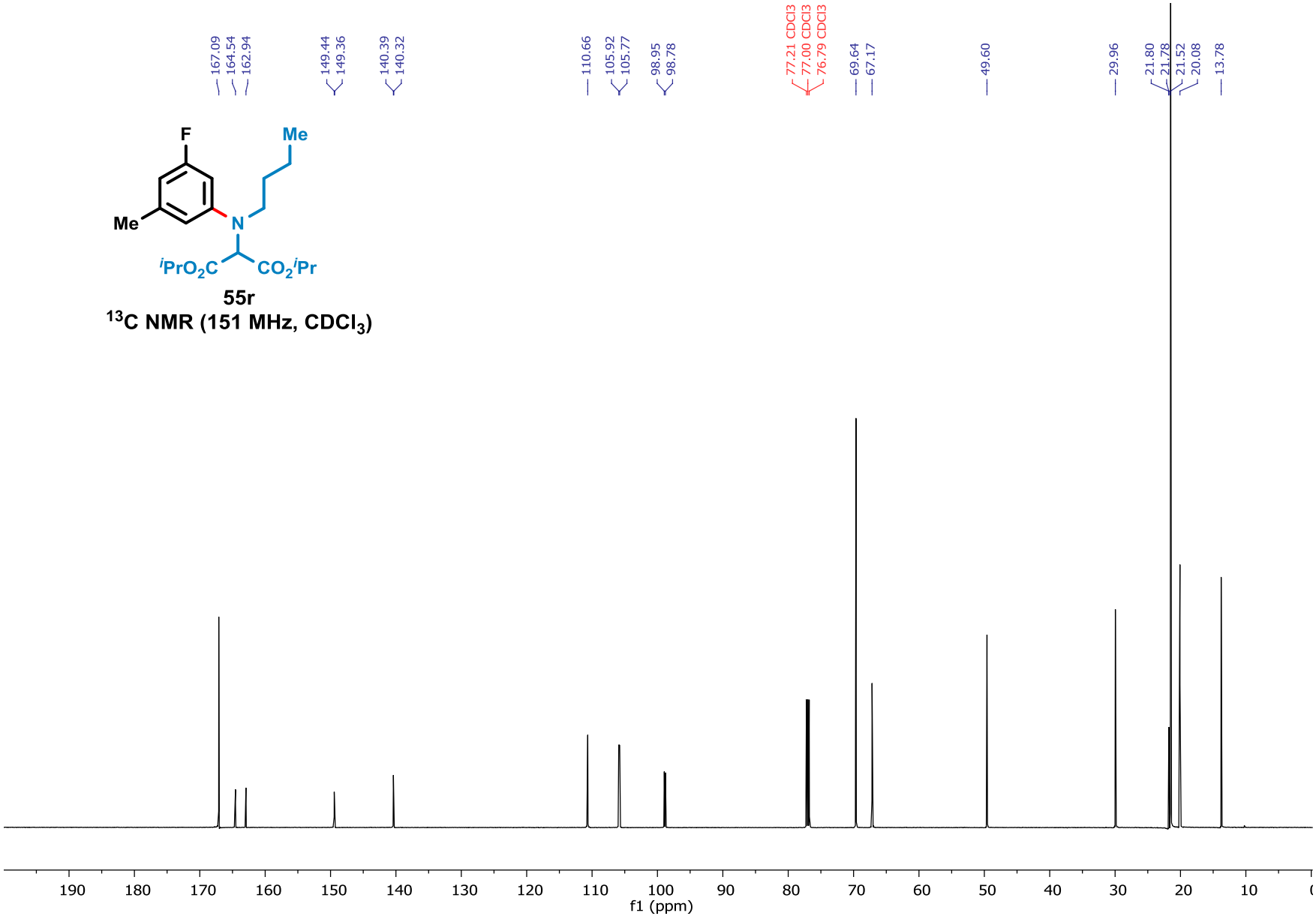
55q

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



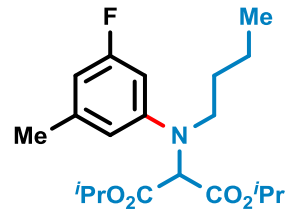
55r

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



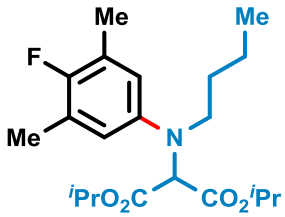
55r

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



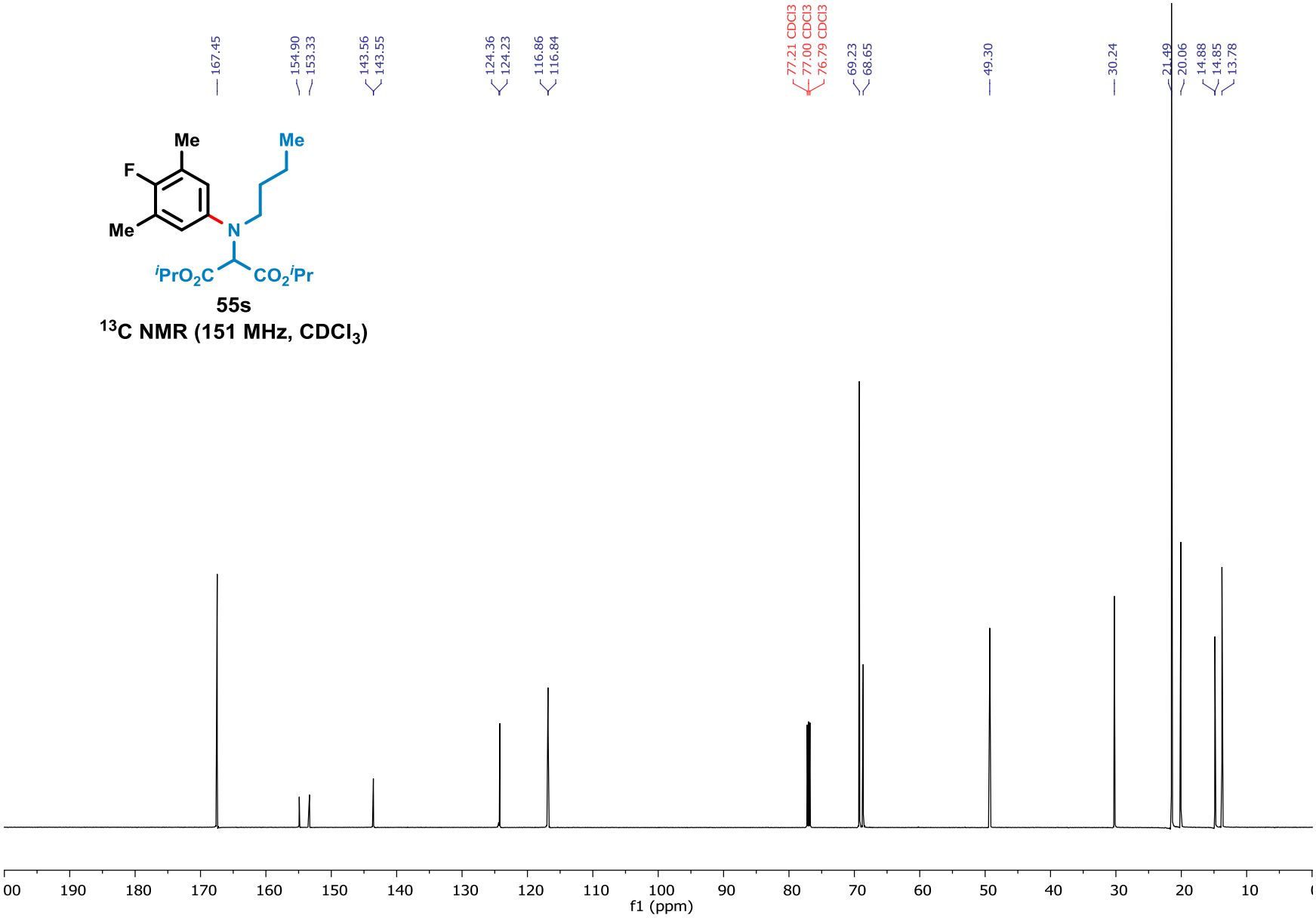
55r

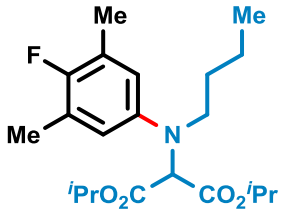
^{19}F NMR (471 MHz, $CDCl_3$)



55s

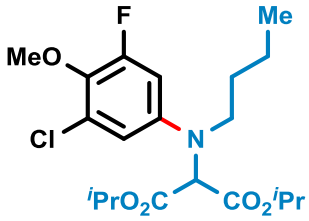
^{1}H NMR (600 MHz, $CDCl_3$)


167.45
154.90
153.33
143.56
143.55
124.36
124.23
116.86
116.84
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.23
68.65
49.30
30.24
21.49
20.06
14.88
14.85
13.78
Me
F
Me
N
Me
iPrO2C
CO2iPr
55s
13C NMR (151 MHz, CDCl3)
f1 (ppm)



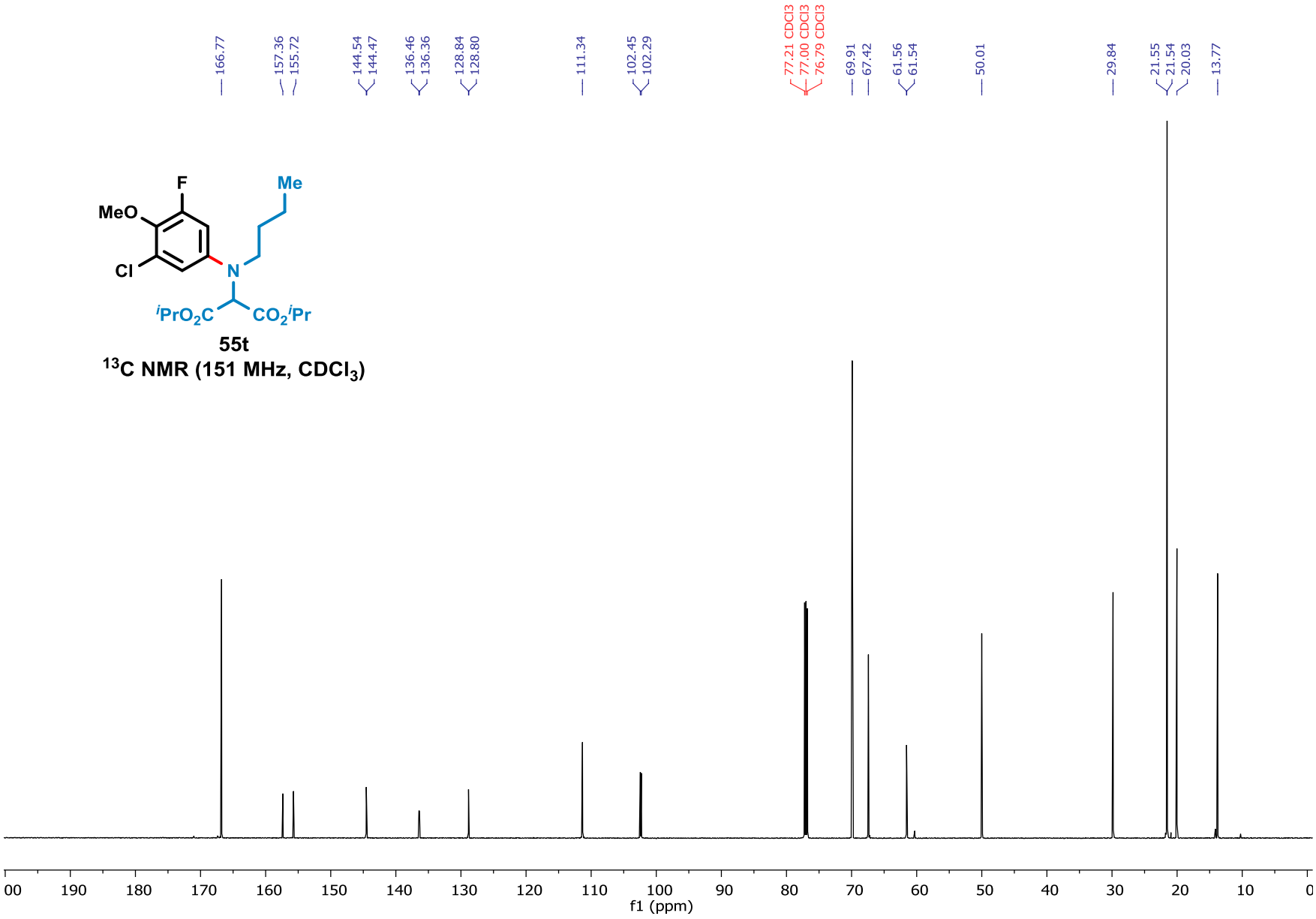
55s

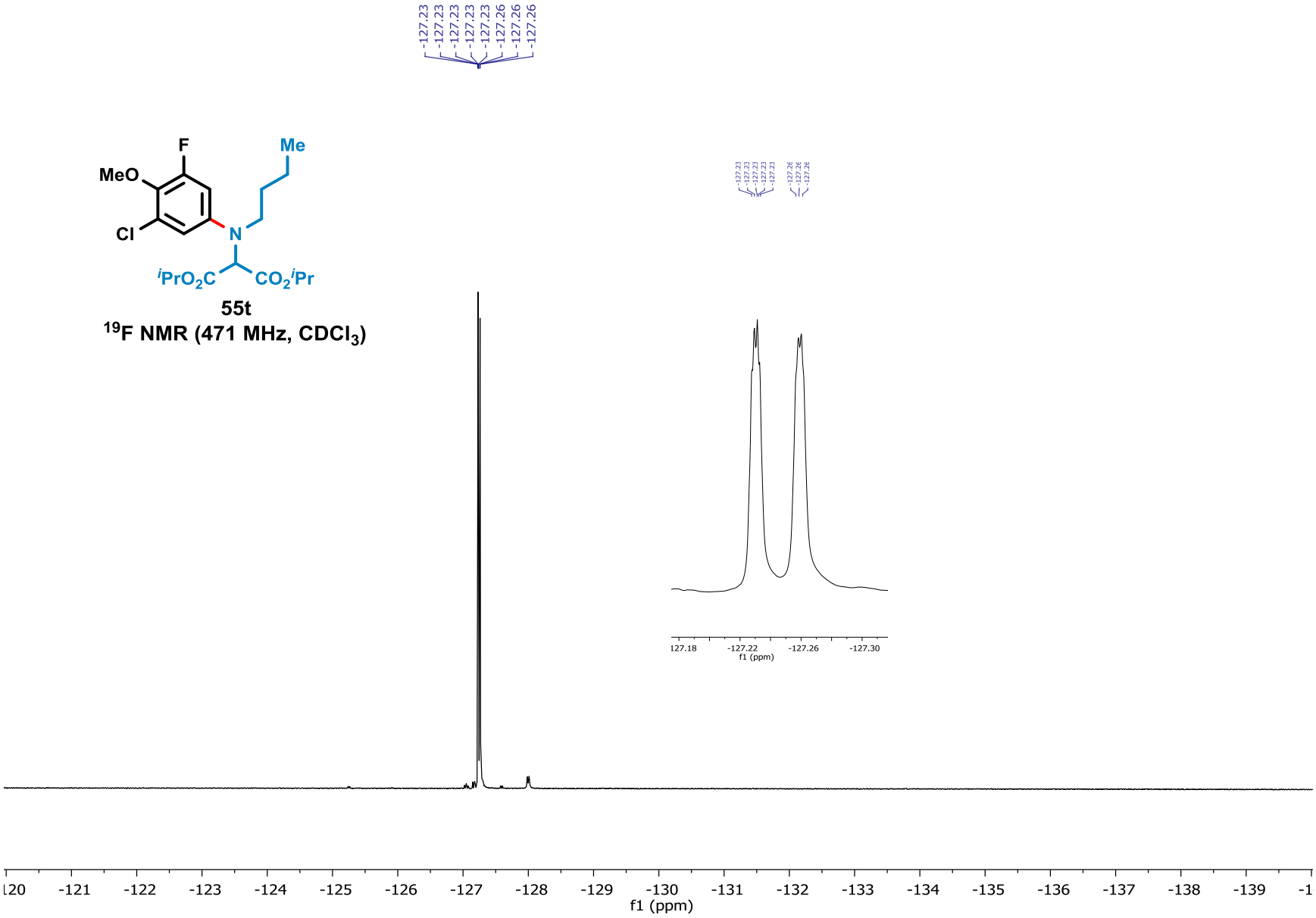
^{19}F NMR (471 MHz, $CDCl_3$)

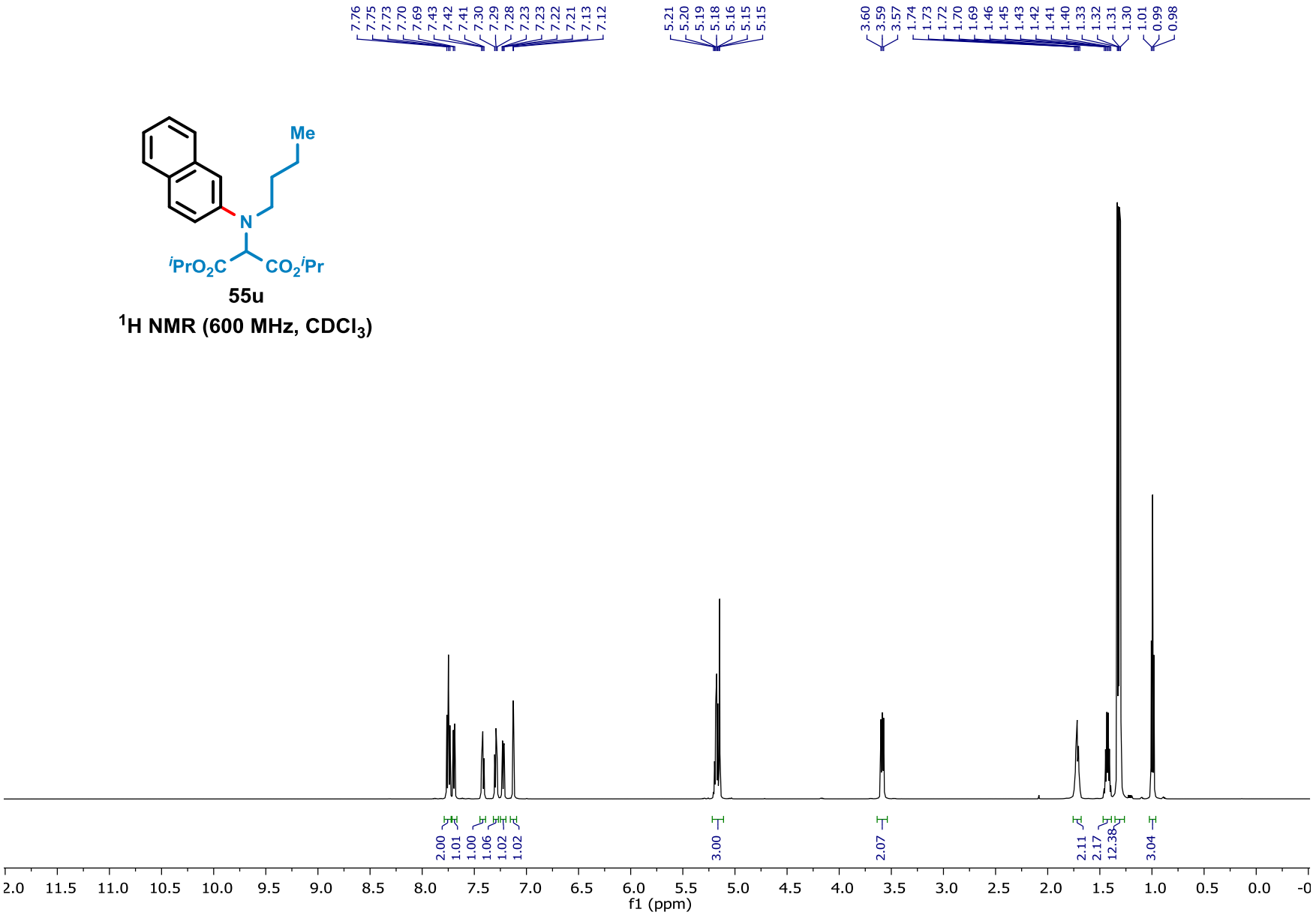


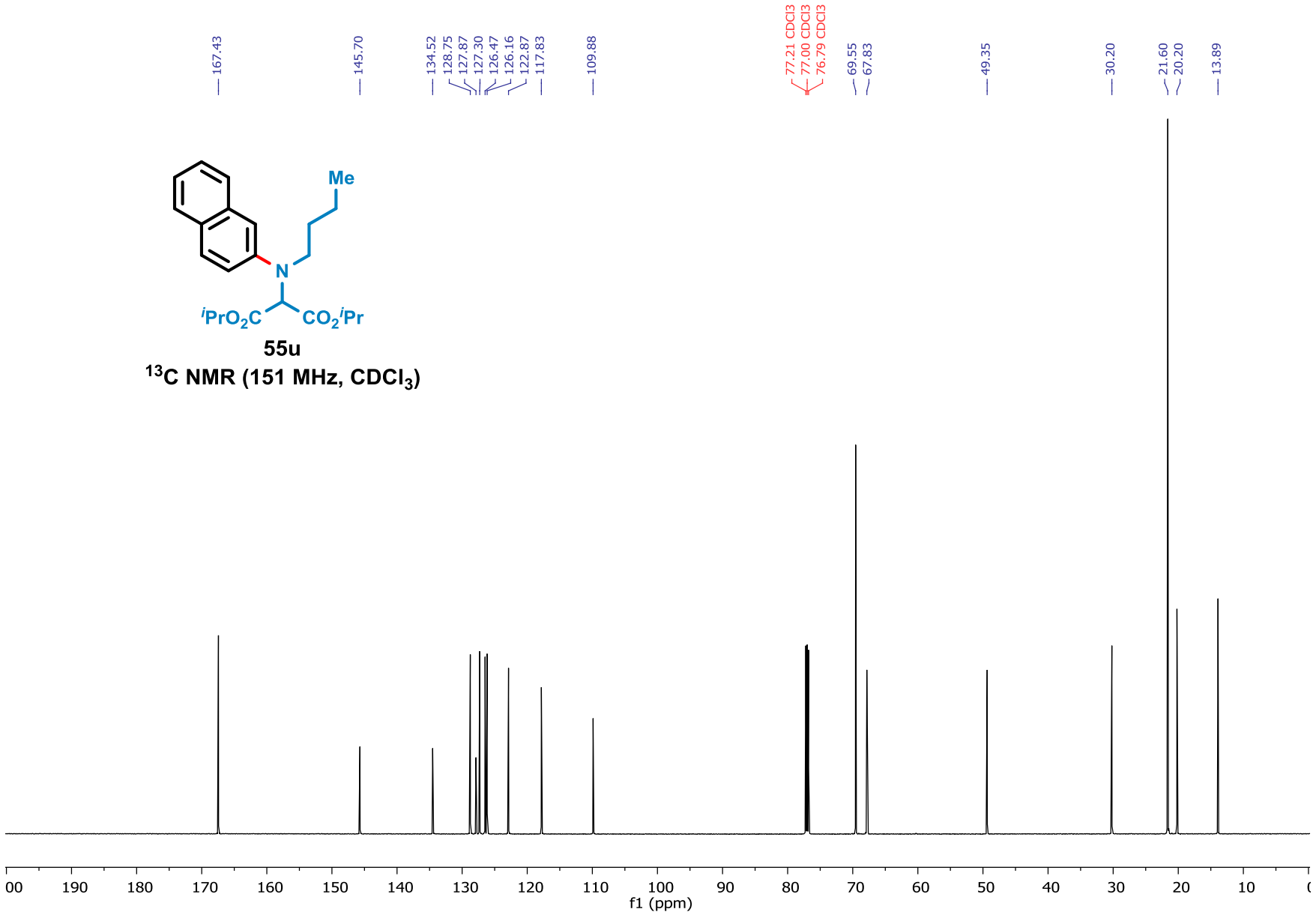
55t

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


166.77
157.36
155.72
144.54
144.47
136.46
136.36
128.84
128.80
111.34
102.45
102.29
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.91
67.42
61.56
61.54
50.01
29.84
21.55
21.54
20.03
13.77
F
Me
MeO
Cl
N
iPrO2C
CO2iPr
55t
13C NMR (151 MHz, CDCl3)
f1 (ppm)

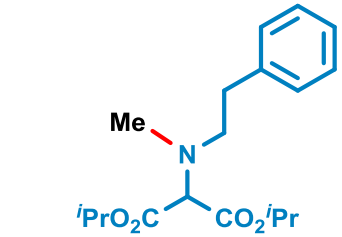

-127.23
-127.23
-127.23
-127.23
-127.23
-127.26
-127.26
-127.26
F
Me
MeO
Cl
N
iPrO2C
CO2iPr
55t
19F NMR (471 MHz, CDCl3)
-127.18
-127.22
-127.26
-127.30
f1 (ppm)
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)


7.76
7.75
7.73
7.70
7.69
7.43
7.42
7.41
7.30
7.29
7.28
7.23
7.23
7.22
7.21
7.13
7.12
5.21
5.20
5.19
5.18
5.16
5.15
5.15
3.60
3.59
3.57
1.74
1.73
1.72
1.70
1.69
1.46
1.45
1.43
1.42
1.41
1.40
1.33
1.32
1.31
1.30
1.01
0.99
0.98
Me
N
iPrO2C
CO2iPr
55u
1H NMR (600 MHz, CDCl3)
2.00
1.01
1.00
1.06
1.02
1.02
3.00
2.07
2.11
2.17
12.38
3.04
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



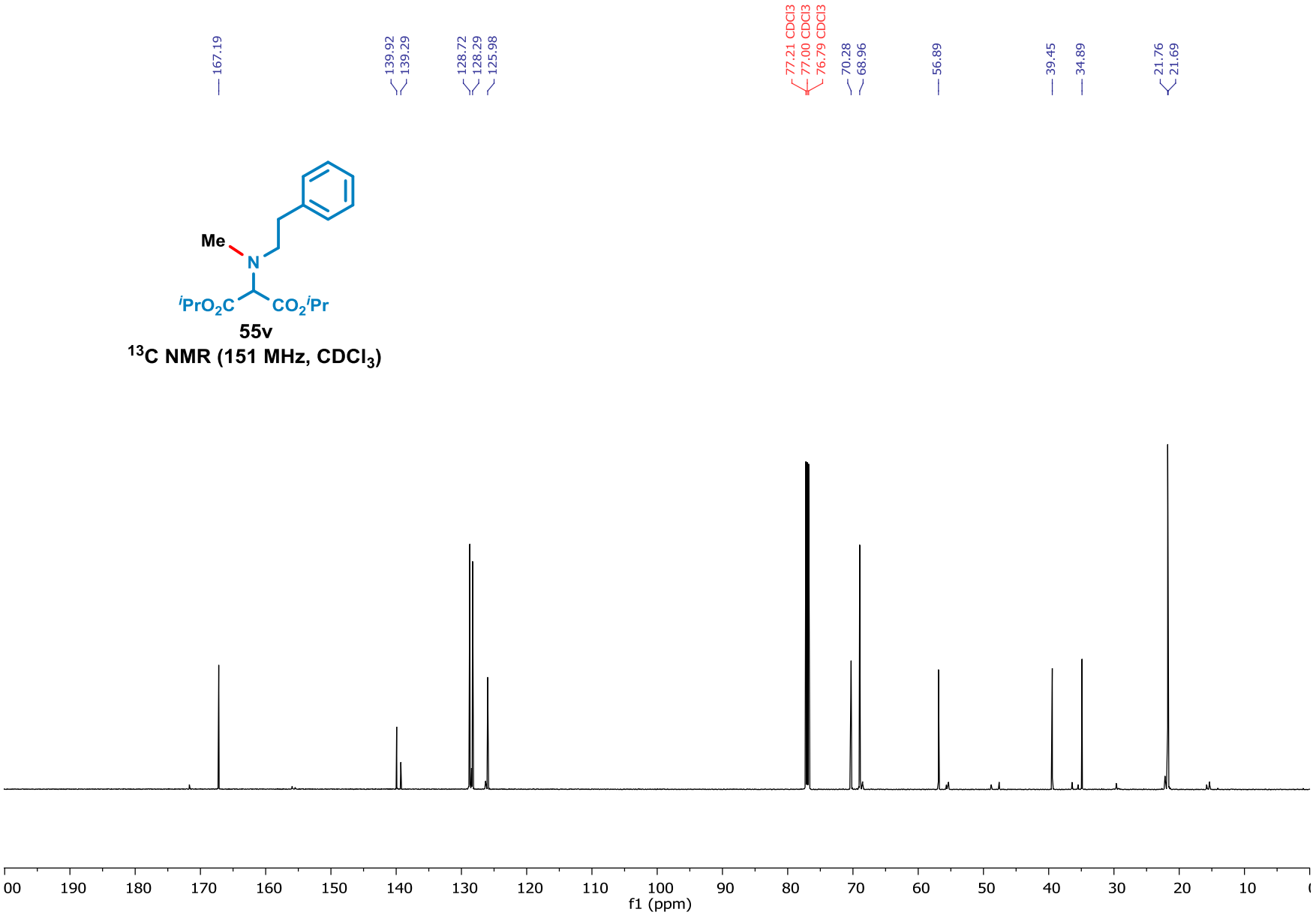
55u

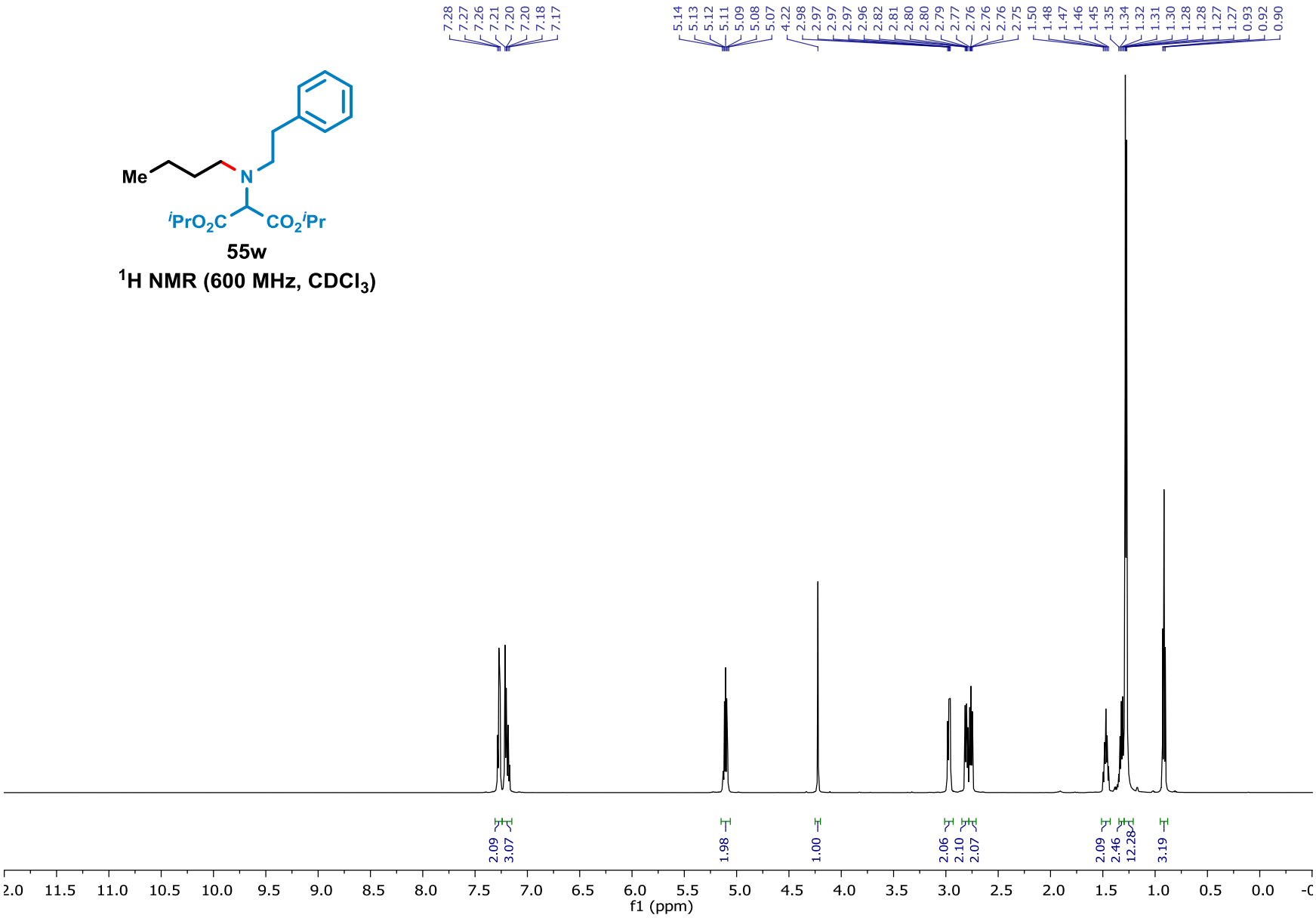
^{13}C NMR (151 MHz, $CDCl_3$)

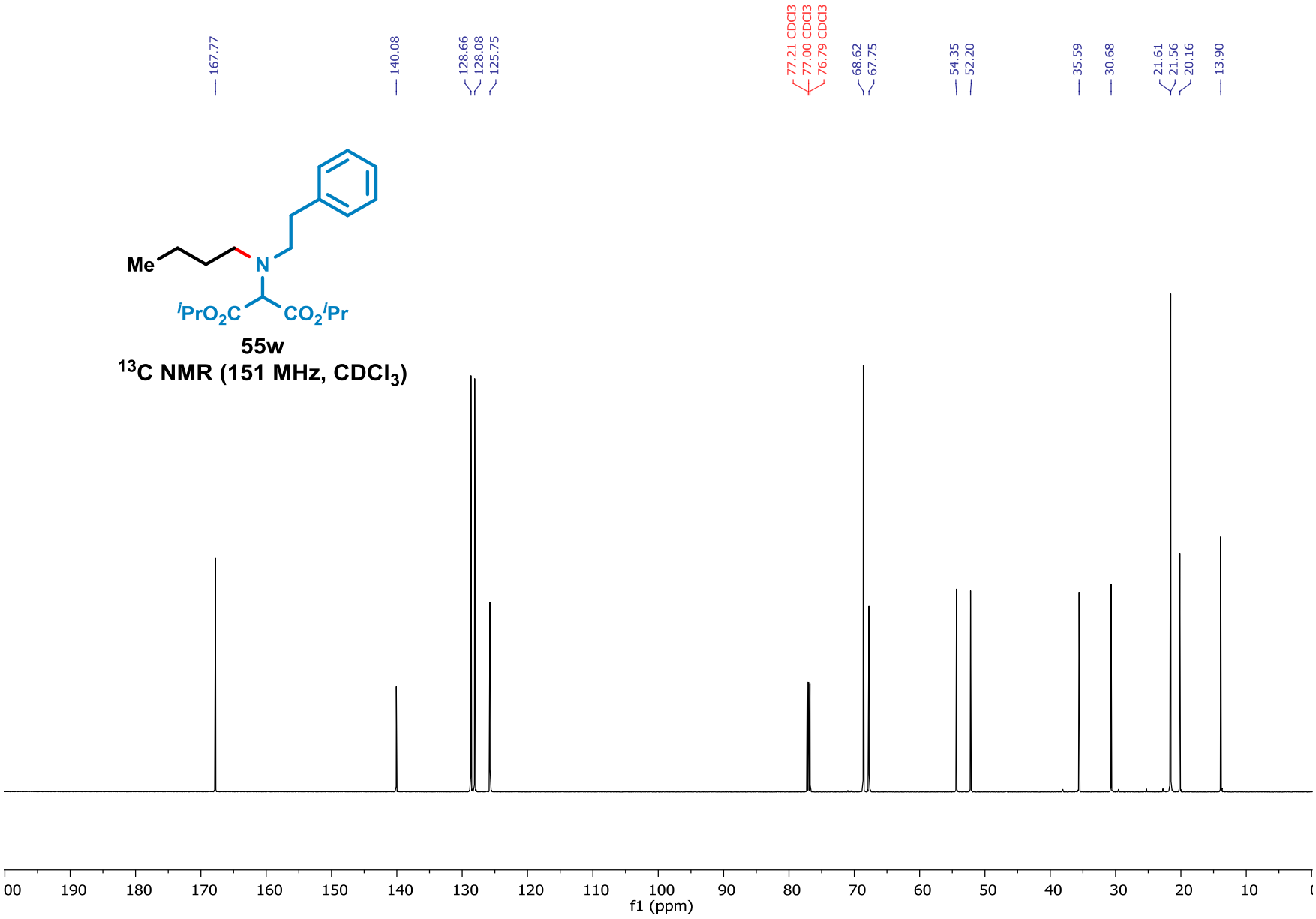


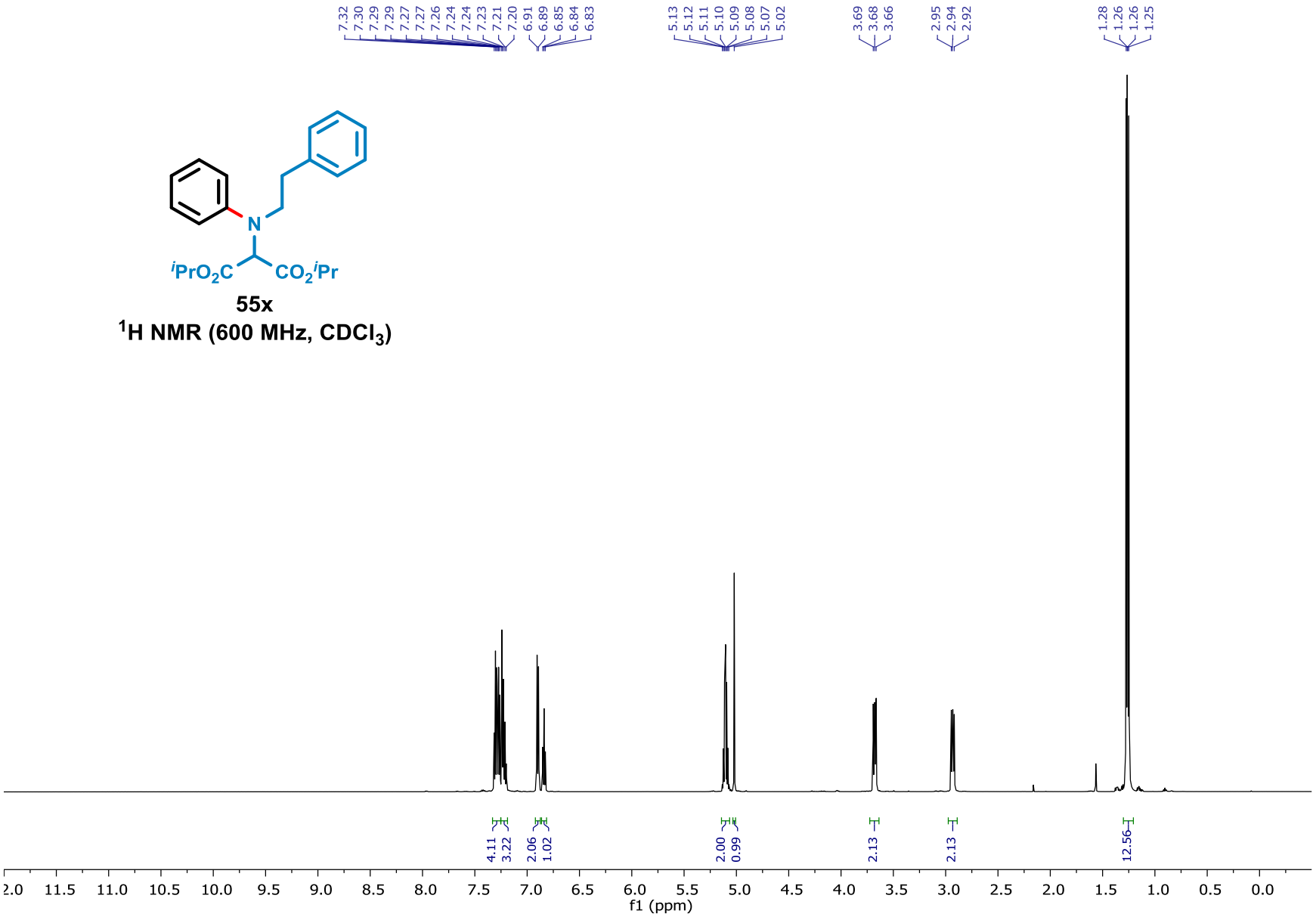
55v

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


167.19
139.92
139.29
128.72
128.29
125.98
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.28
68.96
56.89
39.45
34.89
21.76
21.69
Me
N
iPrO2C
CO2iPr
55v
13C NMR (151 MHz, CDCl3)
f1 (ppm)

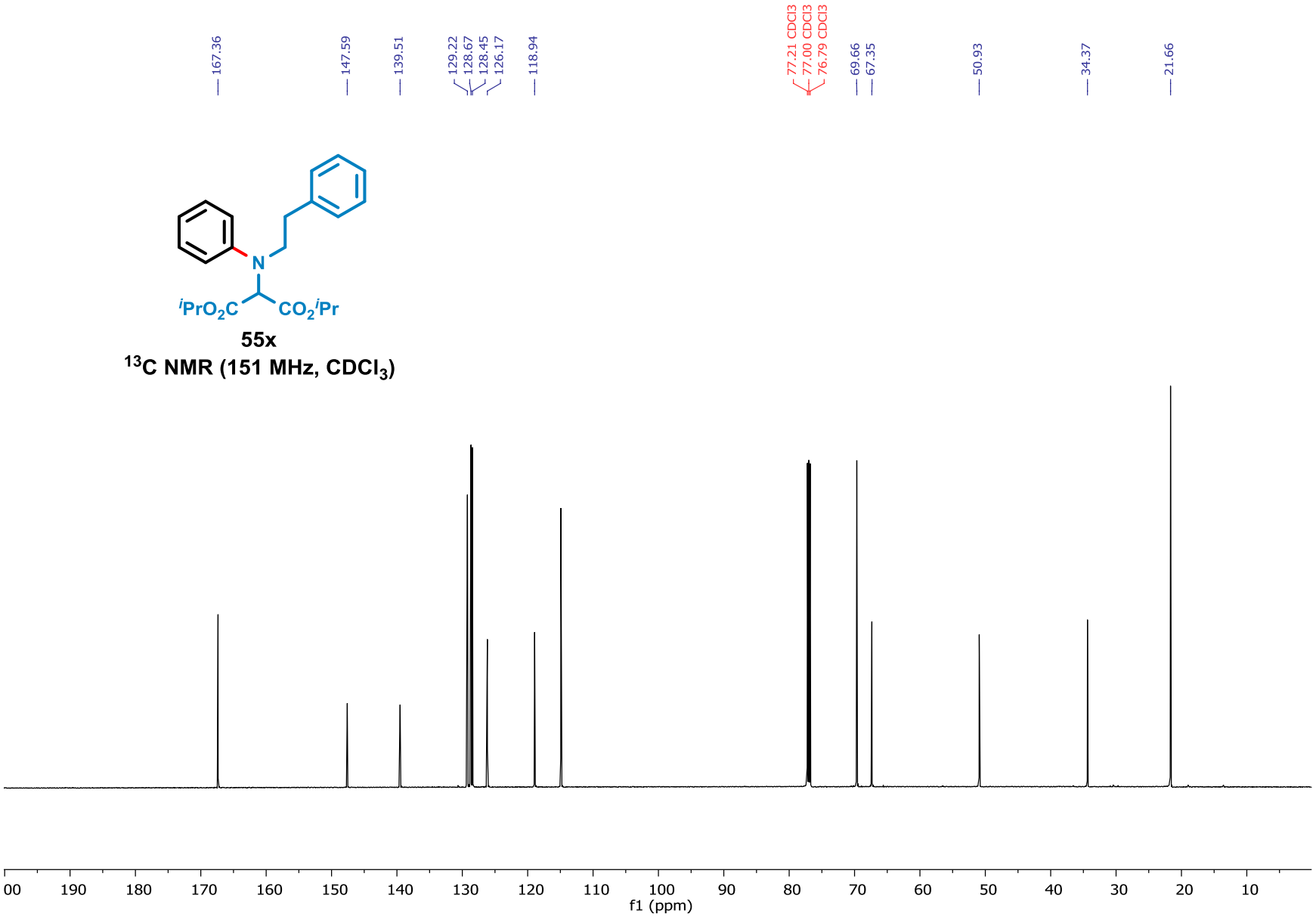

Me
N
iPrO2C
CO2iPr
55w
1H NMR (600 MHz, CDCl3)
f1 (ppm)

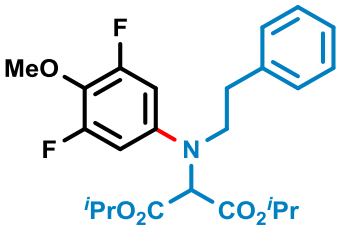

167.77
140.08
128.66
128.08
125.75
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.62
67.75
54.35
52.20
35.59
30.68
21.61
21.56
20.16
13.90
Me
N
iPrO2C
CO2iPr
55w
13C NMR (151 MHz, CDCl3)
f1 (ppm)



55x

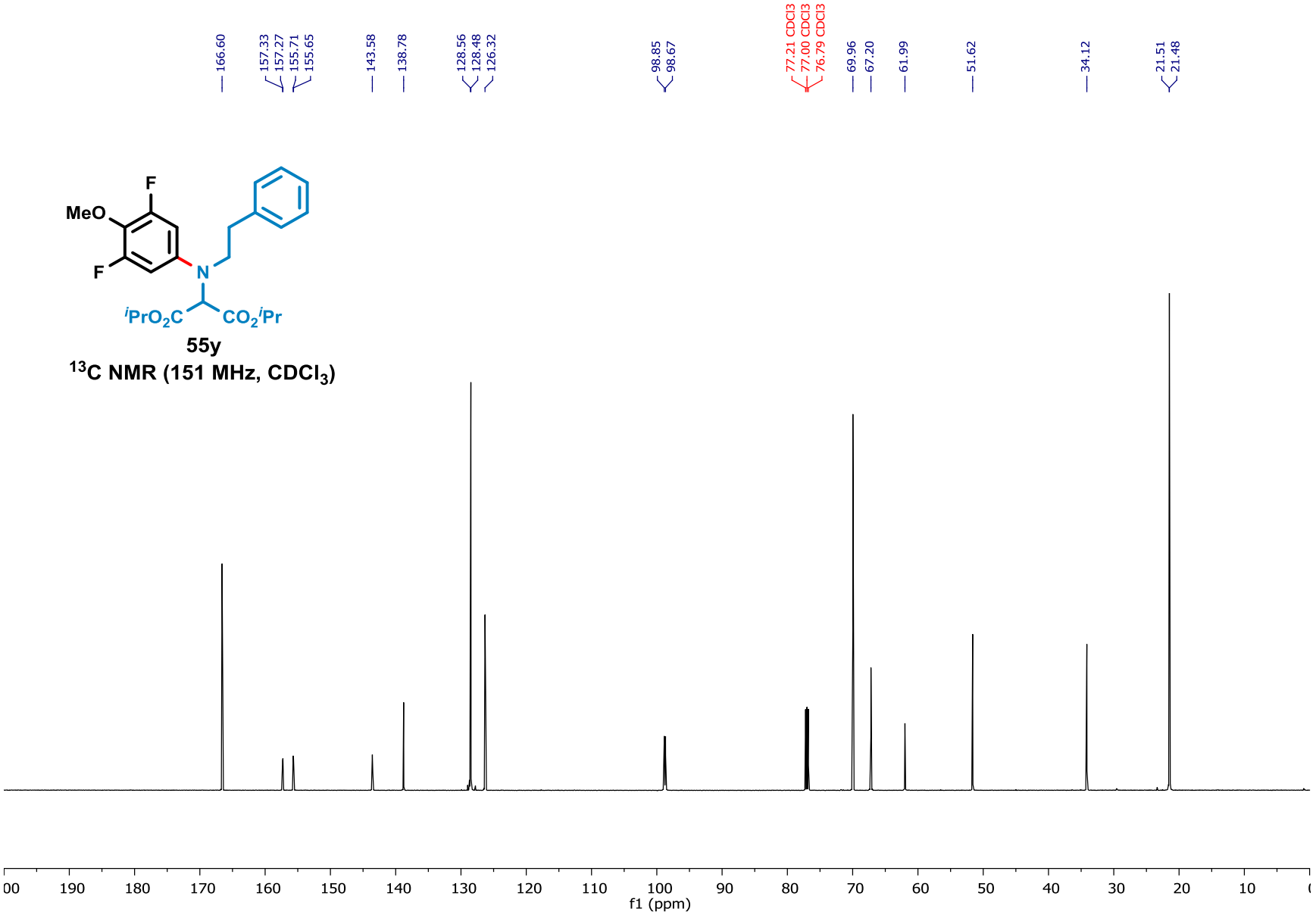
^{1}H NMR (600 MHz, $CDCl_3$)

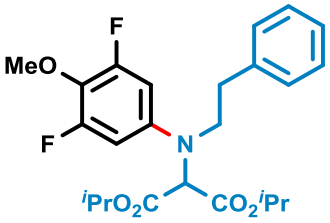

167.36
147.59
139.51
129.22
128.67
128.45
126.17
118.94
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.66
67.35
50.93
34.37
21.66
N
iPrO2C
CO2iPr
55x
13C NMR (151 MHz, CDCl3)
f1 (ppm)



55y

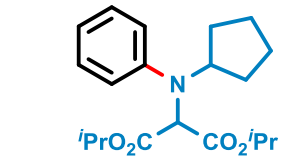
^{1}H NMR (600 MHz, $CDCl_3$)


166.60
157.33
157.27
155.71
155.65
143.58
138.78
128.56
128.48
126.32
98.85
98.67
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.96
67.20
61.99
51.62
34.12
21.51
21.48
F
MeO
F
N
iPrO2C
CO2iPr
55y
13C NMR (151 MHz, CDCl3)
f1 (ppm)



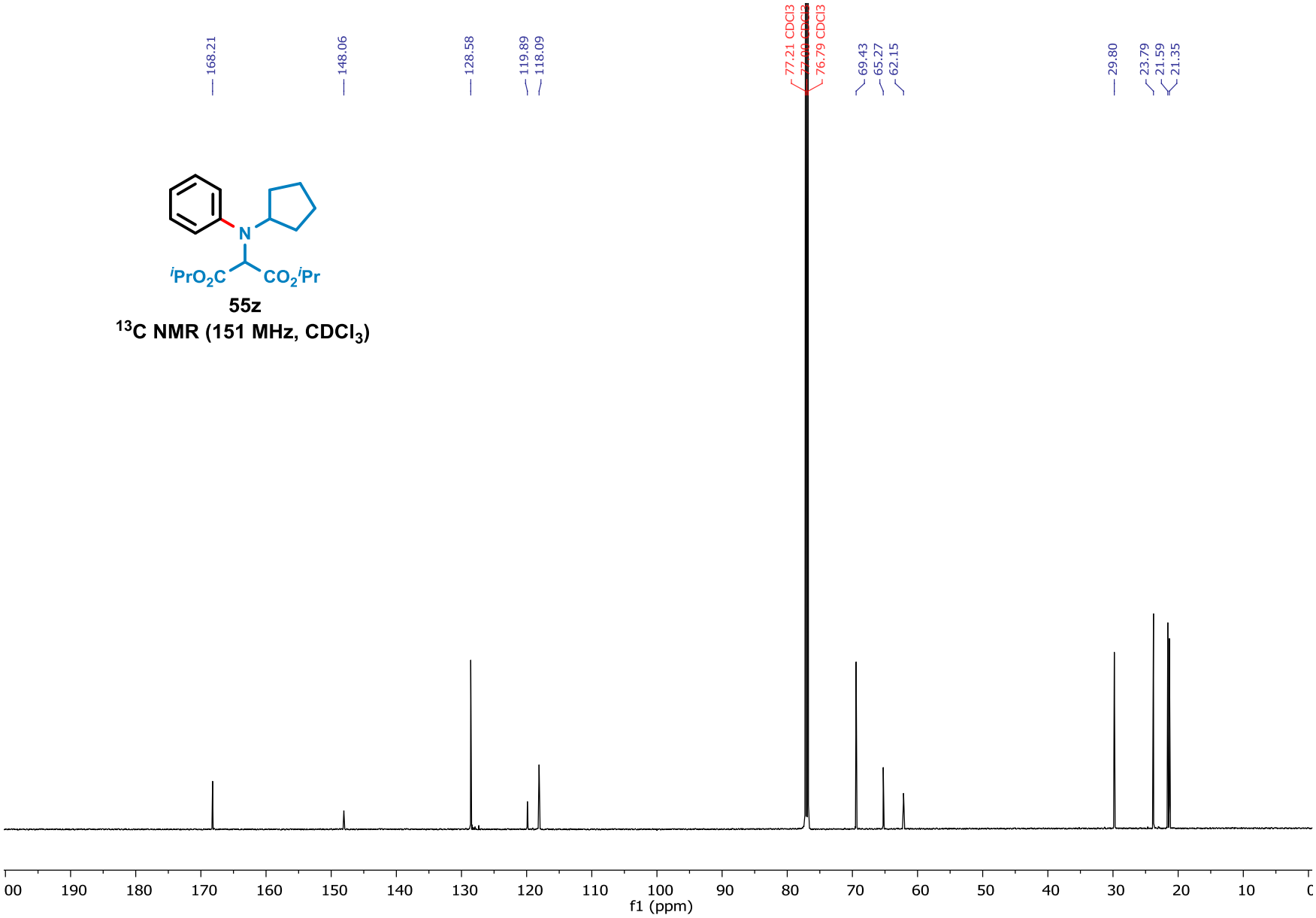
55y

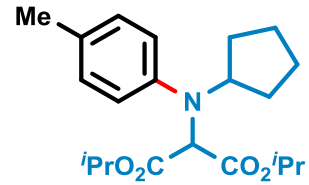
^{19}F NMR (471 MHz, $CDCl_3$)



55z

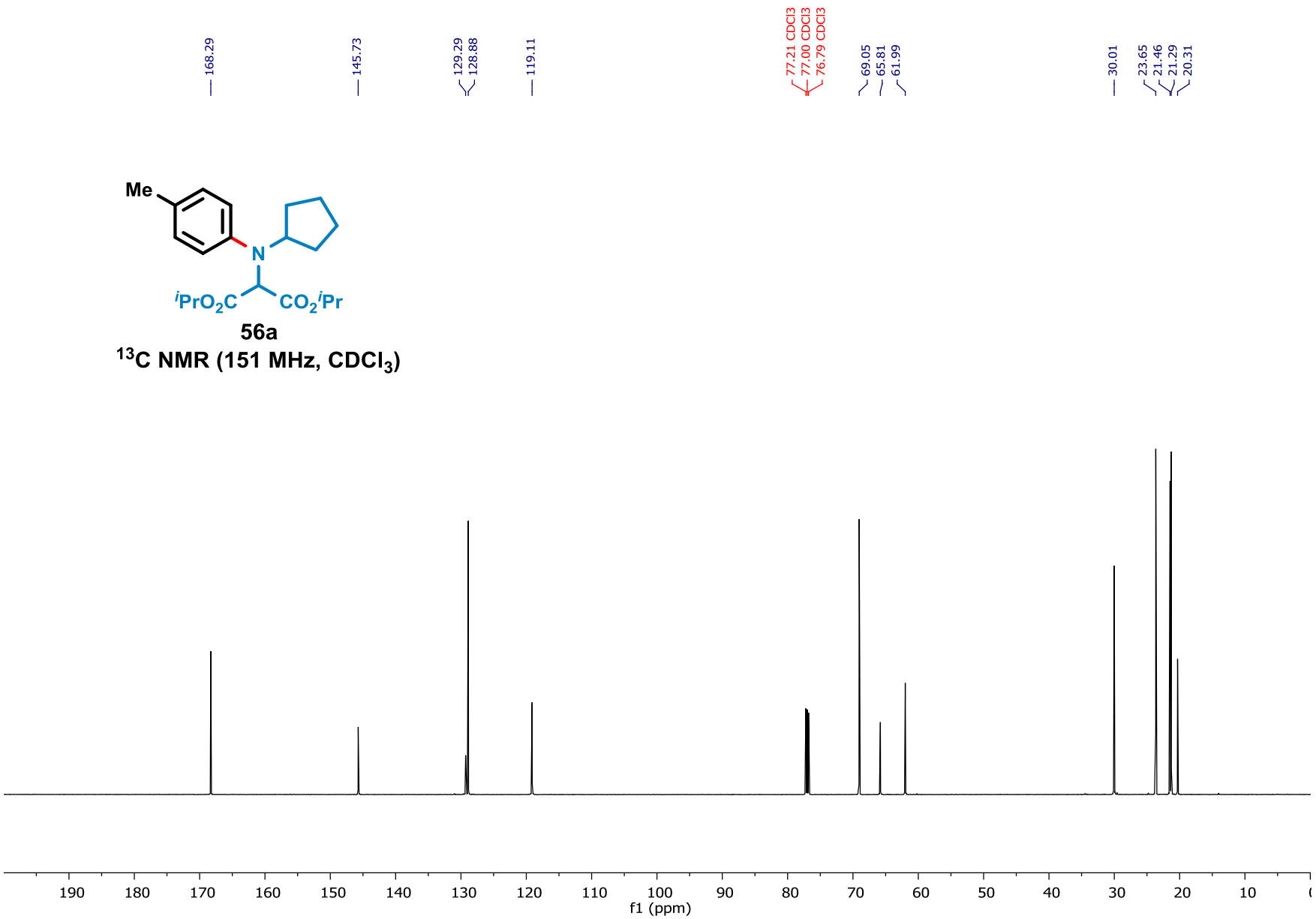
^{1}H NMR (600 MHz, $CDCl_3$)


168.21
148.06
128.58
119.89
118.09
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.43
65.27
62.15
29.80
23.79
21.59
21.35
N
iPrO2C
CO2iPr
55z
13C NMR (151 MHz, CDCl3)
f1 (ppm)



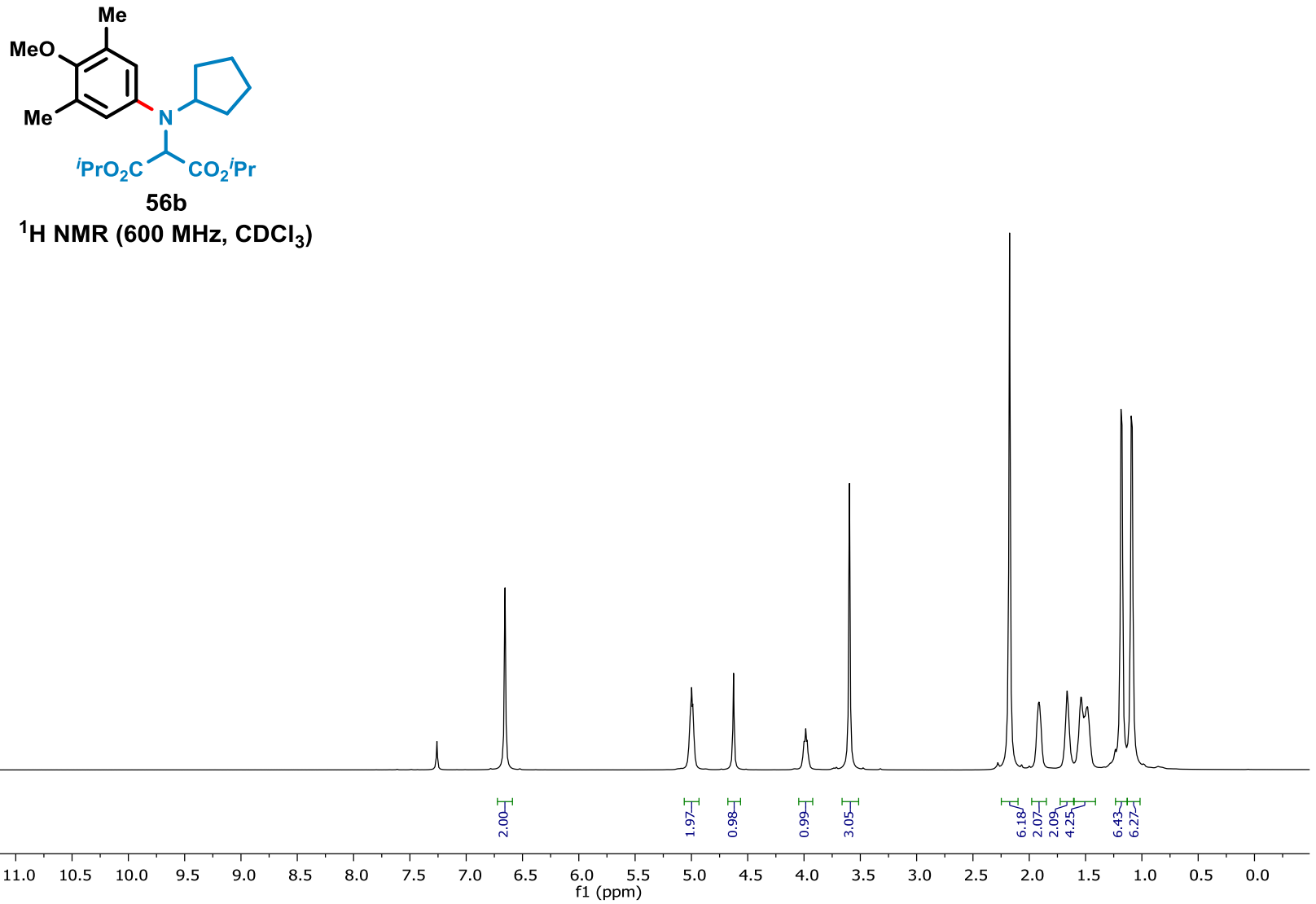
56a

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



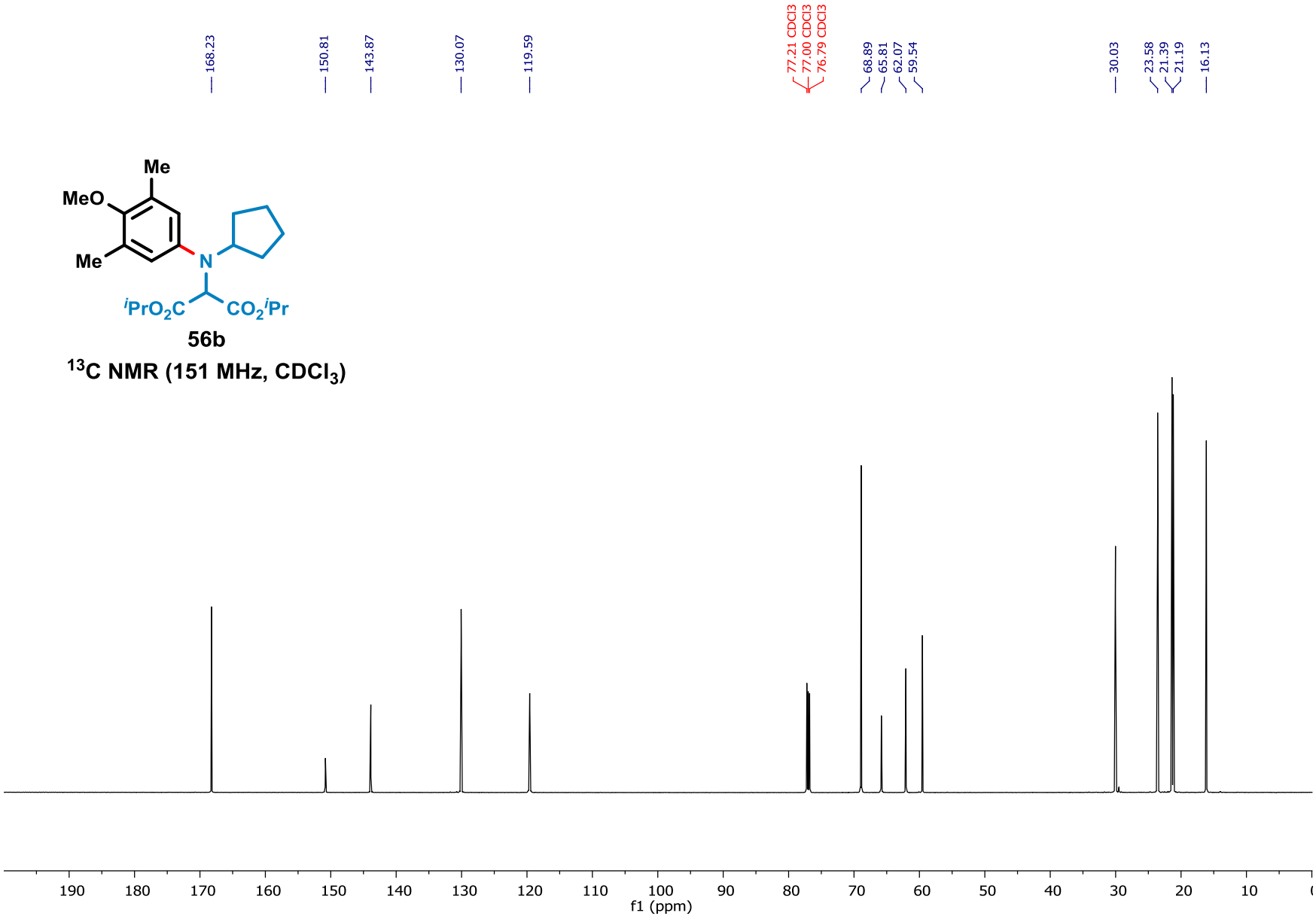
56a

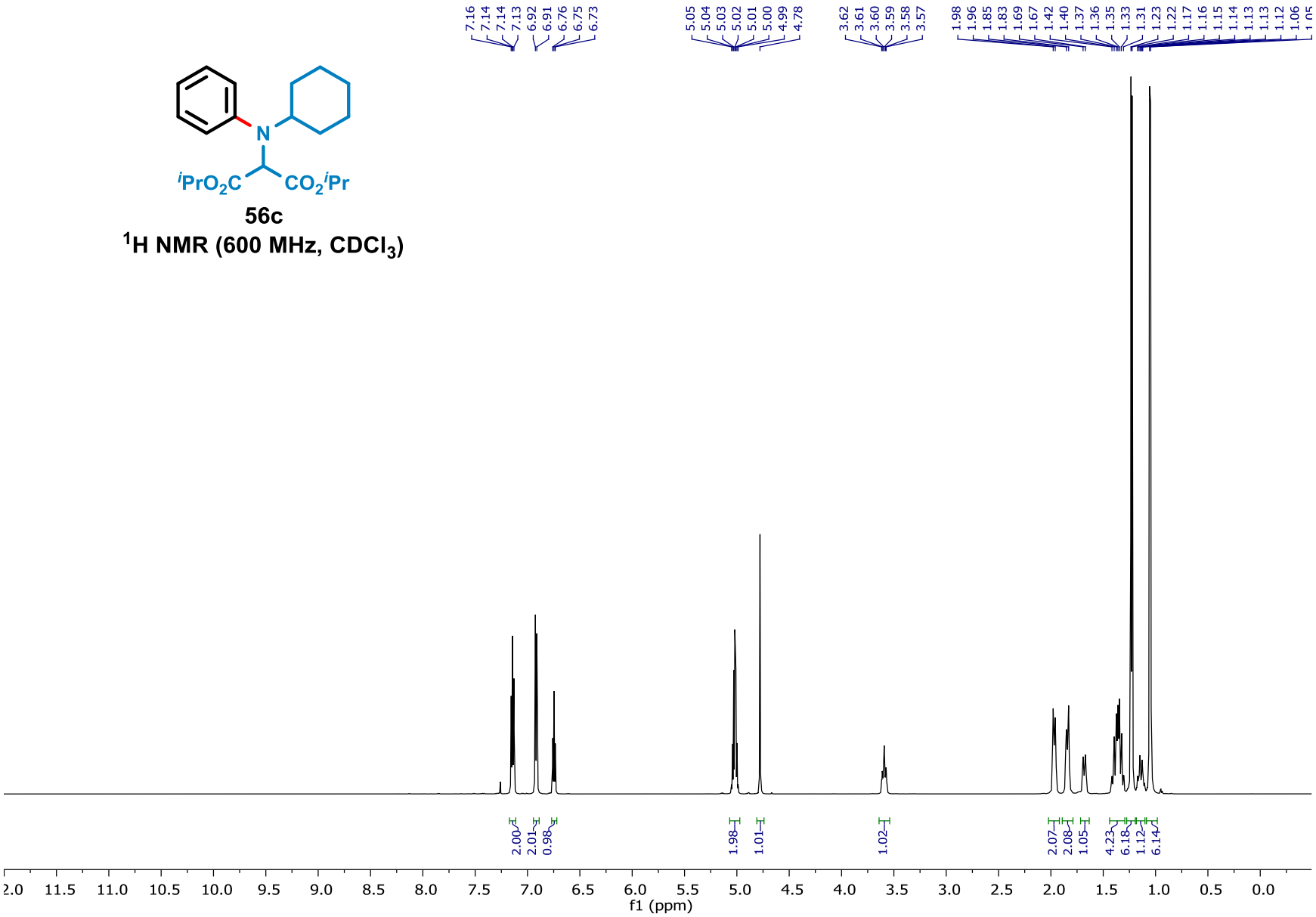
^{13}C NMR (151 MHz, $CDCl_3$)

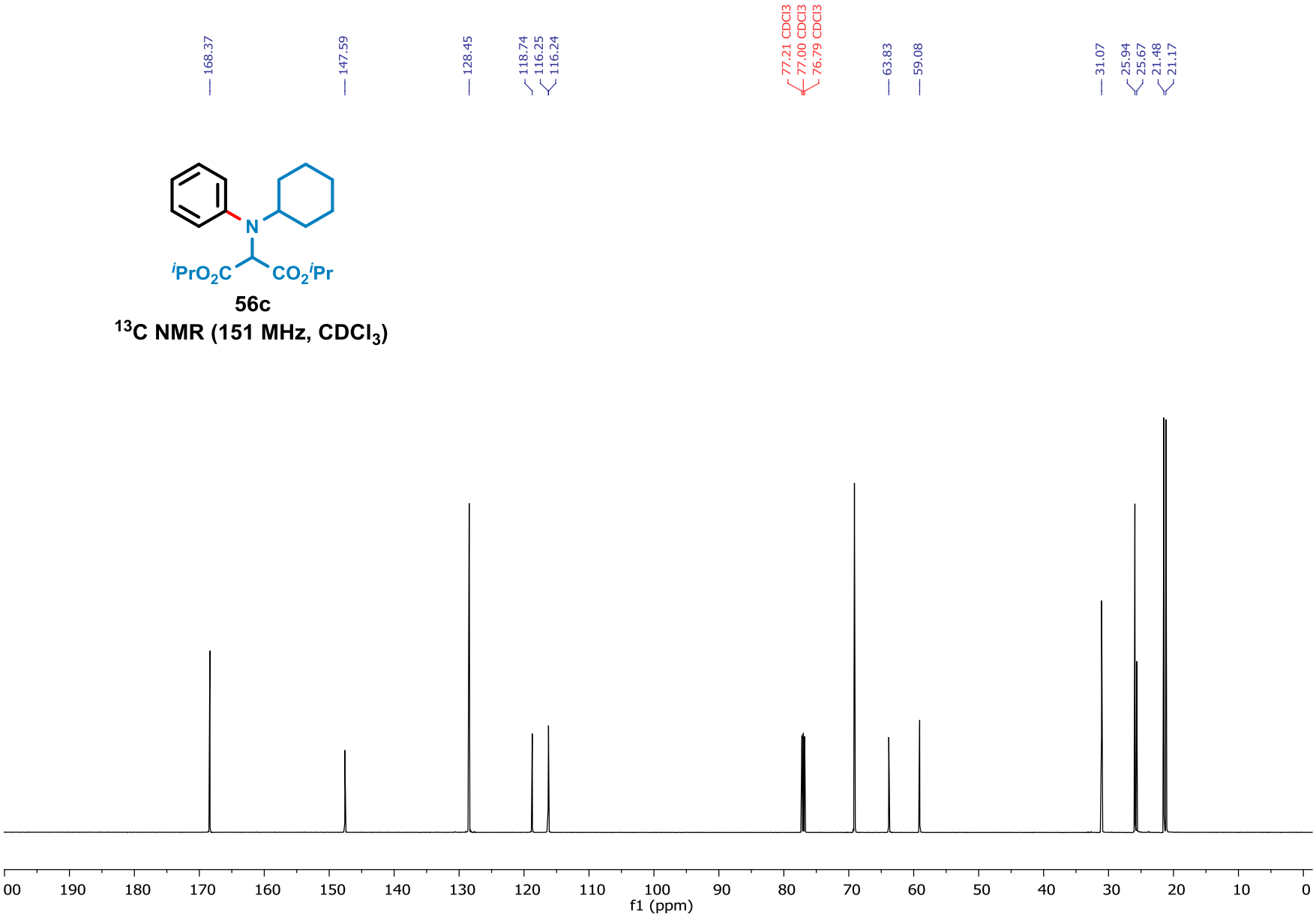


56b

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

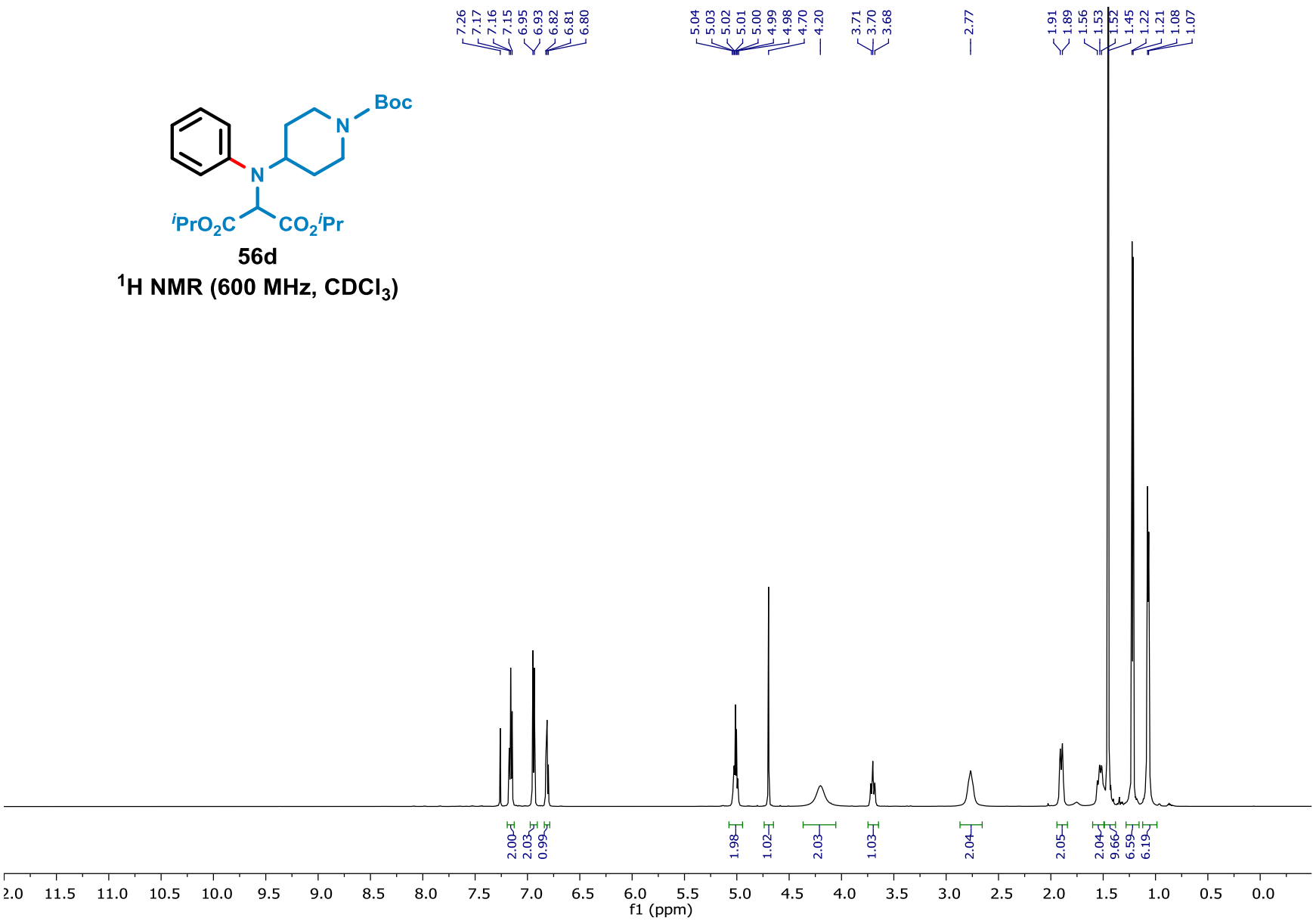

168.23
150.81
143.87
130.07
119.59
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.89
65.81
62.07
59.54
30.03
23.58
21.39
21.19
16.13
Me
MeO
Me
N
iPrO2C
CO2iPr
56b
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


N
iPrO2C
CO2iPr
56c
1H NMR (600 MHz, CDCl3)
f1 (ppm)



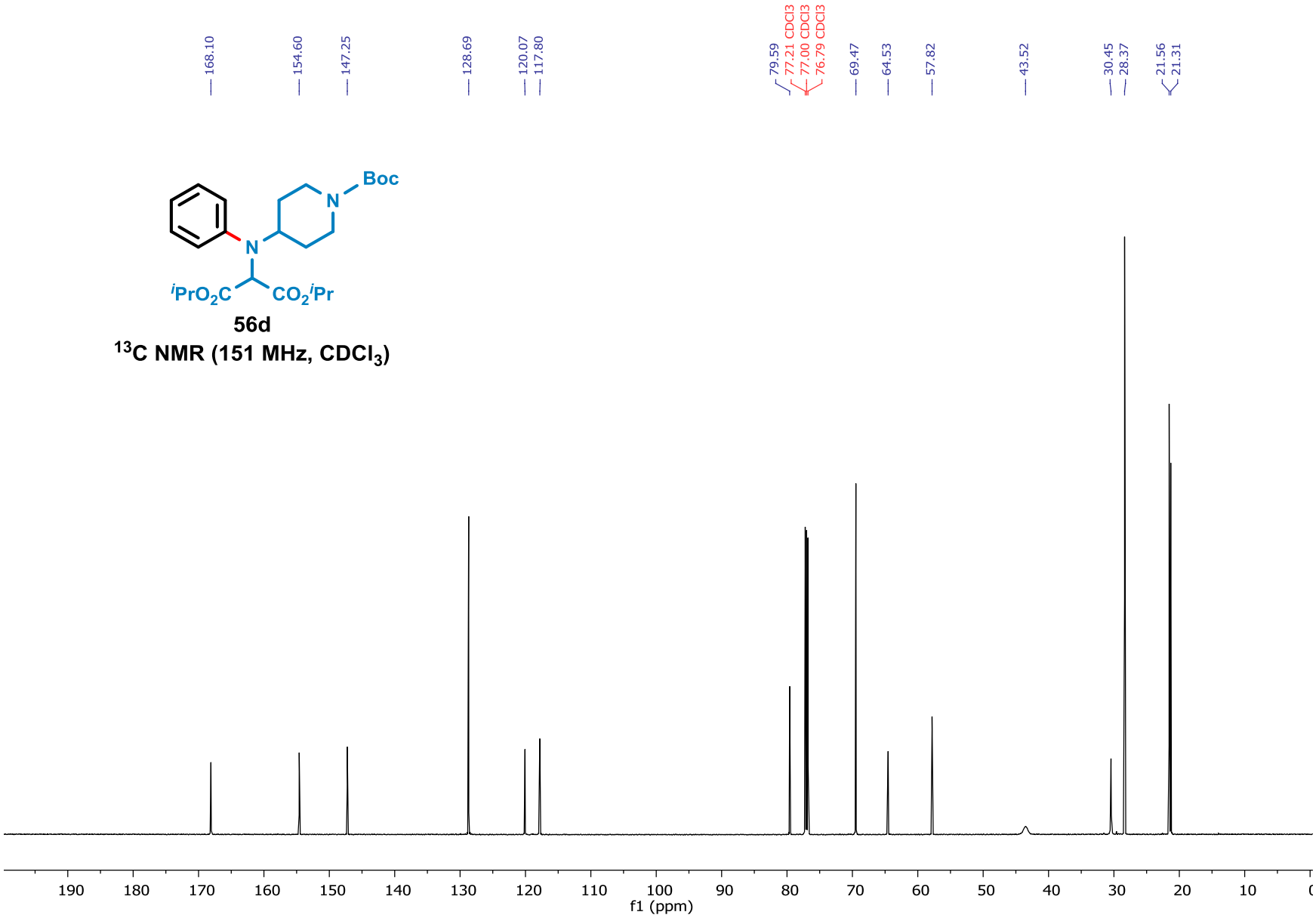
56c

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



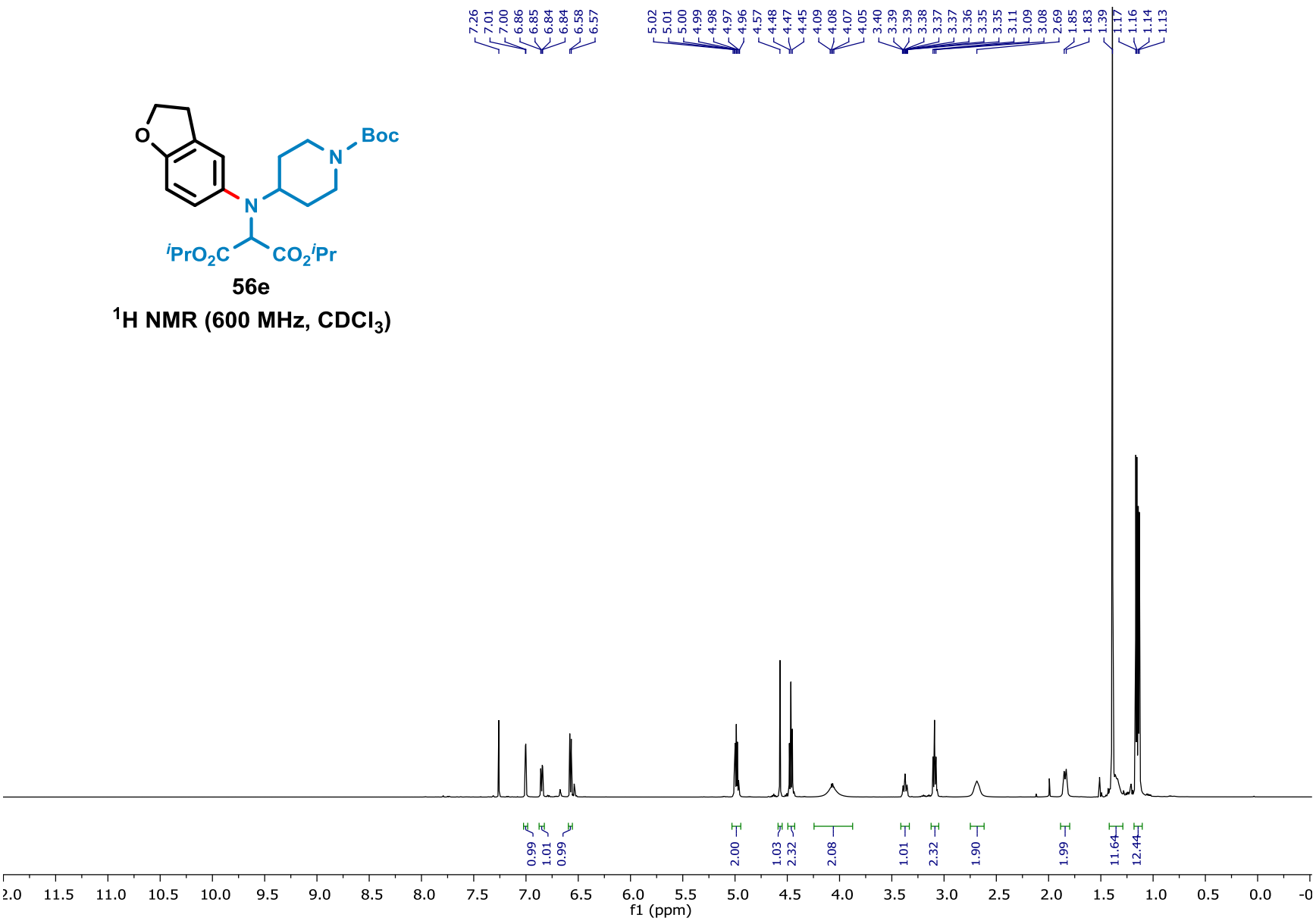
56d

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



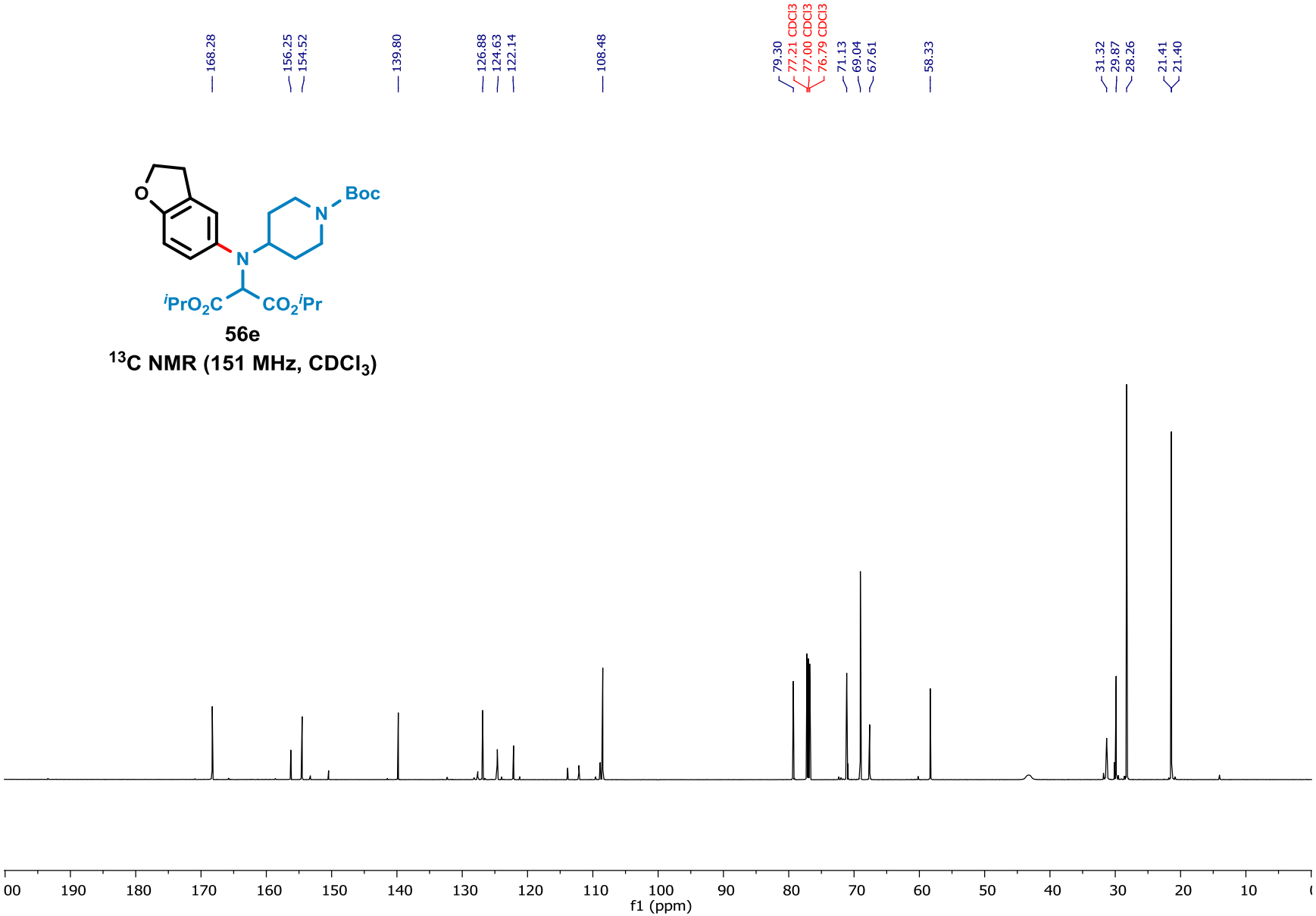
56d

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



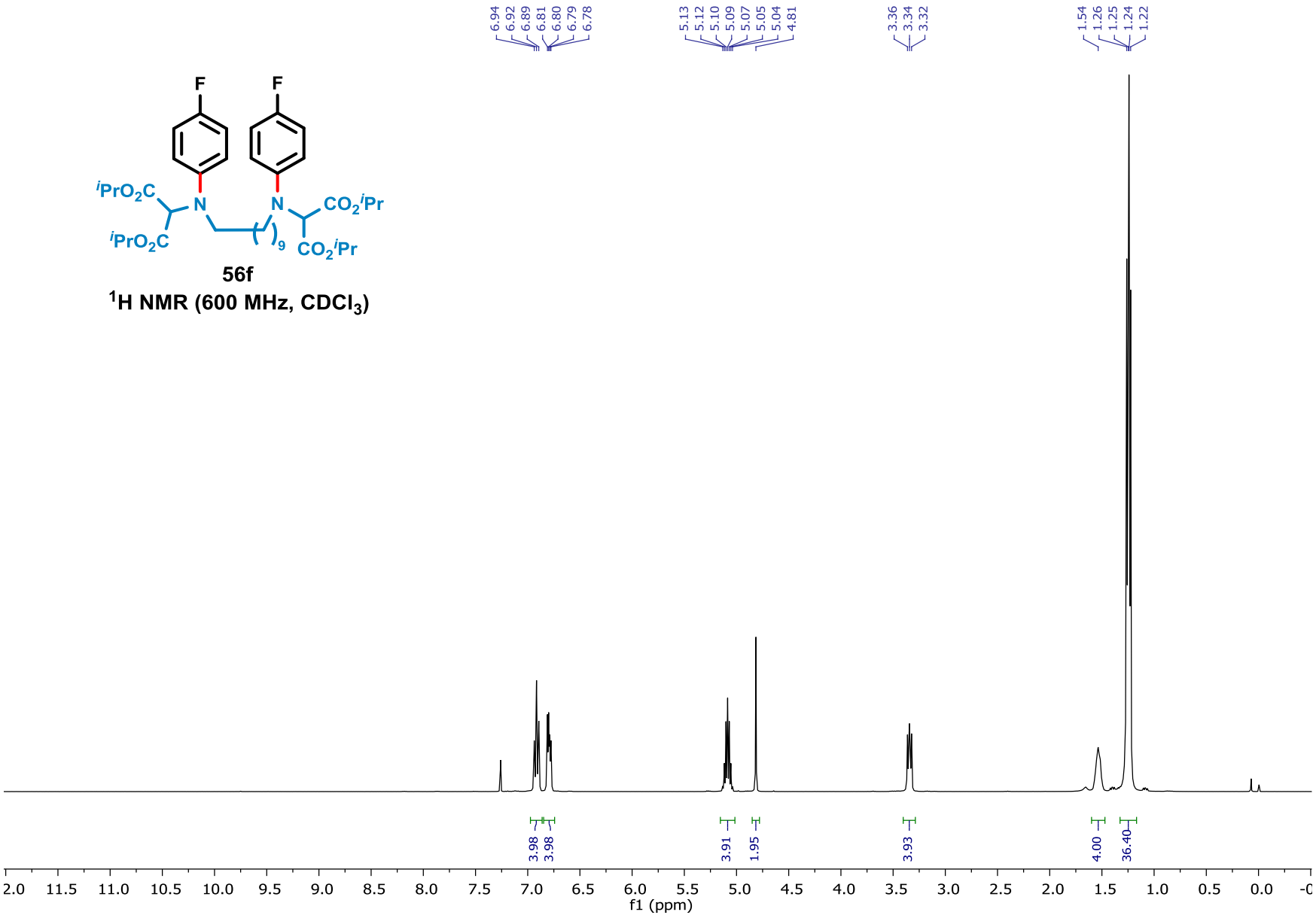
56e

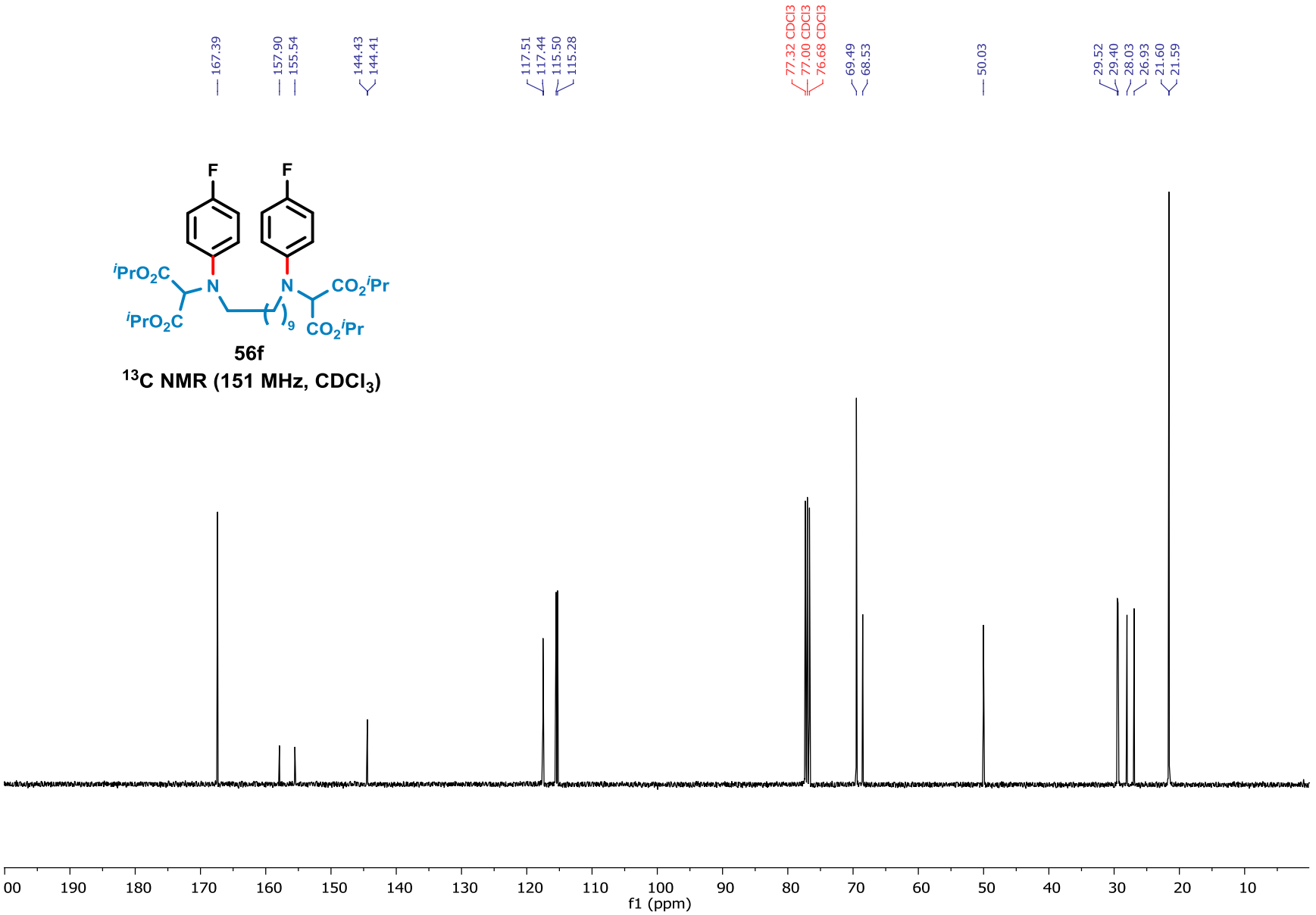
^{1}H NMR (600 MHz, $CDCl_3$)

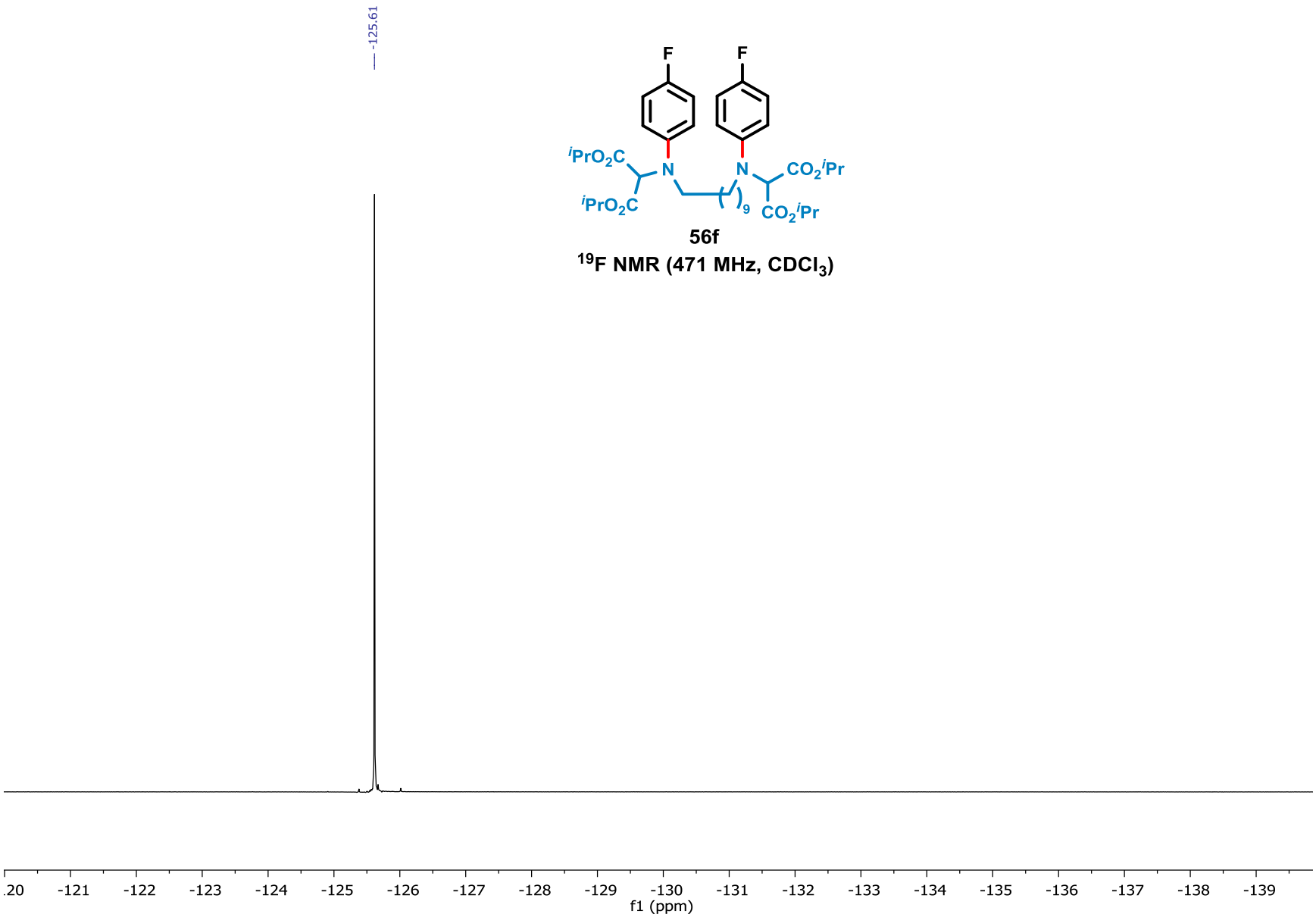


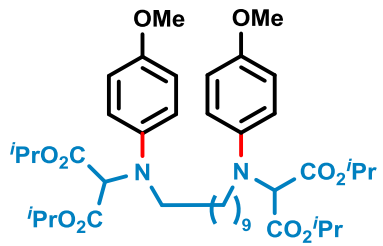
56e

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


F
F
iPrO2C
N
N
CO2iPr
iPrO2C
9
CO2iPr
56f
1H NMR (600 MHz, CDCl3)
6.94
6.92
6.89
6.81
6.80
6.79
6.78
5.13
5.12
5.10
5.09
5.07
5.05
5.04
4.81
3.36
3.34
3.32
1.54
1.26
1.25
1.24
1.22
3.98
3.98
3.91
1.95
3.93
4.00
36.40
f1 (ppm)

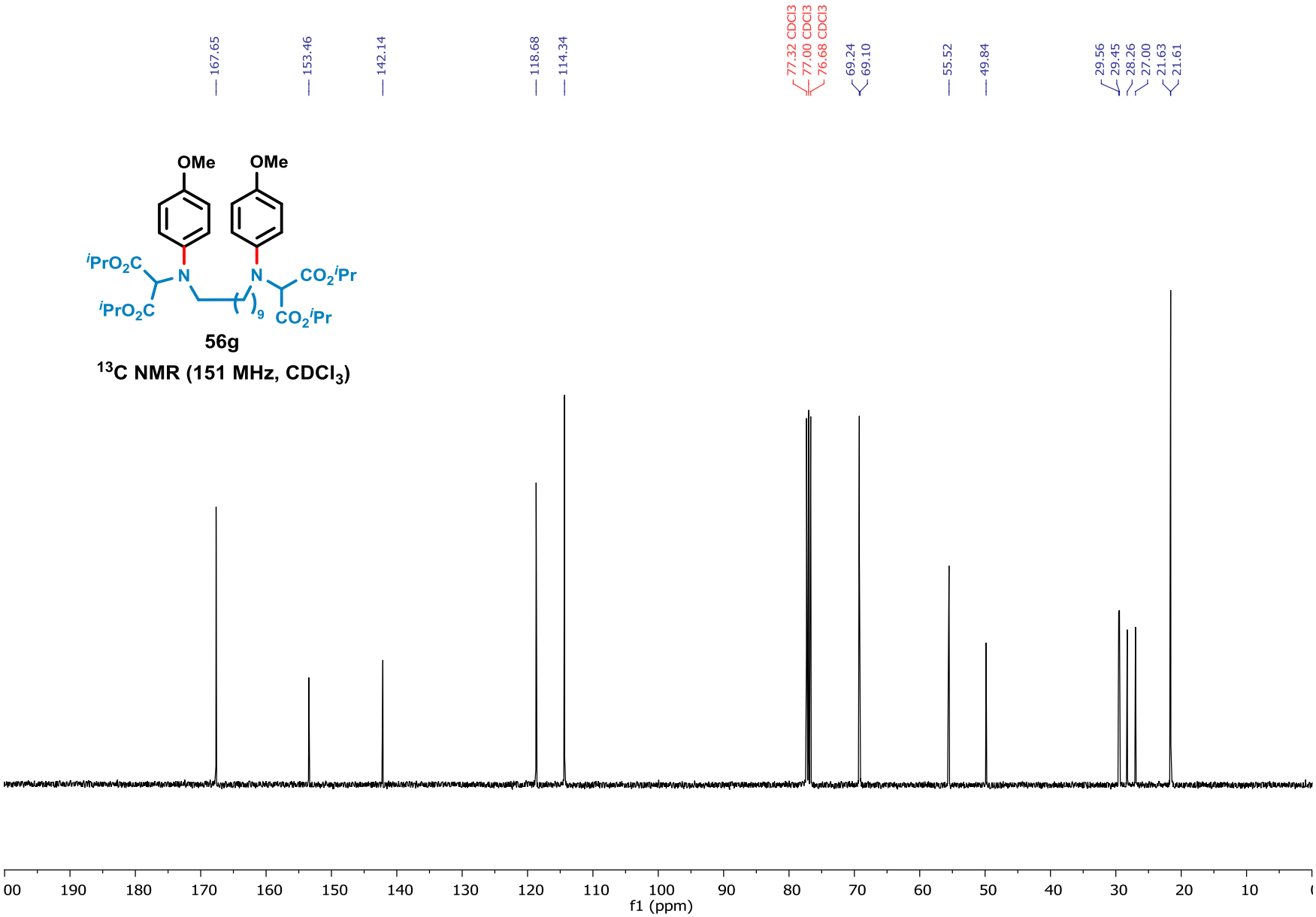

167.39
157.90
155.54
144.43
144.41
117.51
117.44
115.50
115.28
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.49
68.53
50.03
29.52
29.40
28.03
26.93
21.60
21.59
F
F
iPrO2C
iPrO2C
N
N
CO2iPr
CO2iPr
9
56f
13C NMR (151 MHz, CDCl3)
f1 (ppm)

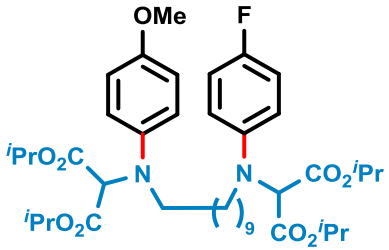

-125.61
F
F
$^{i}PrO_2C$
$^{i}PrO_2C$
N
N
$CO_2{}^{i}Pr$
$CO_2{}^{i}Pr$
9
56f
^{19}F NMR (471 MHz, $CDCl_3$)
.20
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)



56g

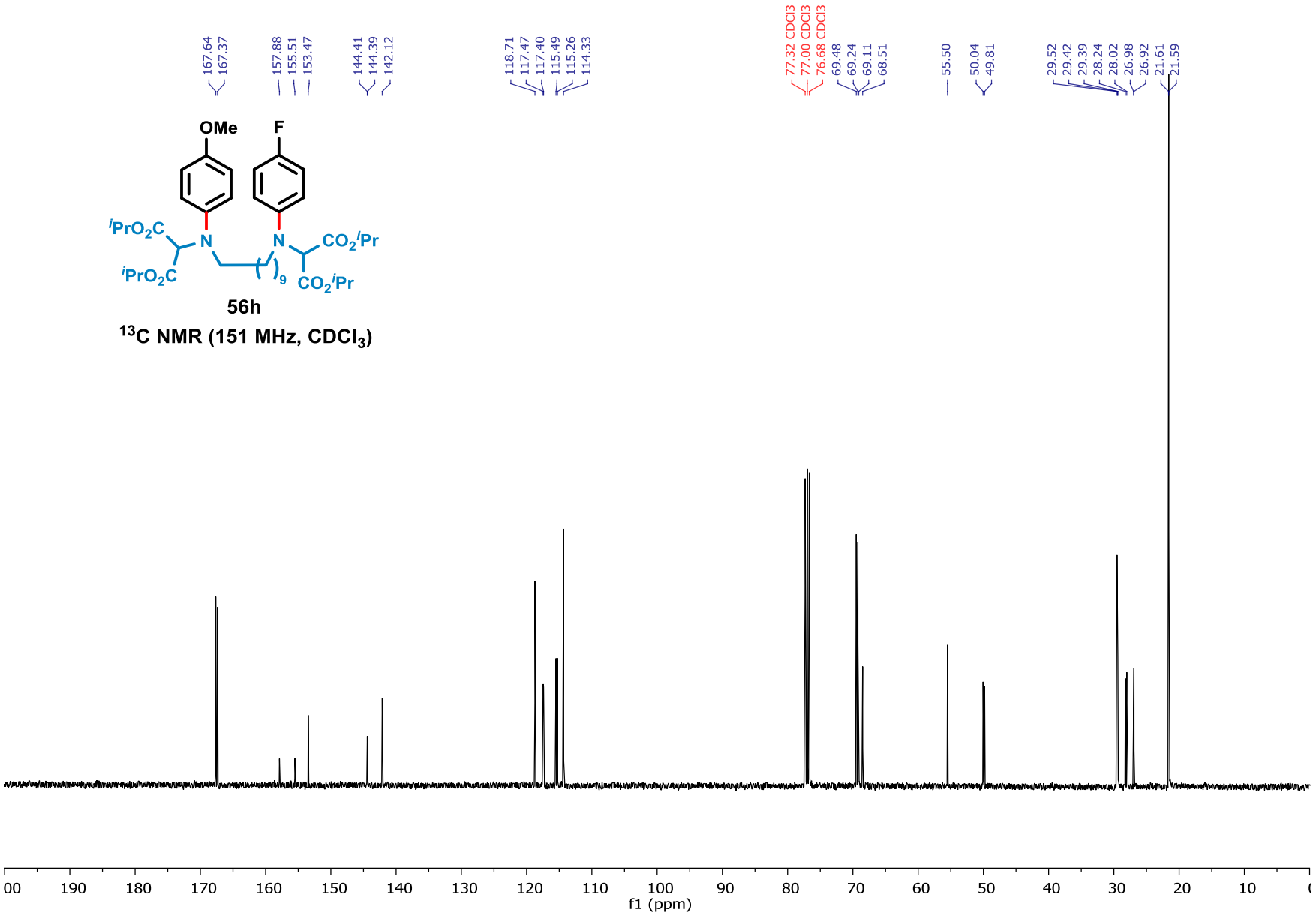
^{1}H NMR (600 MHz, $CDCl_3$)

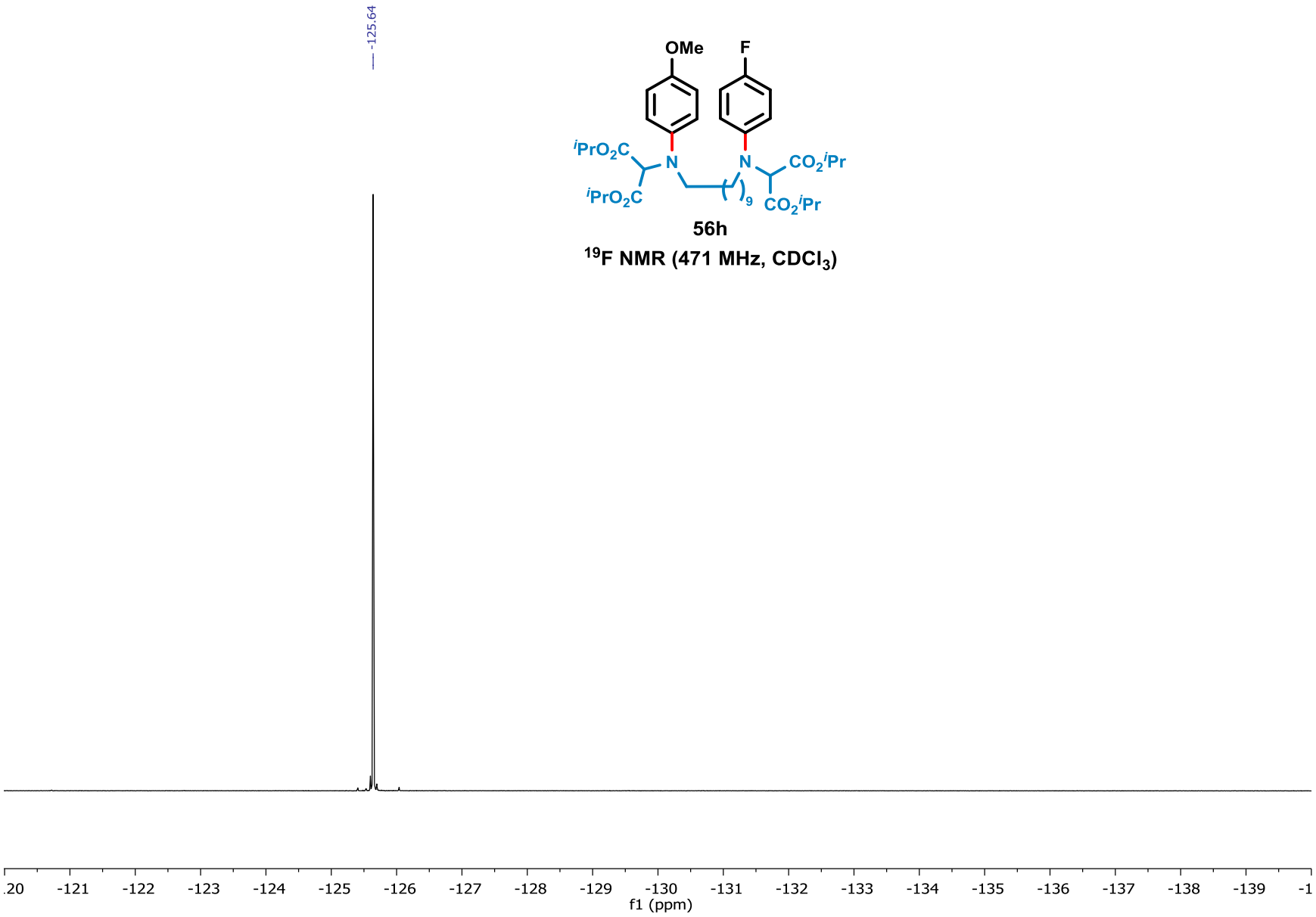

167.65
153.46
142.14
118.68
114.34
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.24
69.10
55.52
49.84
29.56
29.45
28.26
27.00
21.63
21.61
OMe
OMe
iPrO2C
iPrO2C
N
N
CO2iPr
CO2iPr
9
56g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

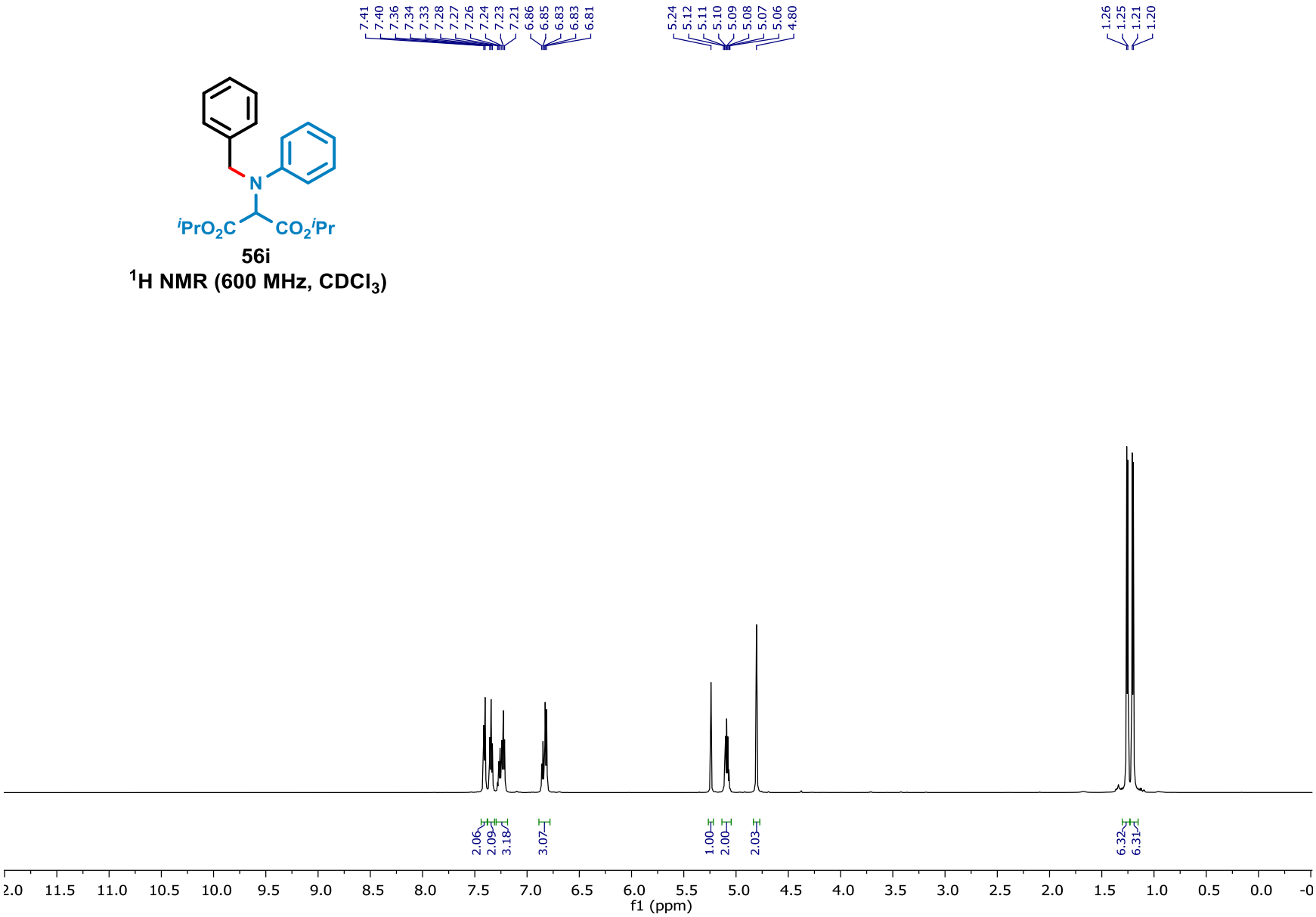


56h

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

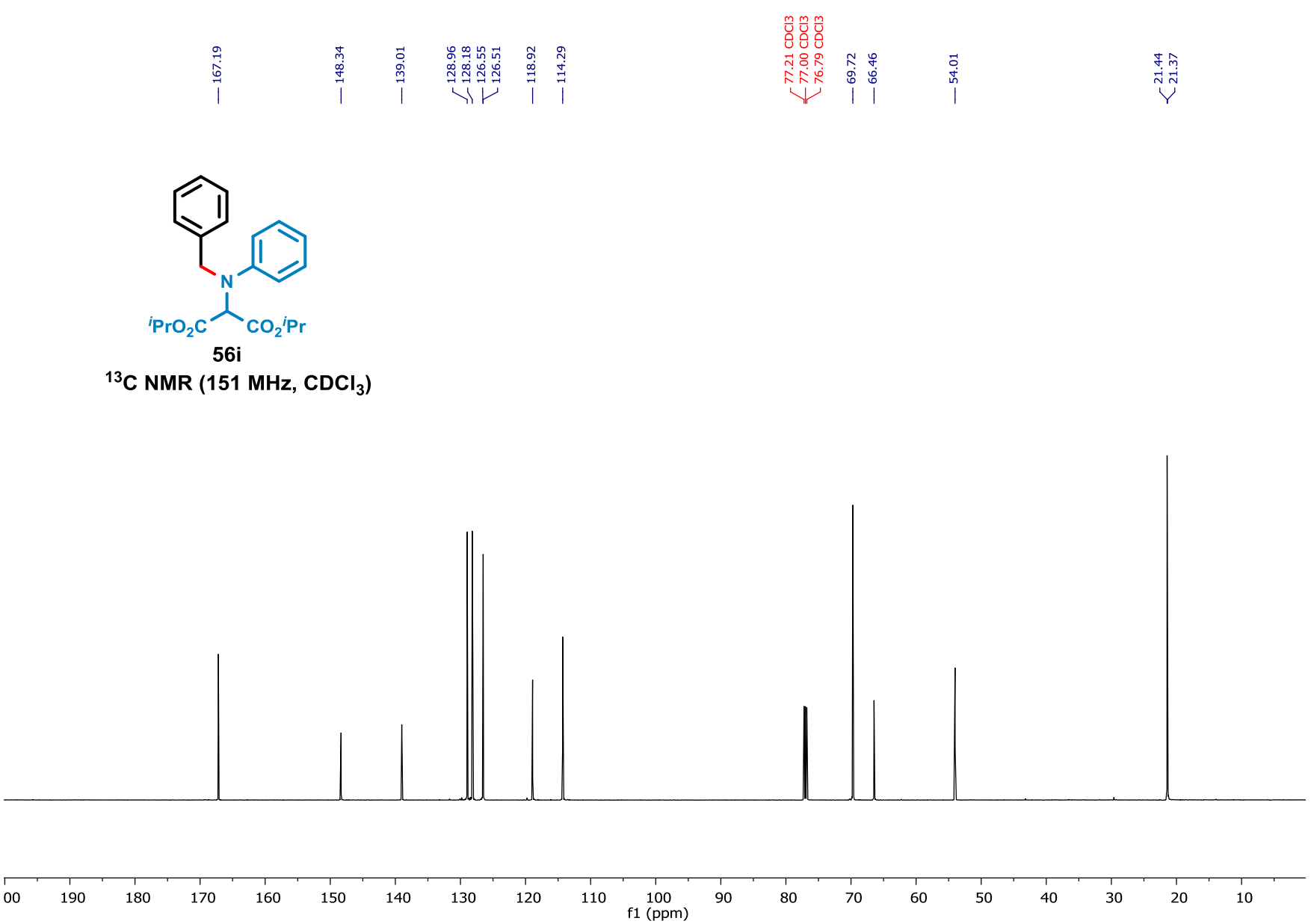

167.64
167.37
157.88
155.51
153.47
144.41
144.39
142.12
118.71
117.47
117.40
115.49
115.26
114.33
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.48
69.24
69.11
68.51
55.50
50.04
49.81
29.52
29.42
29.39
28.24
28.02
26.98
26.92
21.61
21.59
OMe
F
iPrO2C
iPrO2C
N
N
CO2iPr
CO2iPr
9
56h
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-125.64
OMe
F
$^{i}PrO_2C$
$^{i}PrO_2C$
N
N
$CO_2{}^{i}Pr$
$CO_2{}^{i}Pr$
9
56h
^{19}F NMR (471 MHz, $CDCl_3$)
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)



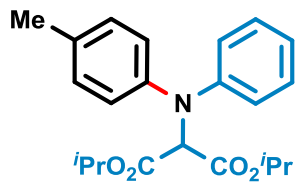
56i

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



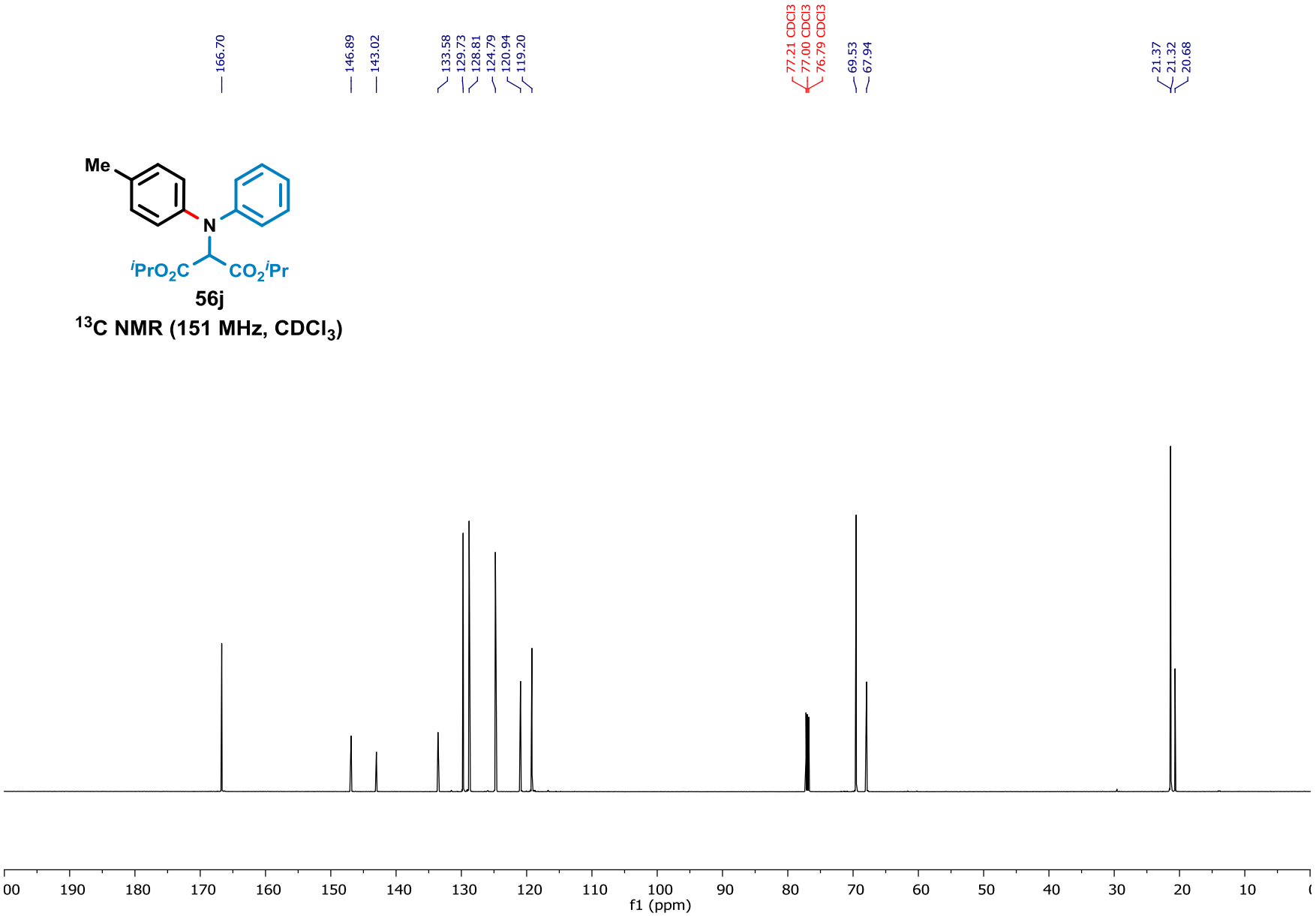
56i

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



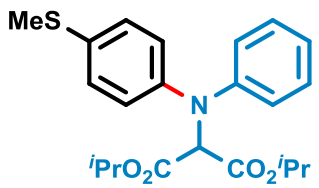
56j

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



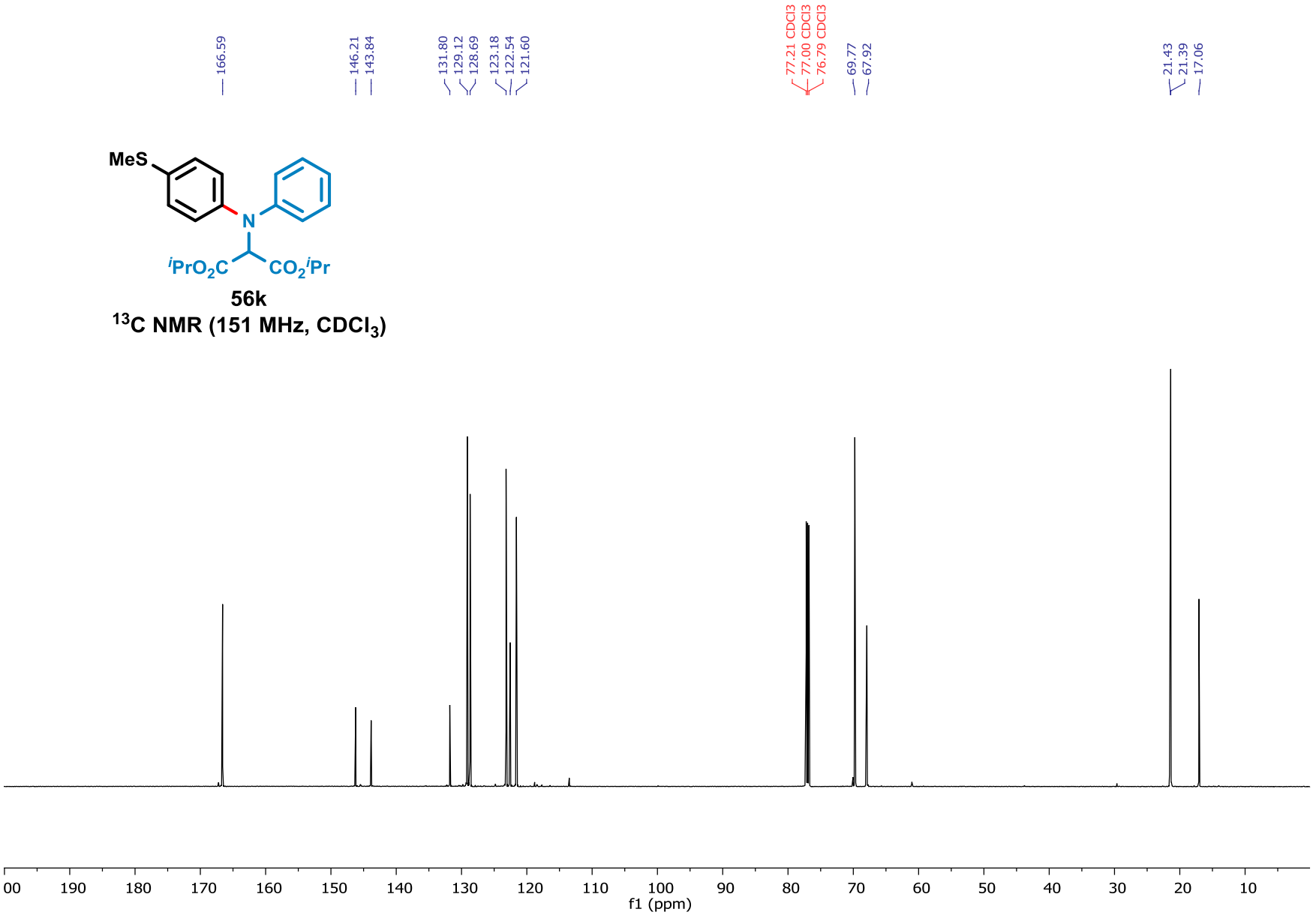
56j

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



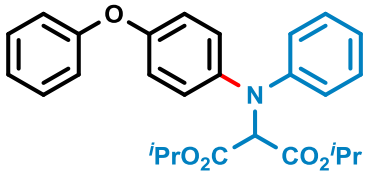
56k

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



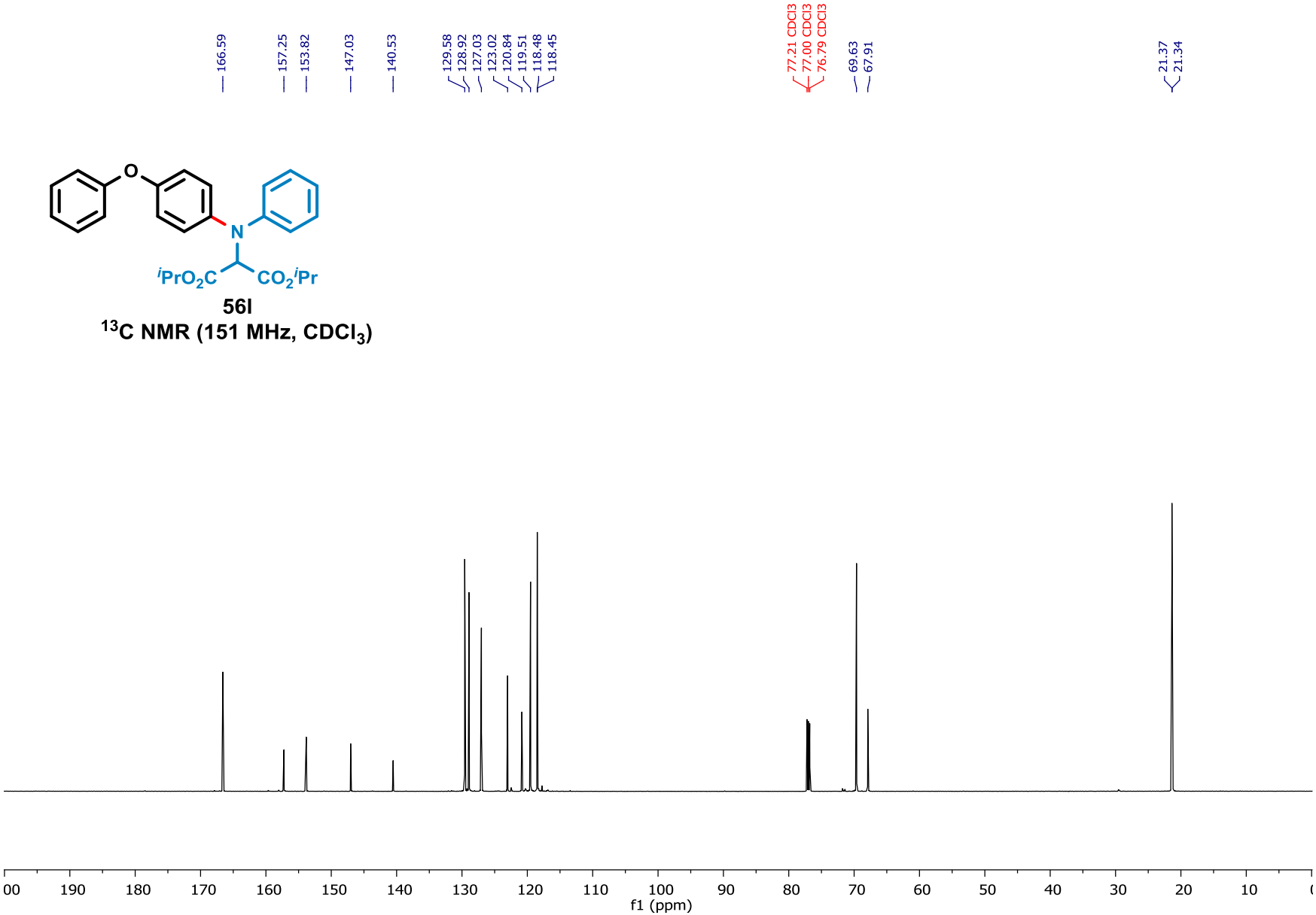
56k

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



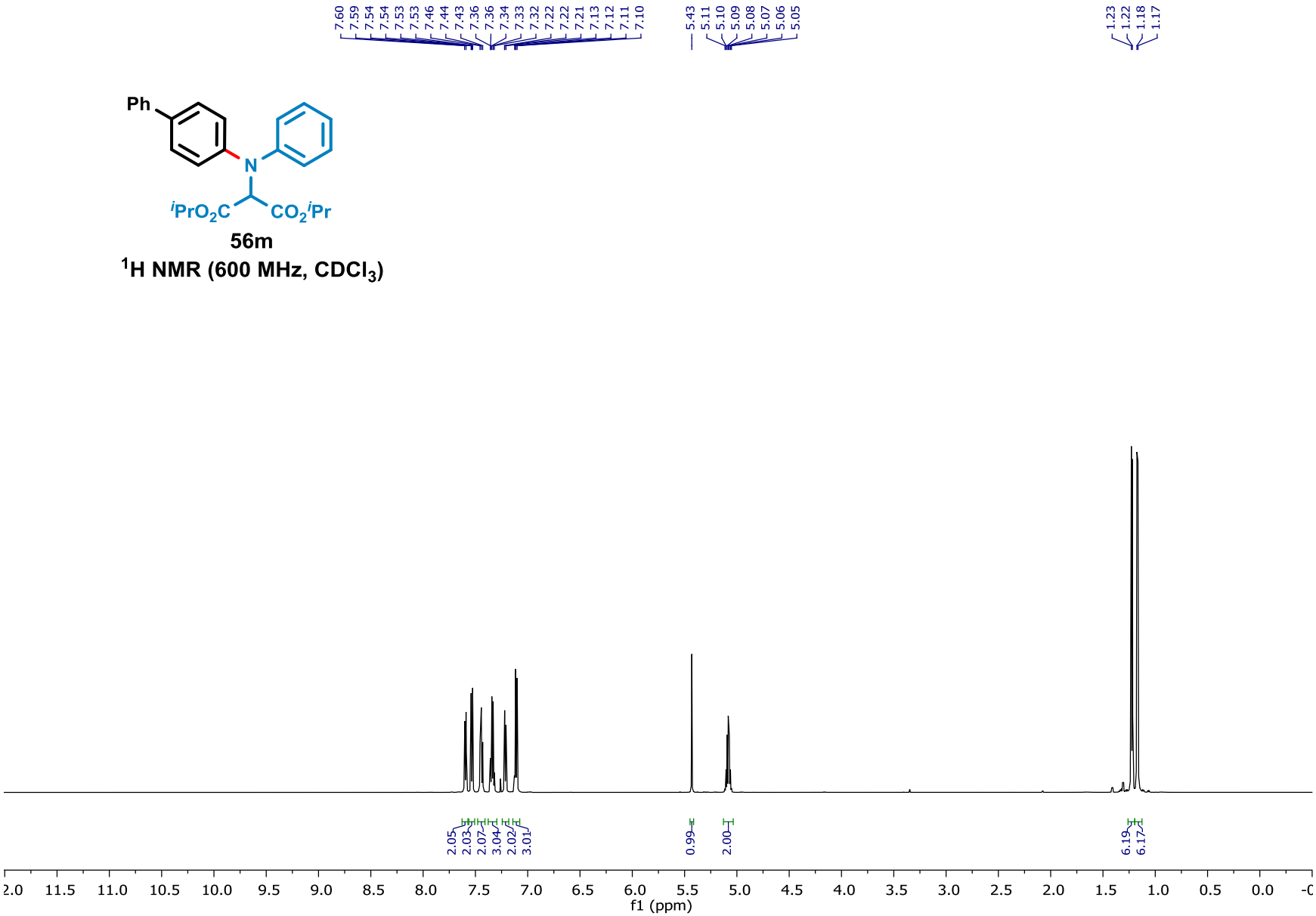
56l

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



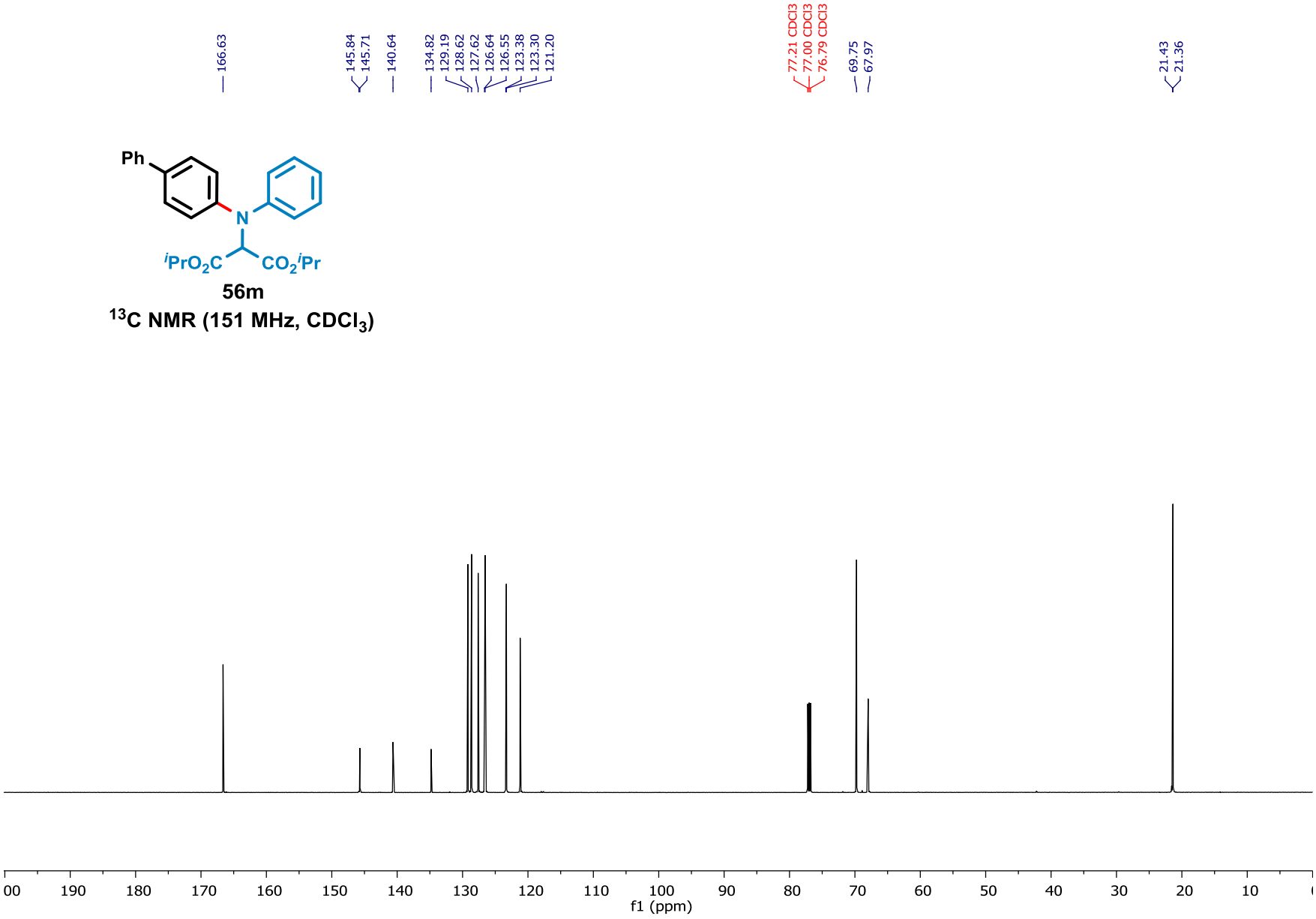
56l

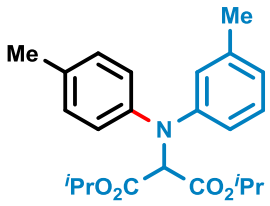
^{13}C NMR (151 MHz, $CDCl_3$)



56m

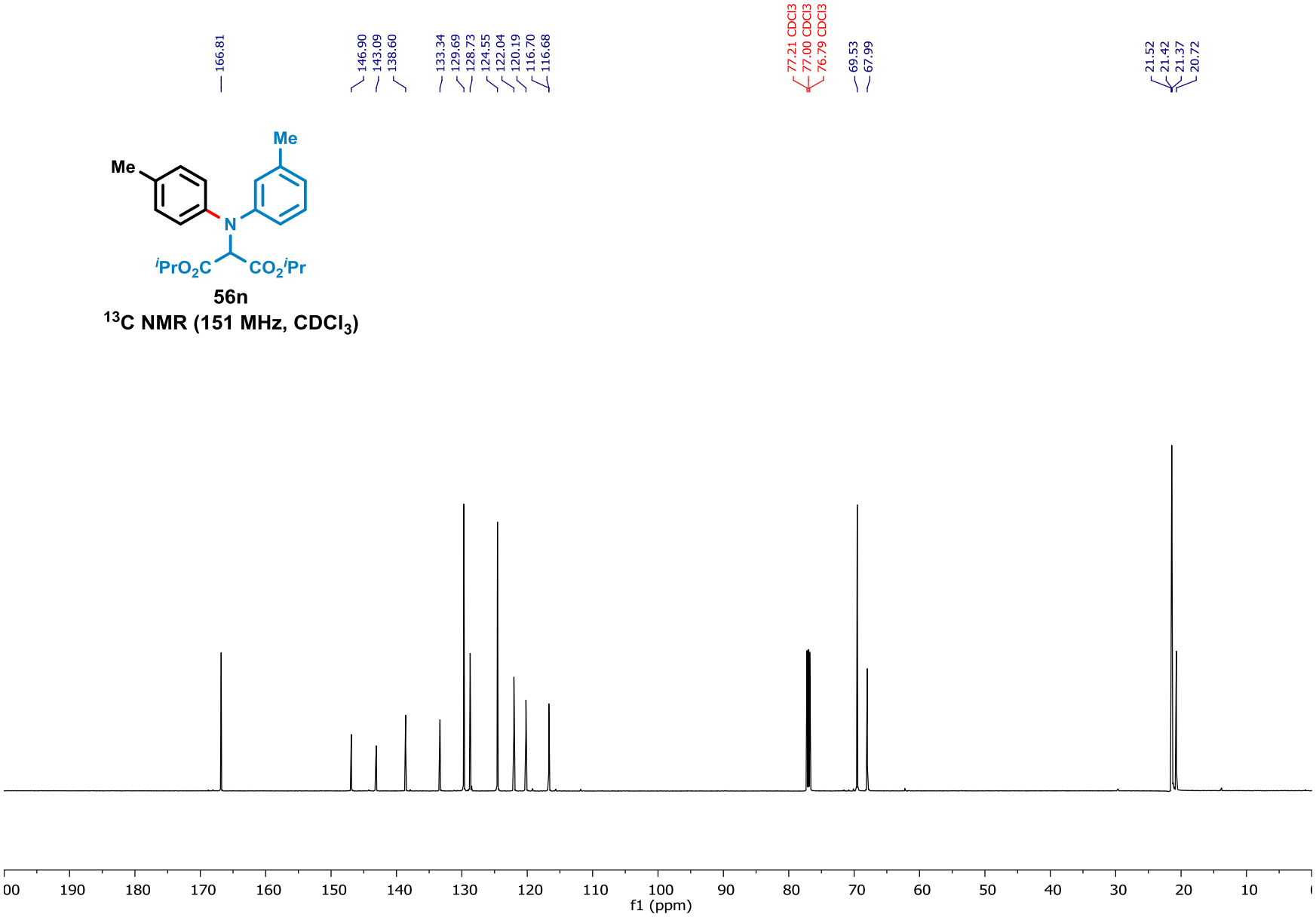
^{1}H NMR (600 MHz, $CDCl_3$)

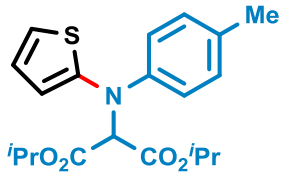

166.63
145.84
145.71
140.64
134.82
129.19
128.62
127.62
126.64
126.55
123.38
123.30
121.20
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.75
67.97
21.43
21.36
Ph
N
iPrO2C
CO2iPr
56m
13C NMR (151 MHz, CDCl3)
f1 (ppm)



56n

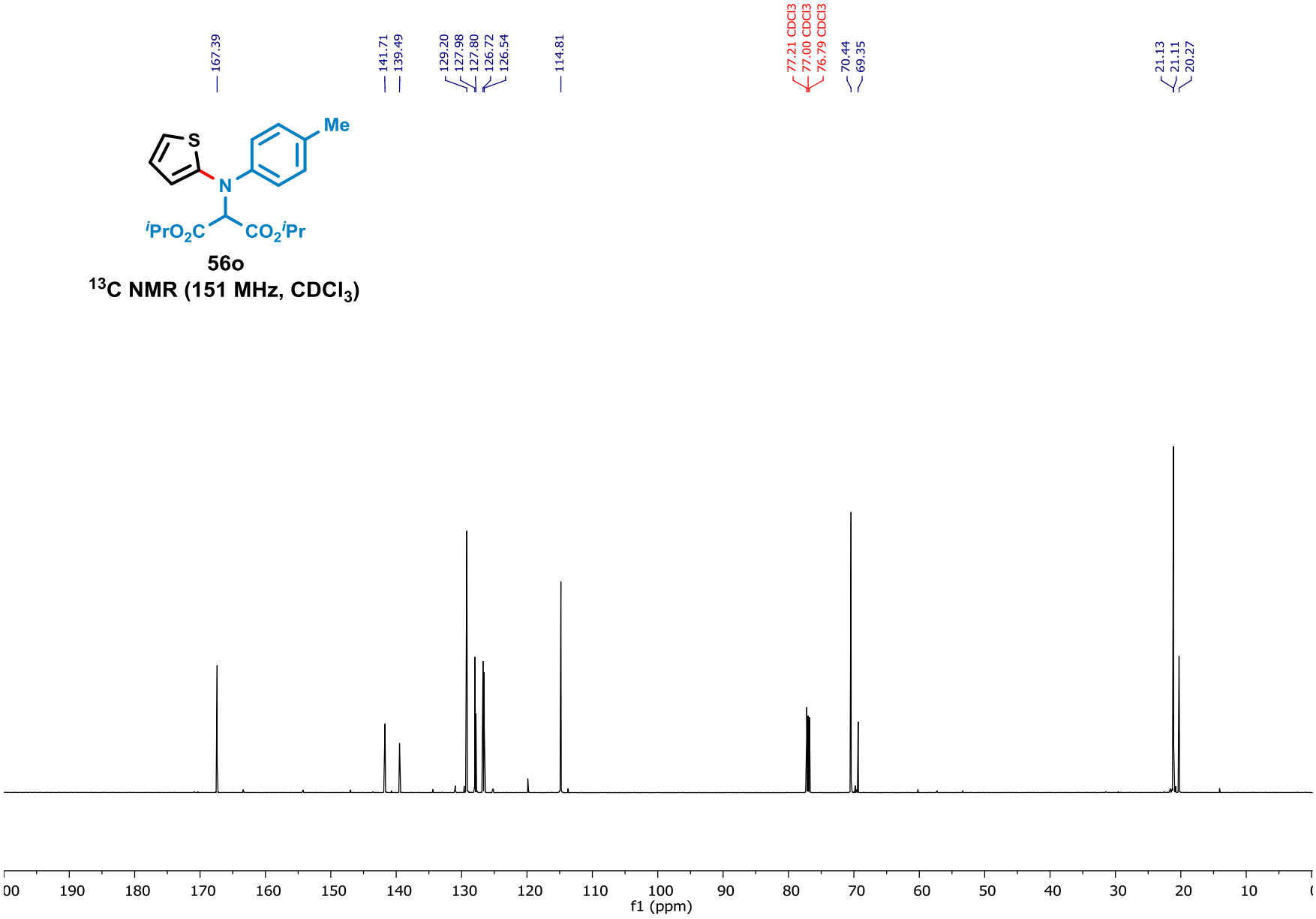
^{1}H NMR (600 MHz, $CDCl_3$)


166.81
146.90
143.09
138.60
133.34
129.69
128.73
124.55
122.04
120.19
116.70
116.68
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.53
67.99
21.52
21.42
21.37
20.72
Me
Me
N
iPrO2C
CO2iPr
56n
13C NMR (151 MHz, CDCl3)
f1 (ppm)



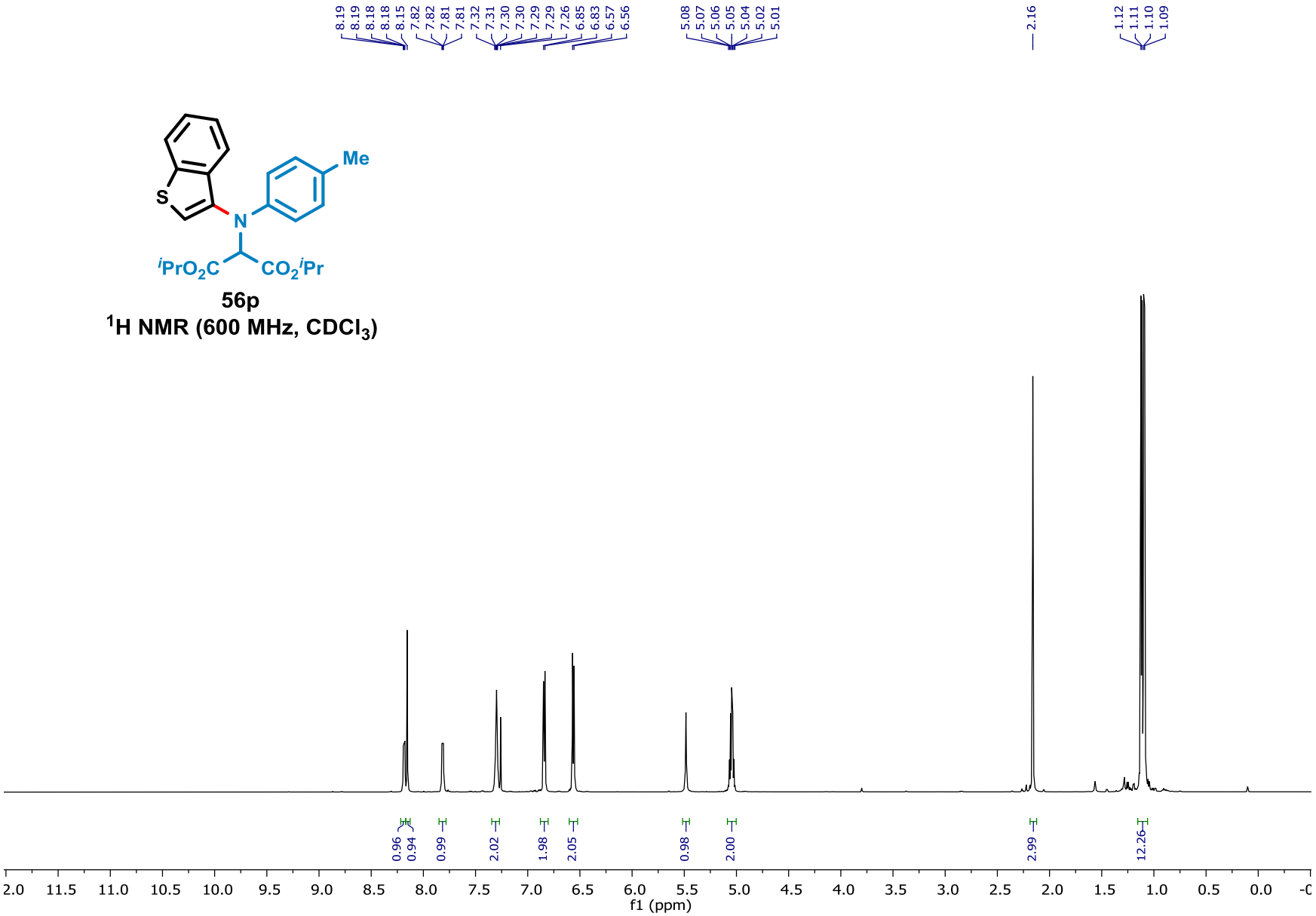
56o

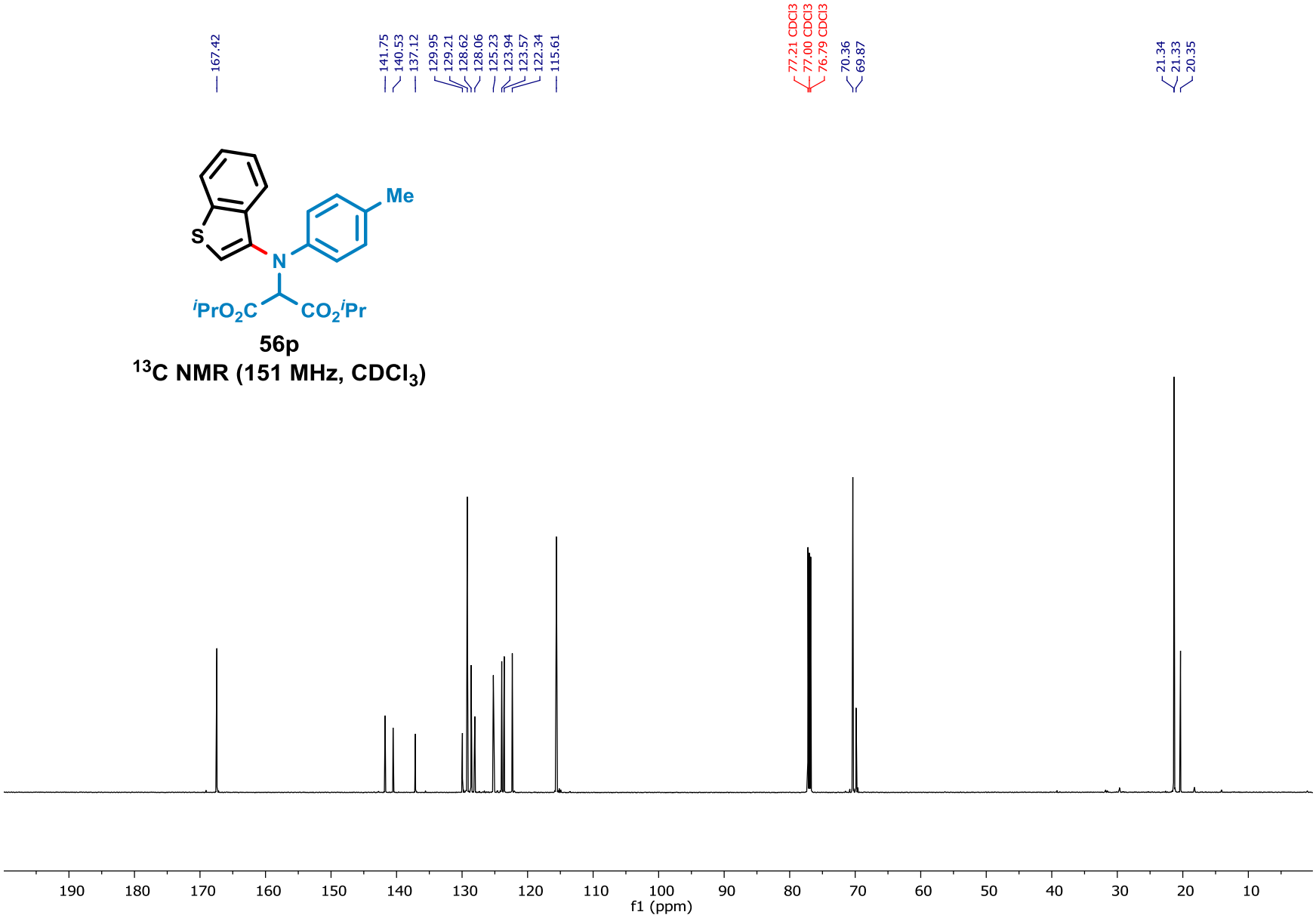
^{1}H NMR (600 MHz, $CDCl_3$)



56o

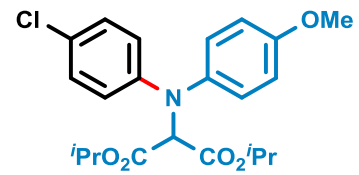
^{13}C NMR (151 MHz, $CDCl_3$)


8.19
8.19
8.18
8.18
8.15
7.82
7.82
7.81
7.81
7.32
7.31
7.30
7.30
7.29
7.29
7.26
6.85
6.83
6.57
6.56
5.08
5.07
5.06
5.05
5.04
5.02
5.01
2.16
1.12
1.11
1.10
1.09
Me
S
N
iPrO2C
CO2iPr
56p
1H NMR (600 MHz, CDCl3)
0.96
0.94
0.99
2.02
1.98
2.05
0.98
2.00
2.99
12.26
f1 (ppm)



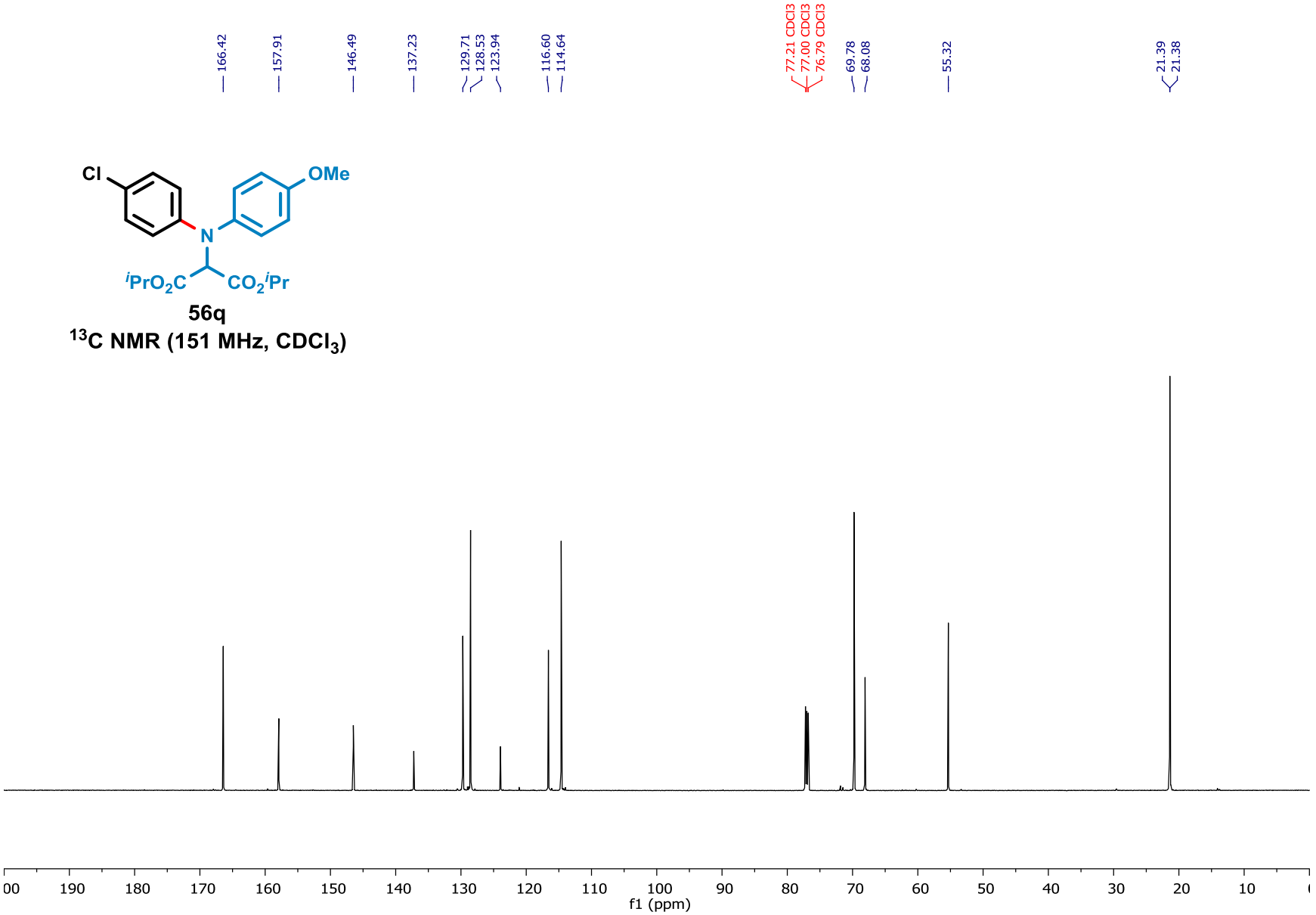
56p

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



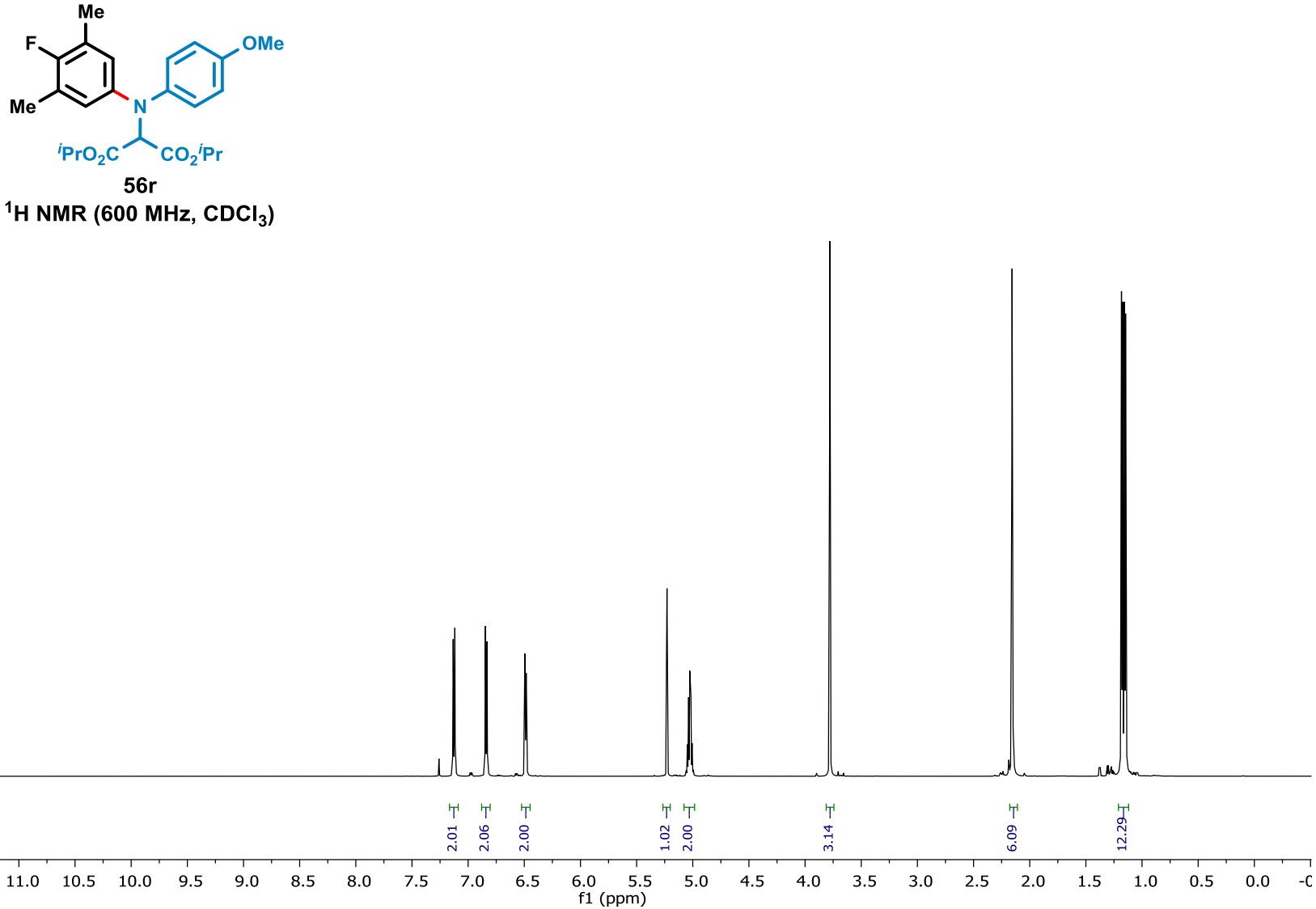
56q

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



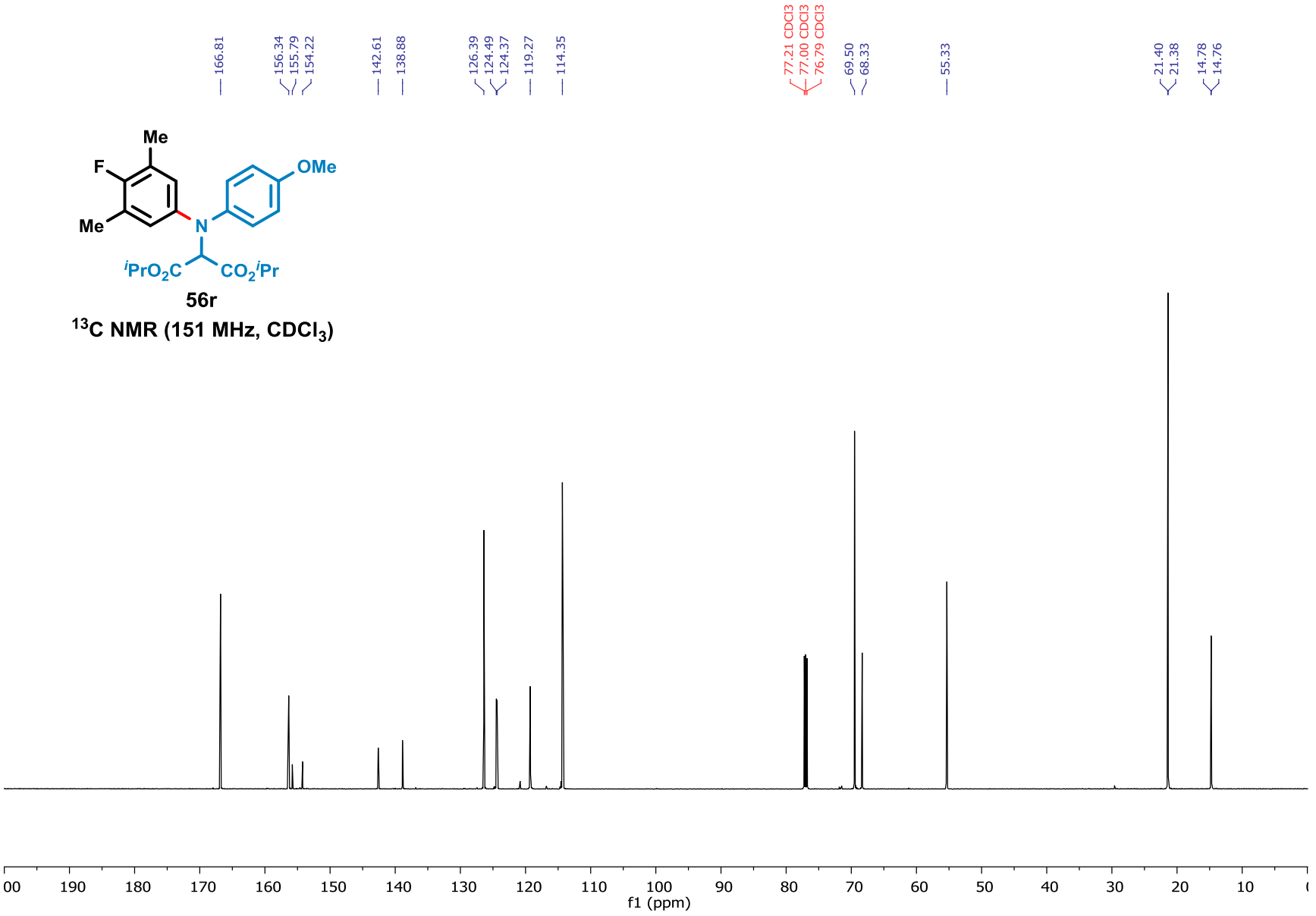
56q

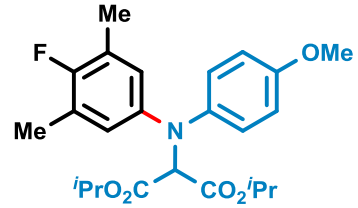
^{13}C NMR (151 MHz, $CDCl_3$)



56r

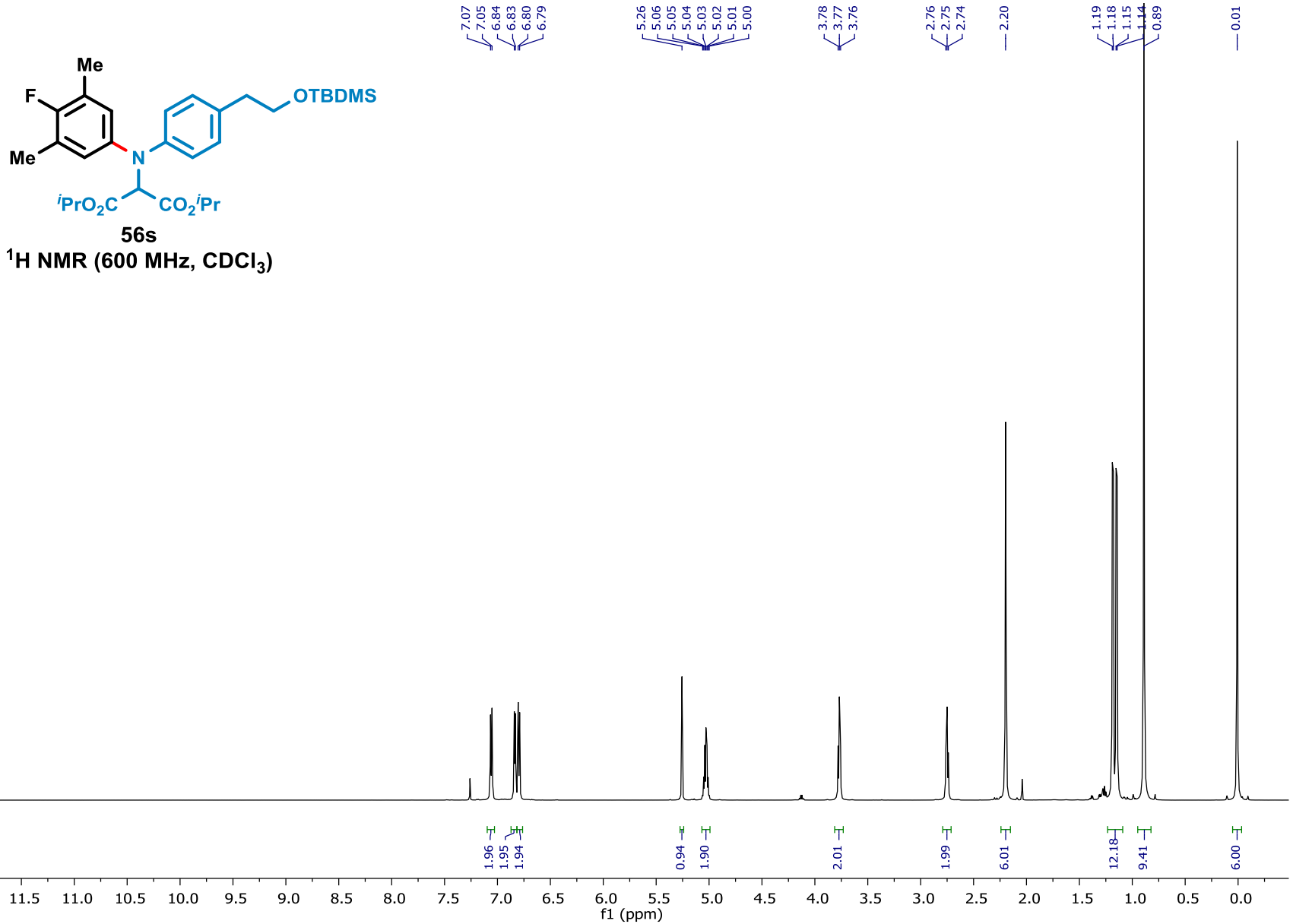
^{1}H NMR (600 MHz, $CDCl_3$)

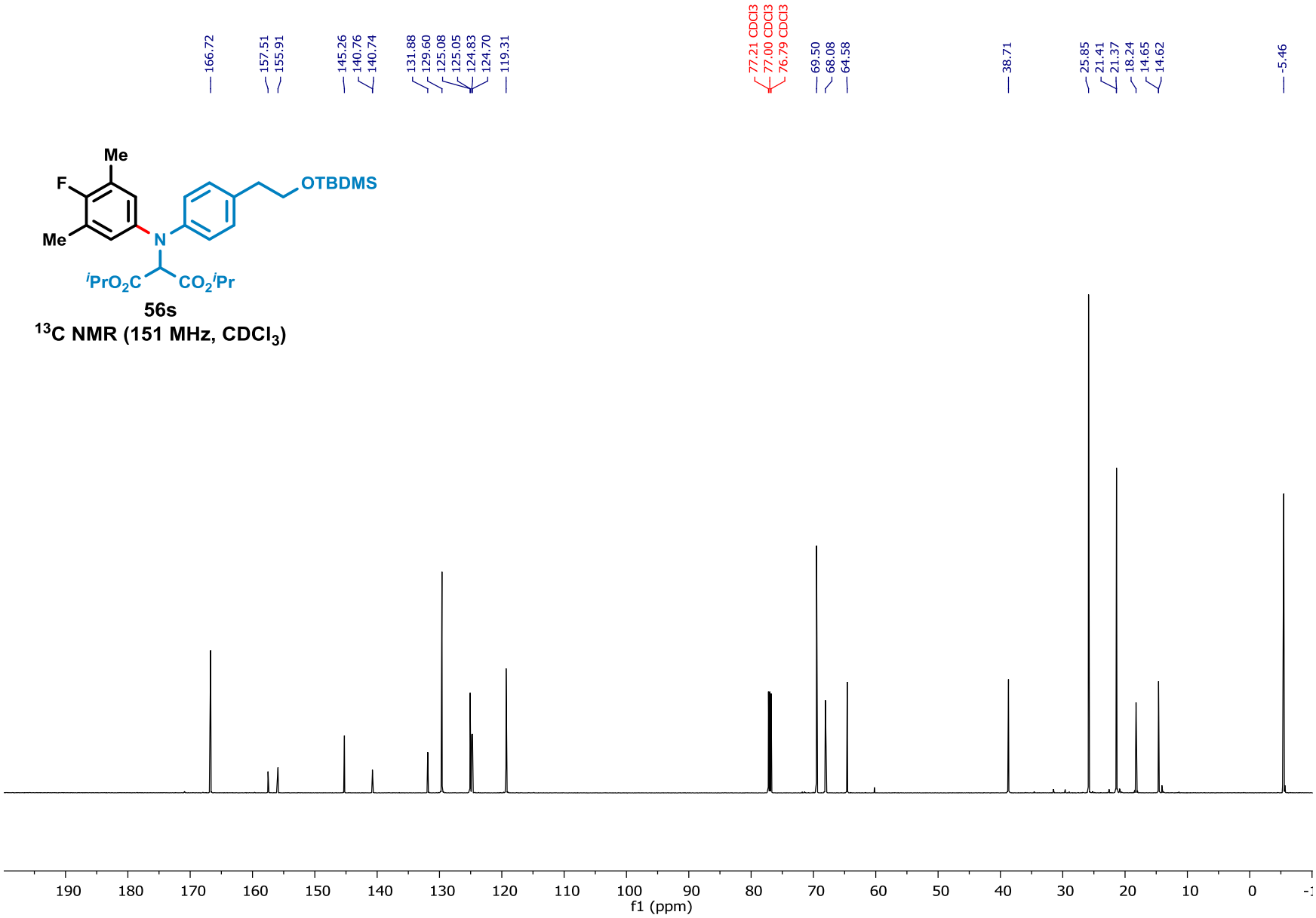

166.81
156.34
155.79
154.22
142.61
138.88
126.39
124.49
124.37
119.27
114.35
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.50
68.33
55.33
21.40
21.38
14.78
14.76
Me
F
Me
N
OMe
iPrO2C
CO2iPr
56r
13C NMR (151 MHz, CDCl3)
f1 (ppm)

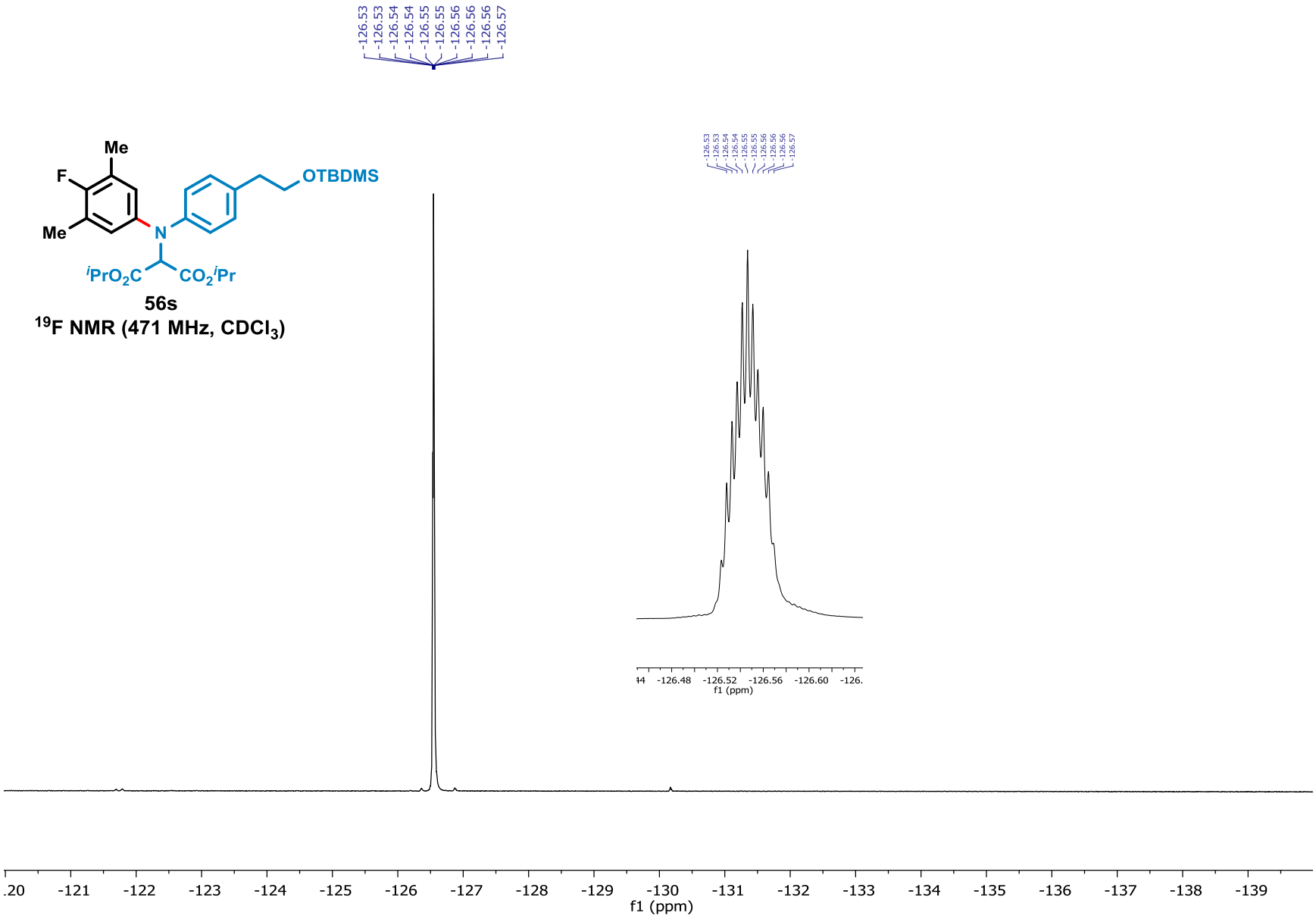


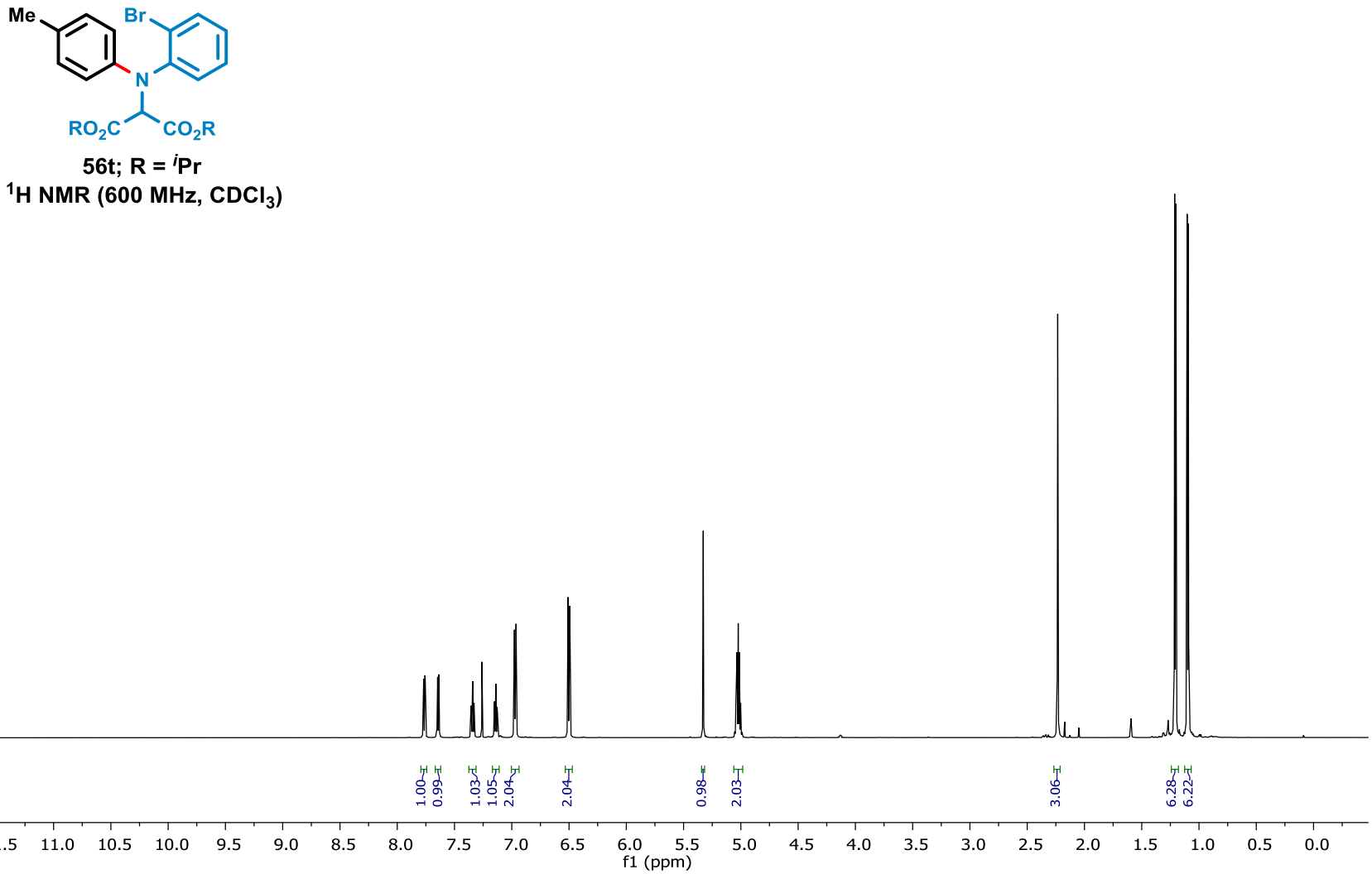
56r

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


Me
F
Me
N
OTBDMS
iPrO2C
CO2iPr
56s
1H NMR (600 MHz, CDCl3)
7.07
7.05
6.84
6.83
6.80
6.79
5.26
5.06
5.05
5.04
5.03
5.02
5.01
5.00
3.78
3.77
3.76
2.76
2.75
2.74
2.20
1.19
1.18
1.15
1.14
0.89
0.01
1.96
1.95
1.94
0.94
1.90
2.01
1.99
6.01
12.18
9.41
6.00
f1 (ppm)

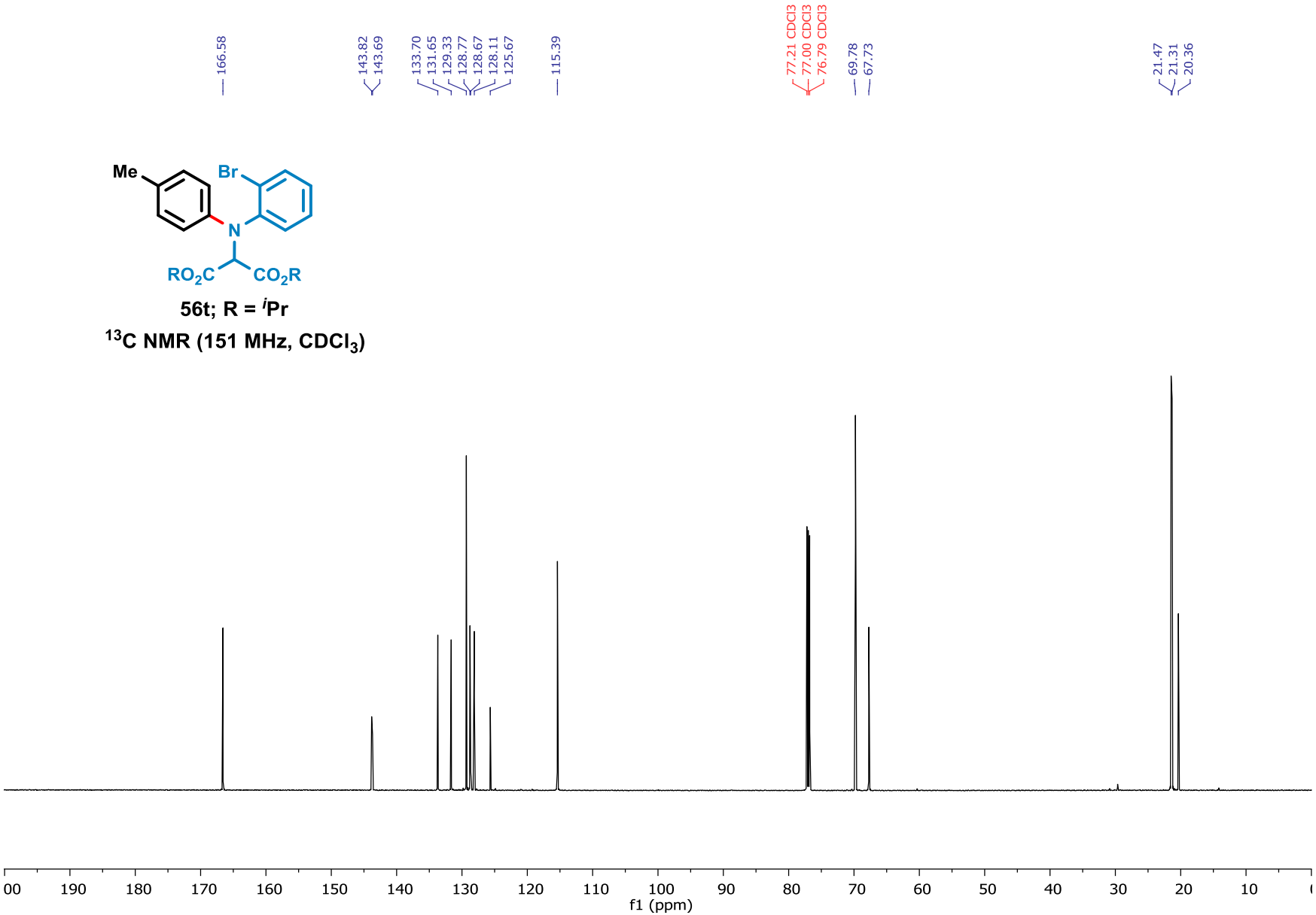

166.72
157.51
155.91
145.26
140.76
140.74
131.88
129.60
125.08
125.05
124.83
124.70
119.31
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.50
68.08
64.58
38.71
25.85
21.41
21.37
18.24
14.65
14.62
-5.46
Me
F
Me
N
OTBDMS
iPrO2C
CO2iPr
56s
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-126.53
-126.53
-126.54
-126.54
-126.55
-126.55
-126.56
-126.56
-126.56
-126.57
Me
F
Me
N
OTBDMS
iPrO2C
CO2iPr
56s
19F NMR (471 MHz, CDCl3)
-126.48
-126.52
-126.56
-126.60
f1 (ppm)
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)



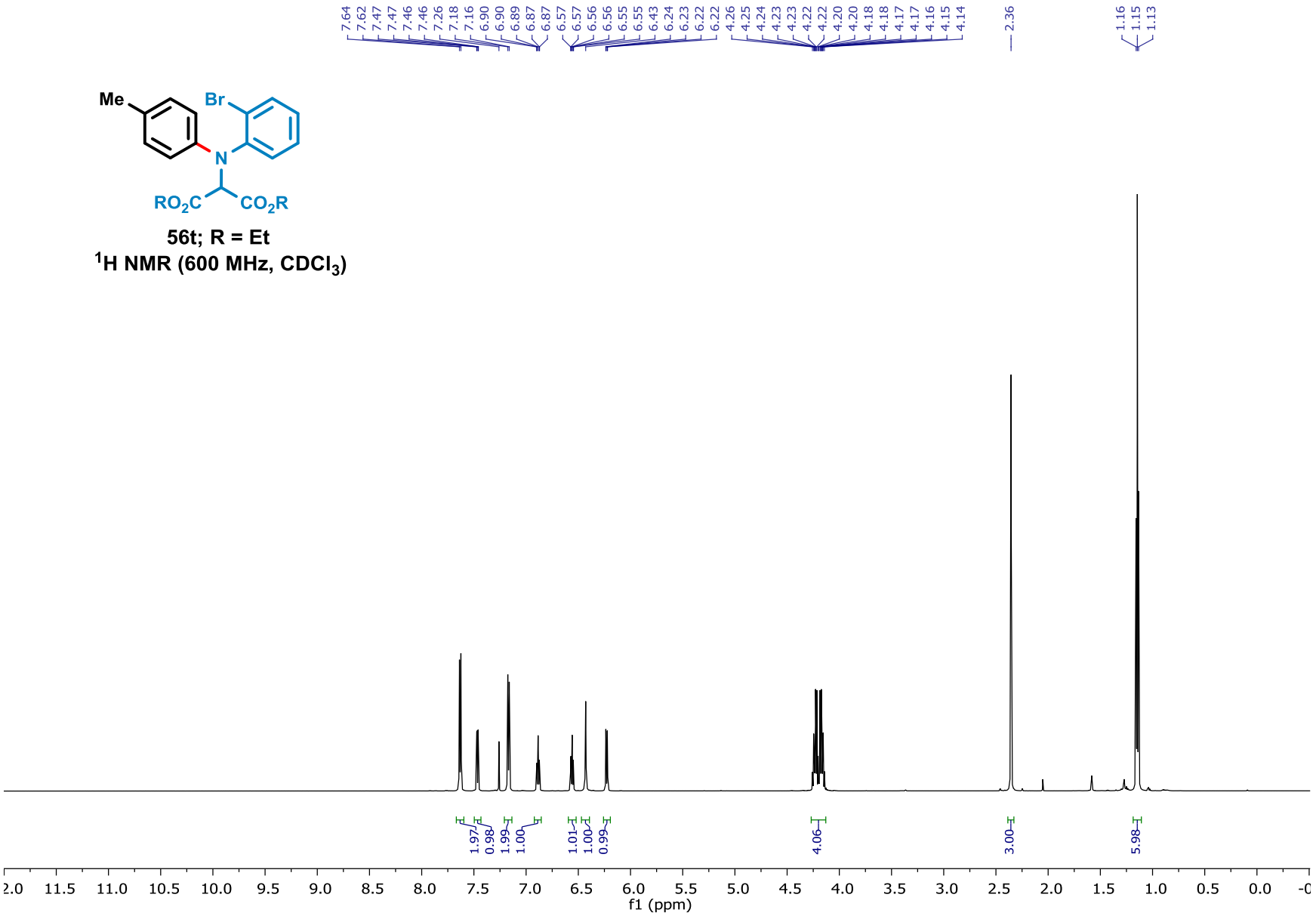
56t; R = ^{i}Pr

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



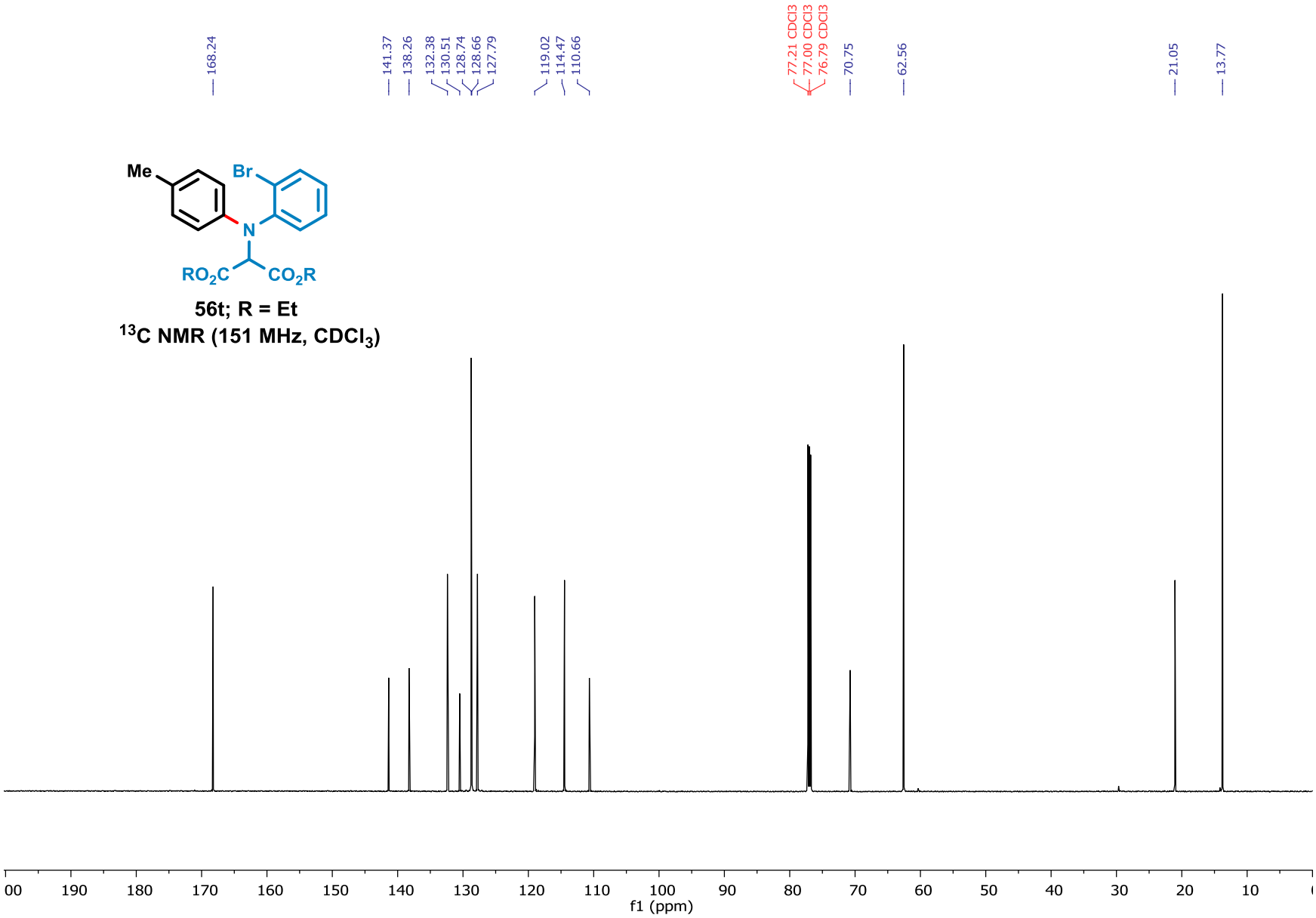
56t; R = ^{i}Pr

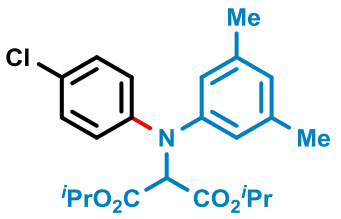
^{13}C NMR (151 MHz, $CDCl_3$)



56t; R = Et

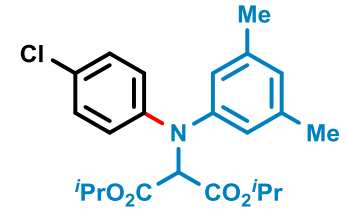
^{1}H NMR (600 MHz, $CDCl_3$)


168.24
141.37
138.26
132.38
130.51
128.74
128.66
127.79
119.02
114.47
110.66
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.75
62.56
21.05
13.77
Me
Br
N
RO2C
CO2R
56t; R = Et
13C NMR (151 MHz, CDCl3)
f1 (ppm)



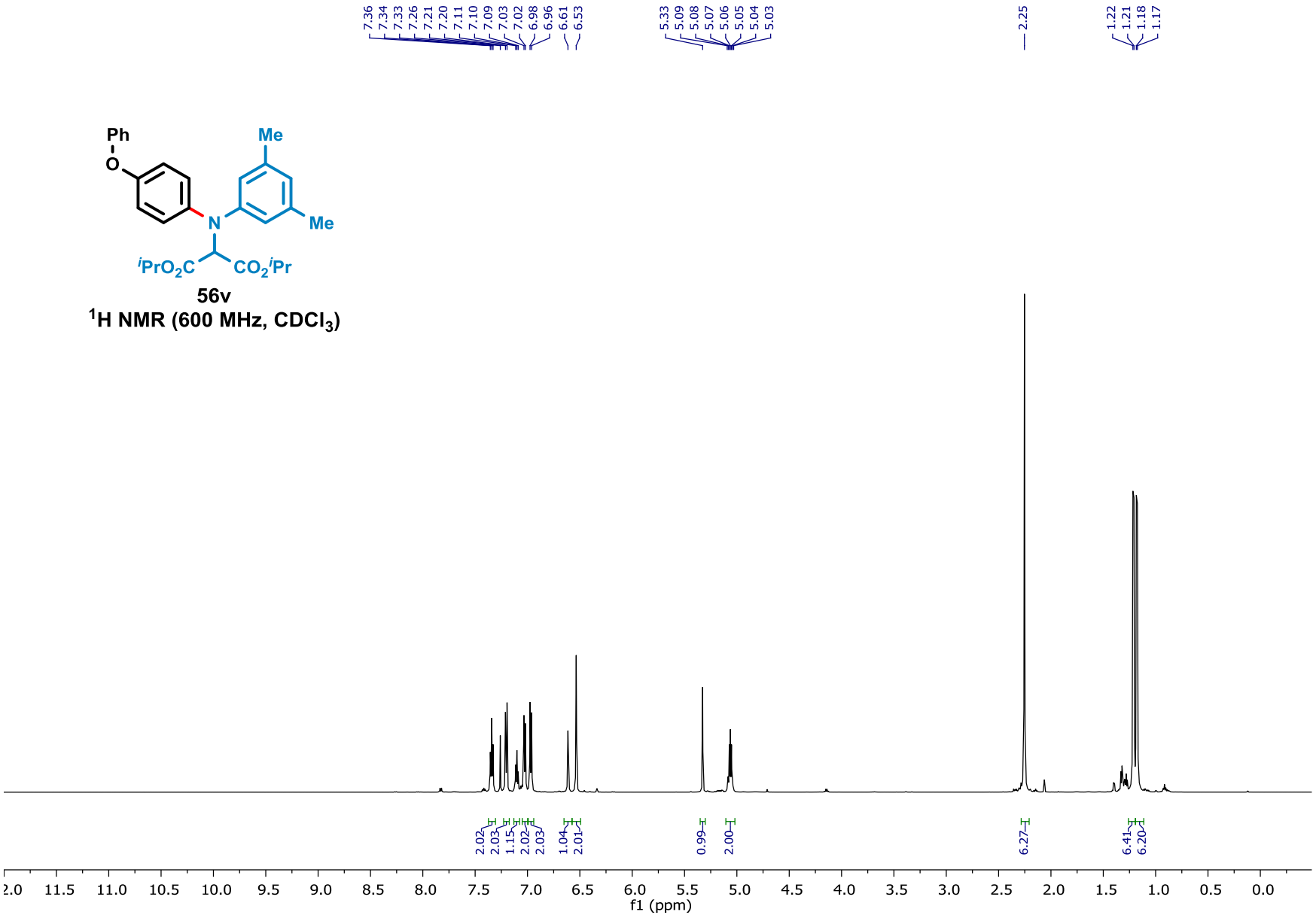
56u

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



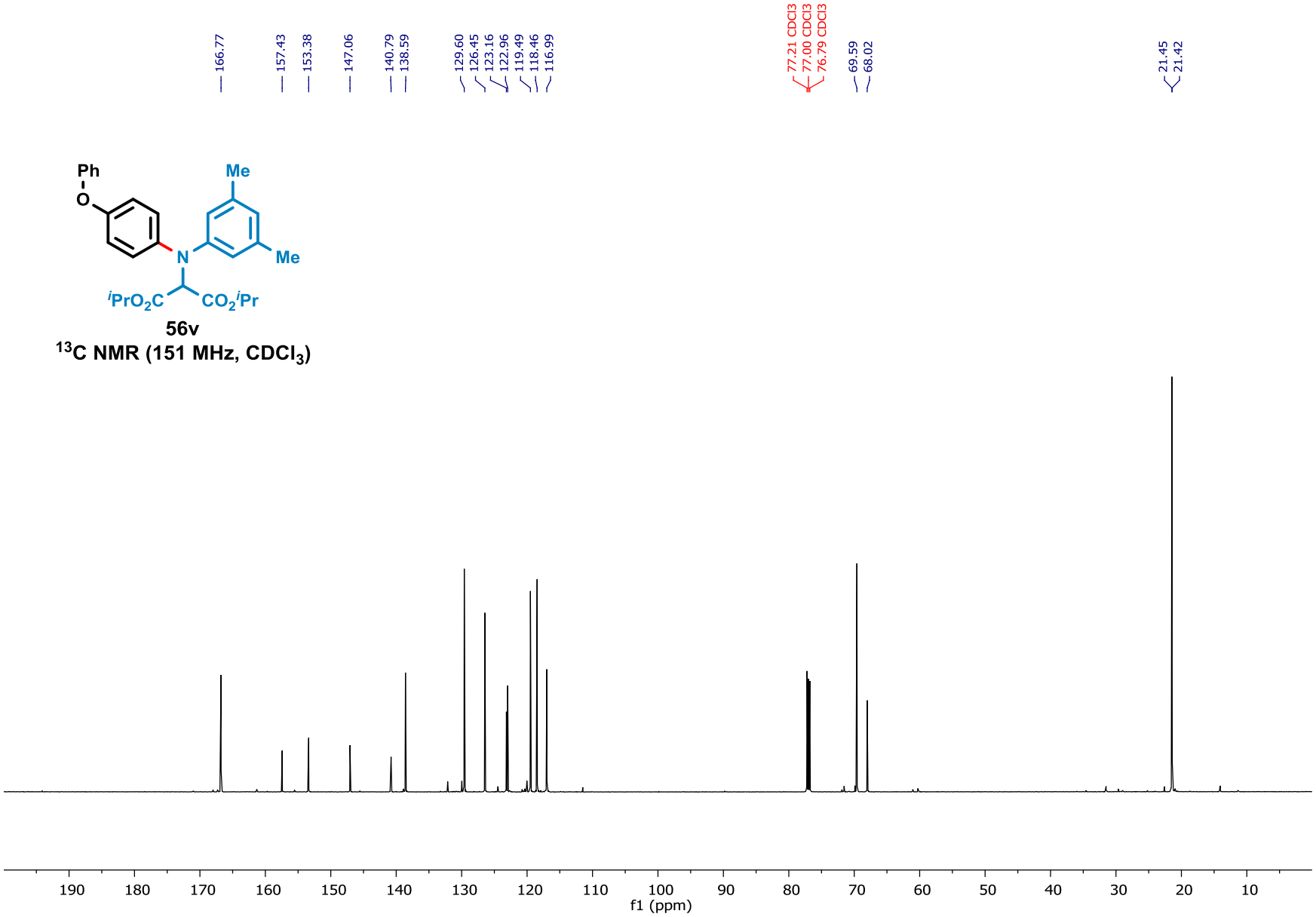
56u

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



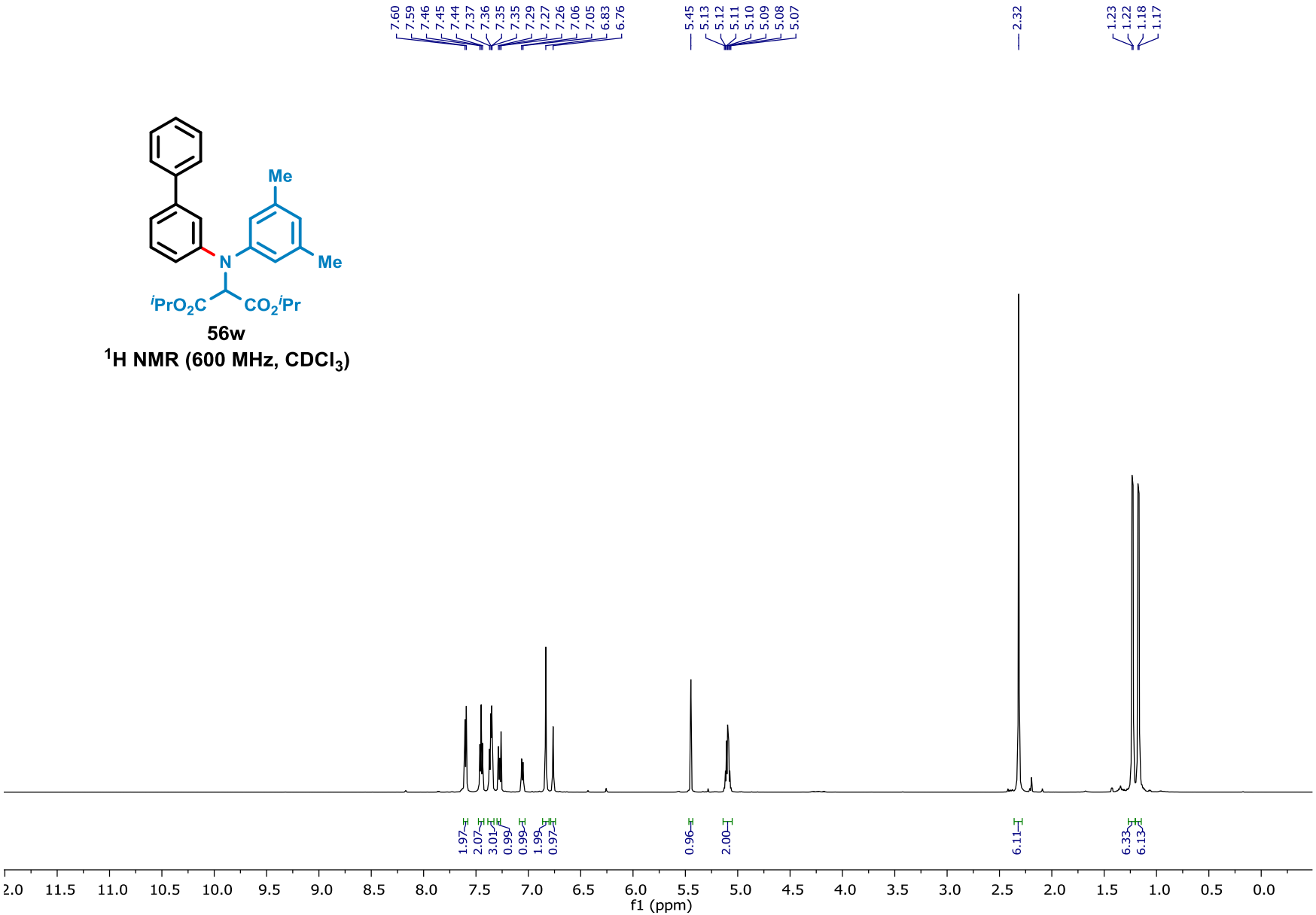
56v

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



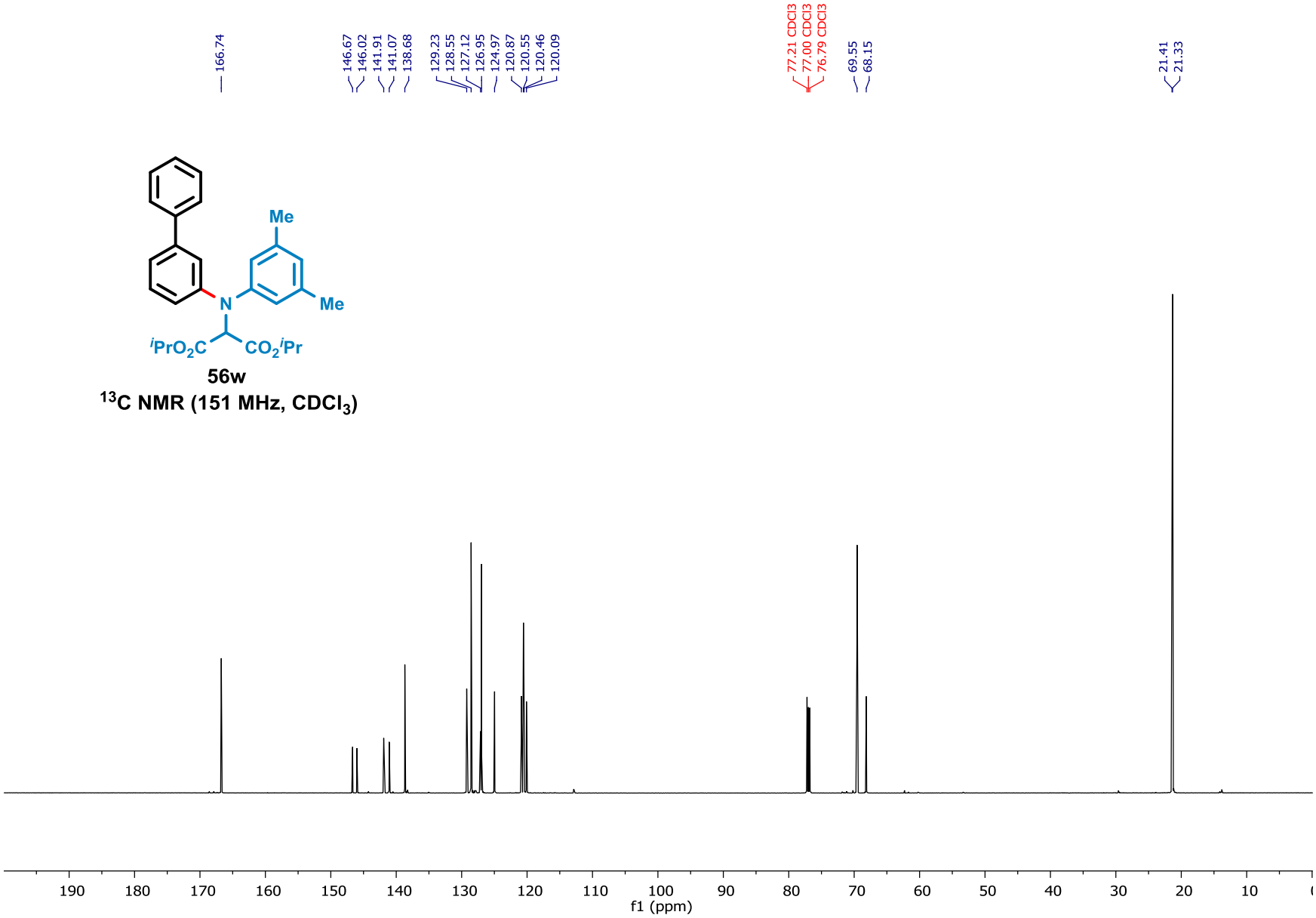
56v

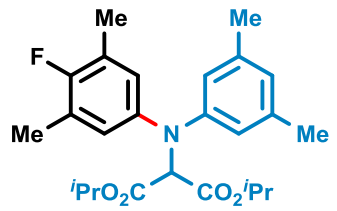
^{13}C NMR (151 MHz, $CDCl_3$)



56w

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

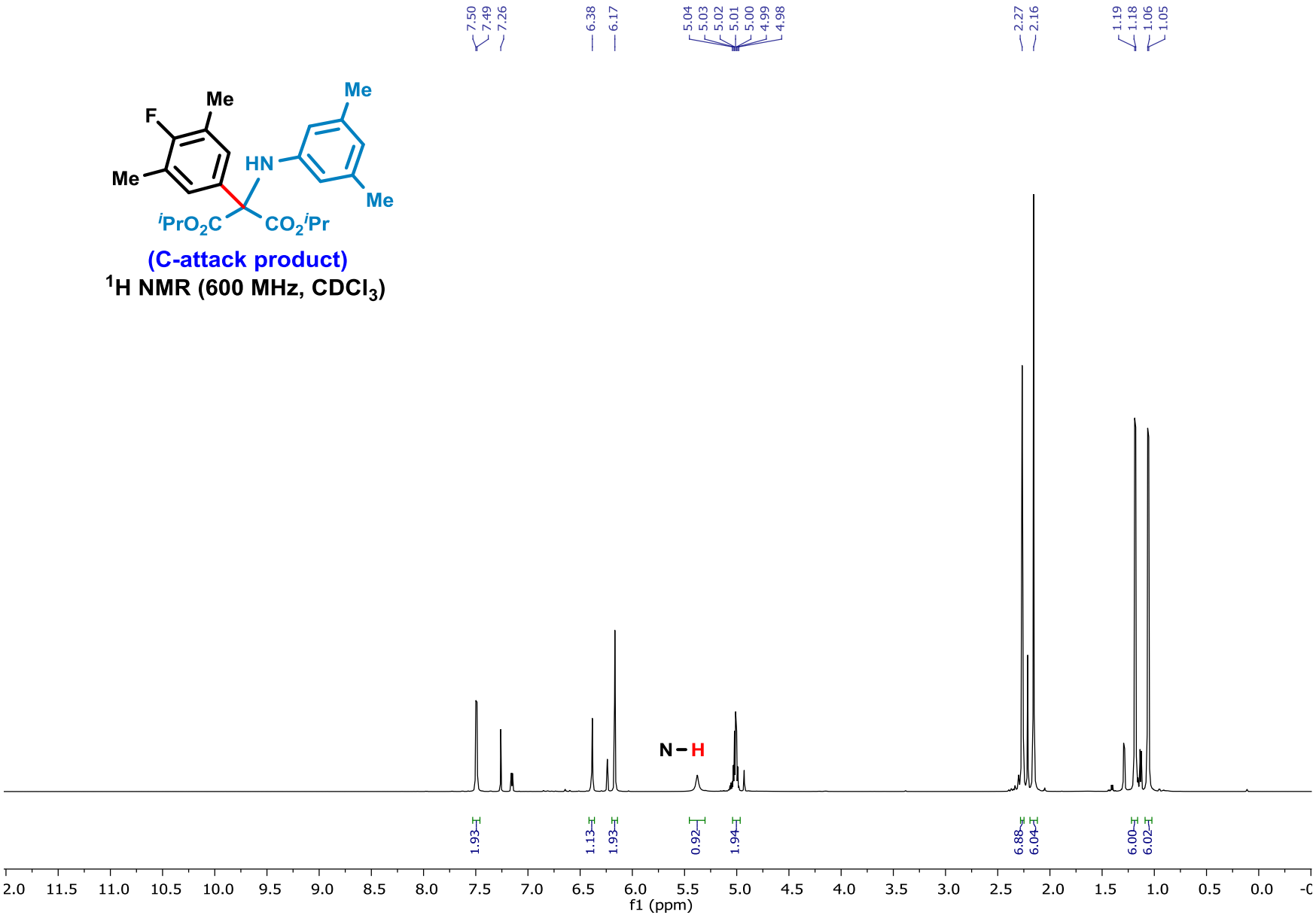

166.74
146.67
146.02
141.91
141.07
138.68
129.23
128.55
127.12
126.95
124.97
120.87
120.55
120.46
120.09
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.55
68.15
21.41
21.33
Me
Me
N
iPrO2C
CO2iPr
56w
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

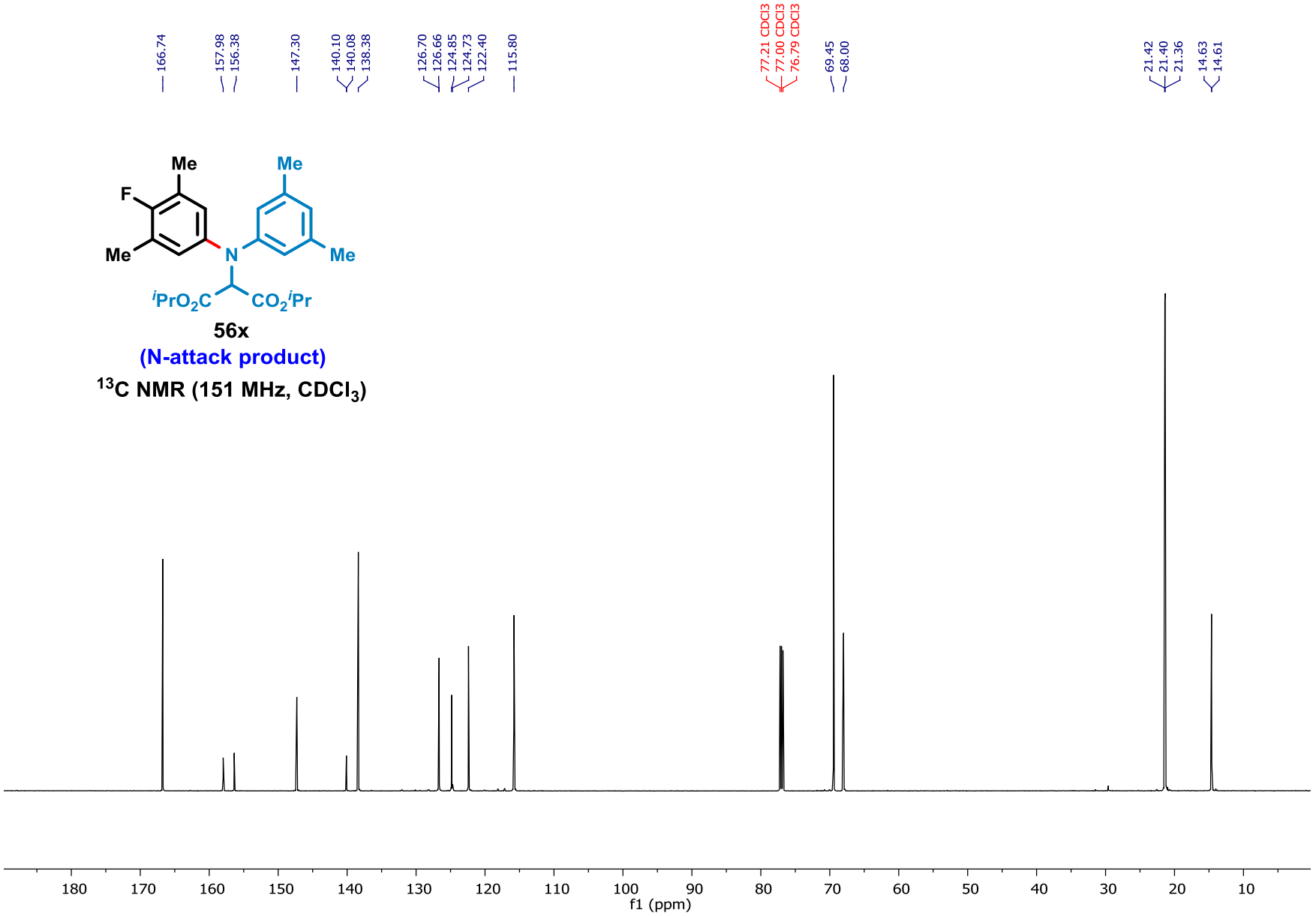


56x

(N-attack product)

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

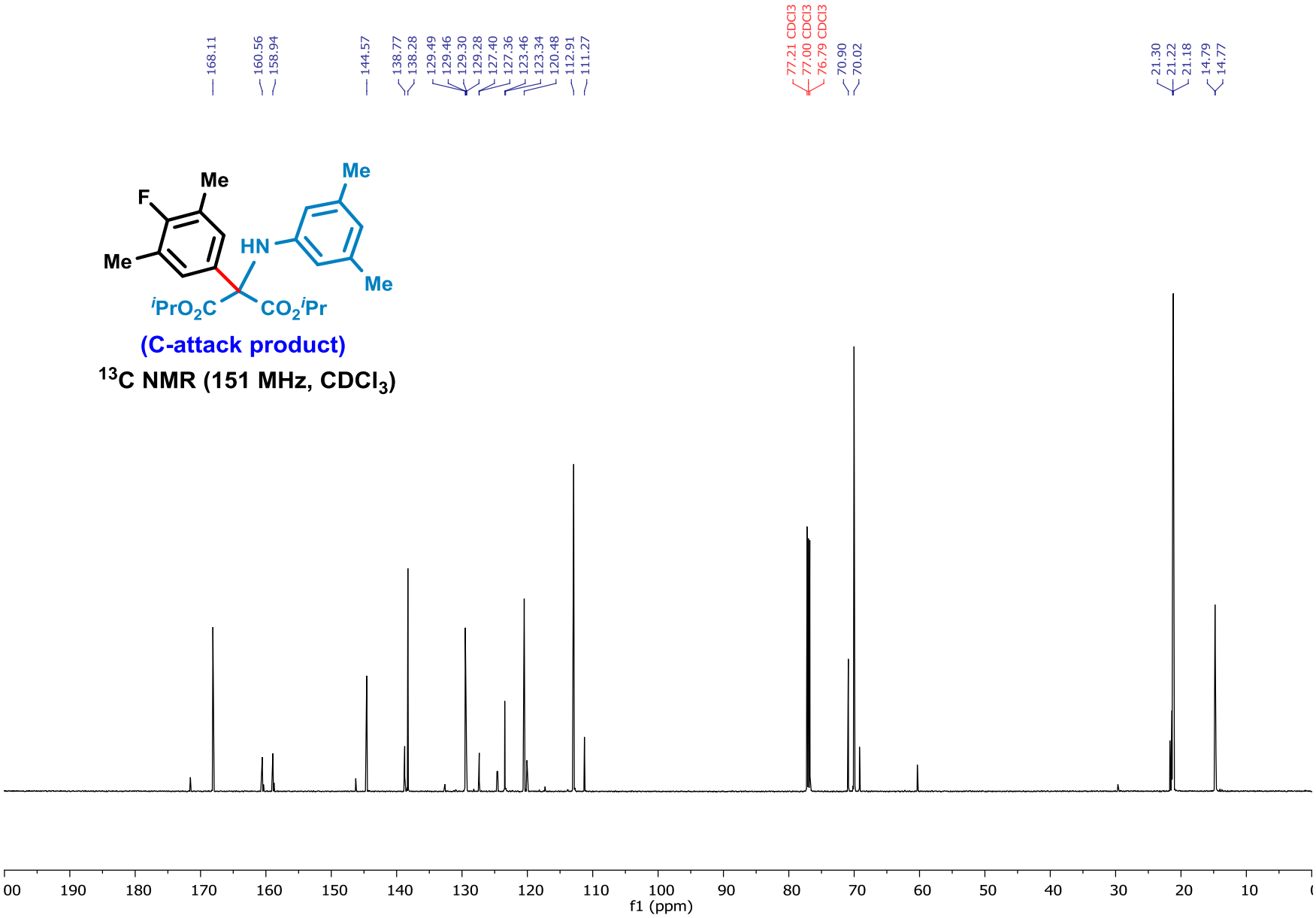

Me
F
Me
HN
Me
Me
$^{i}PrO_2C$
$CO_2{}^{i}Pr$
(C-attack product)
^{1}H NMR (600 MHz, $CDCl_3$)
7.50
7.49
7.26
6.38
6.17
5.04
5.03
5.02
5.01
5.00
4.99
4.98
2.27
2.16
1.19
1.18
1.06
1.05
N–H
1.93
1.13
1.93
0.92
1.94
6.88
6.04
6.00
6.02
f1 (ppm)

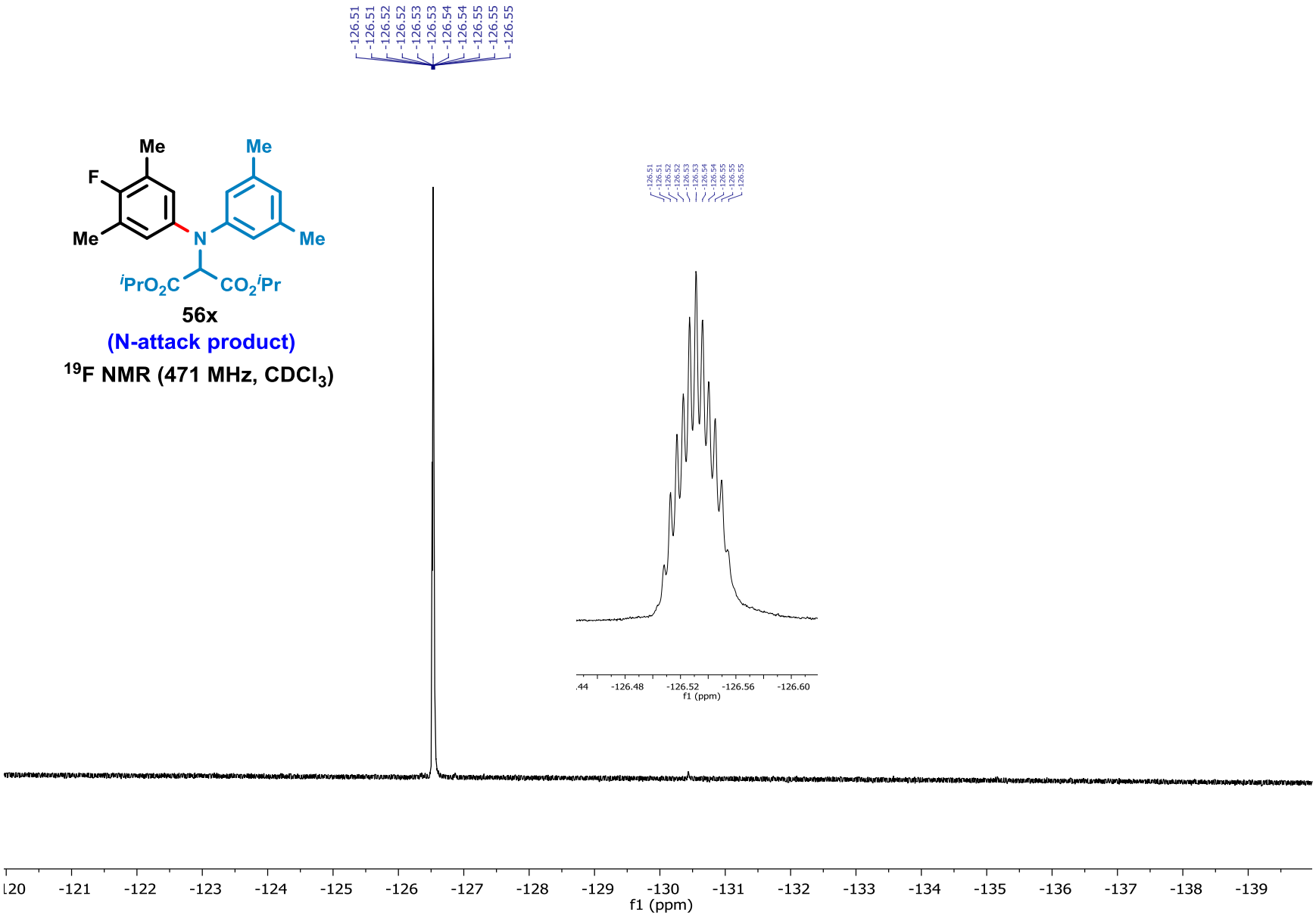


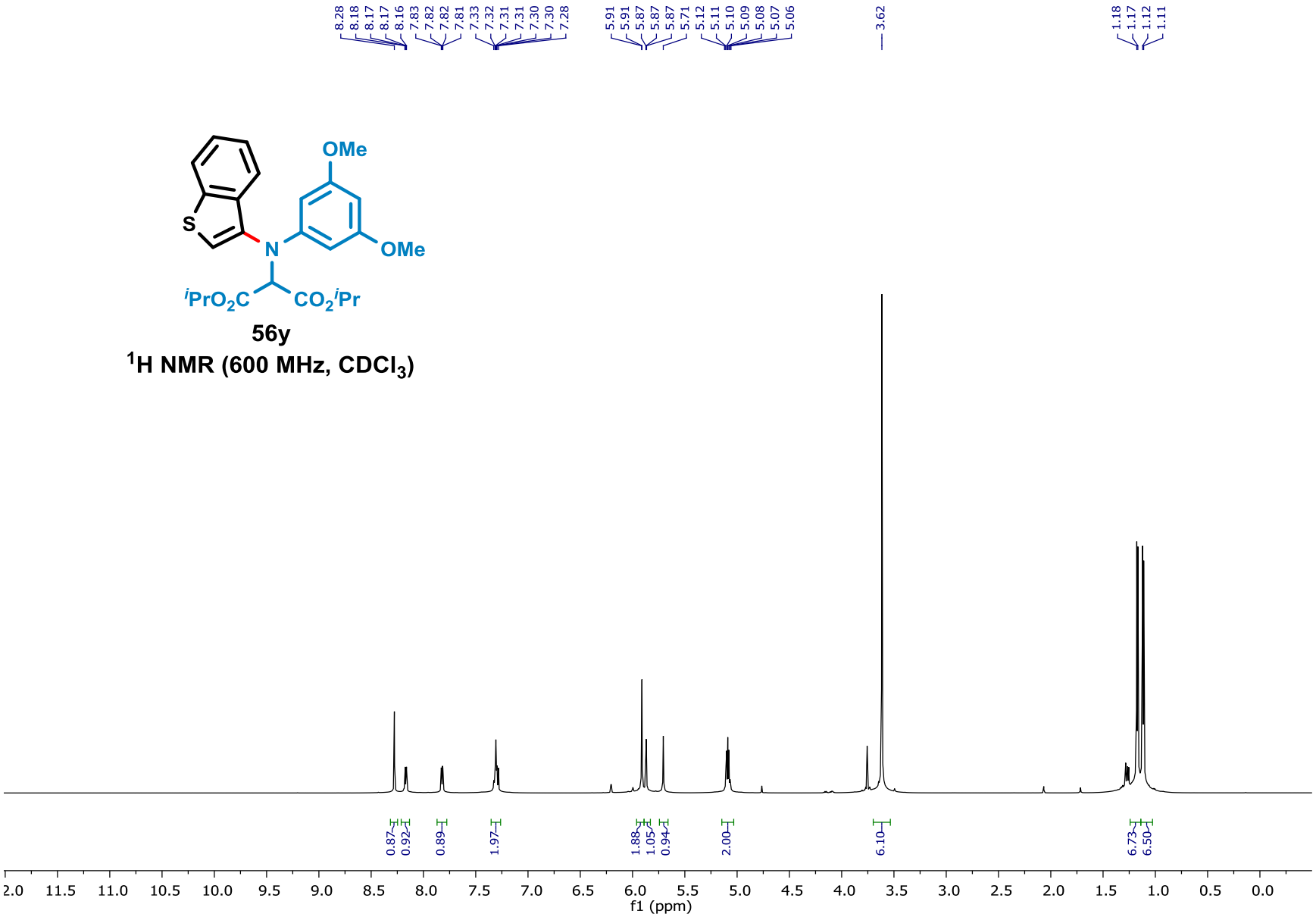
56x

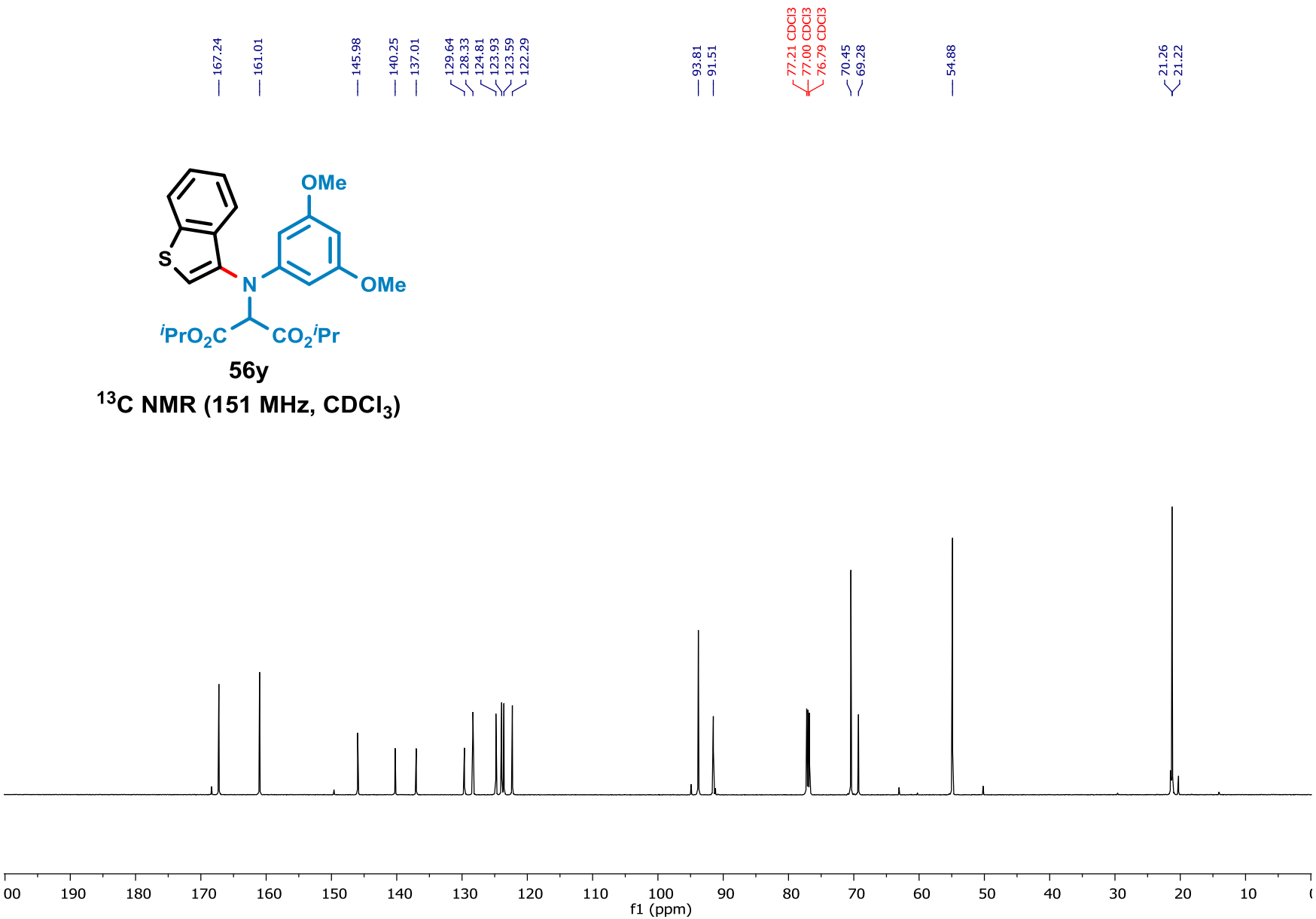
(N-attack product)

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


168.11
160.56
158.94
144.57
138.77
138.28
129.49
129.46
129.30
129.28
127.40
127.36
123.46
123.34
120.48
112.91
111.27
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.90
70.02
21.30
21.22
21.18
14.79
14.77
Me
F
Me
HN
Me
Me
iPrO2C
CO2iPr
(C-attack product)
13C NMR (151 MHz, CDCl3)
f1 (ppm)

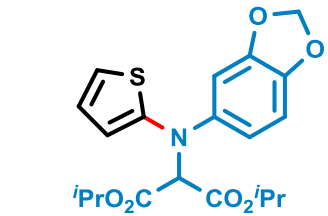

-126.51
-126.51
-126.52
-126.52
-126.53
-126.53
-126.54
-126.54
-126.55
-126.55
Me
F
Me
N
Me
Me
iPrO2C
CO2iPr
56x
(N-attack product)
19F NMR (471 MHz, CDCl3)
.44
-126.48
-126.52
-126.56
-126.60
f1 (ppm)
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)


8.28
8.18
8.17
8.17
8.16
7.83
7.82
7.82
7.81
7.33
7.32
7.31
7.31
7.30
7.30
7.28
5.91
5.91
5.87
5.87
5.87
5.71
5.12
5.11
5.10
5.09
5.08
5.07
5.06
3.62
1.18
1.17
1.12
1.11
OMe
OMe
S
N
iPrO2C
CO2iPr
56y
1H NMR (600 MHz, CDCl3)
0.87
0.92
0.89
1.97
1.88
1.05
0.94
2.00
6.10
6.73
6.50
f1 (ppm)



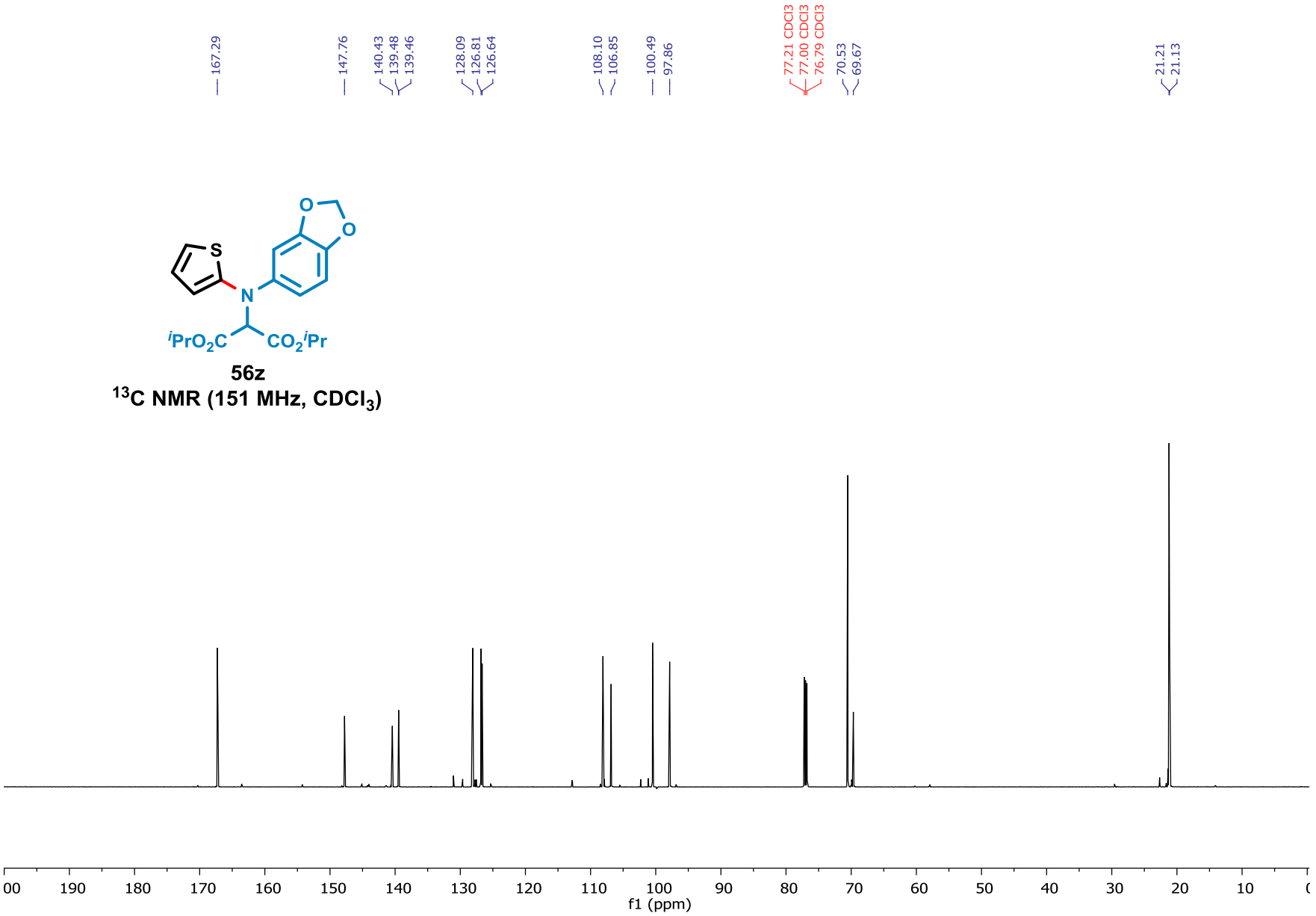
56y

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



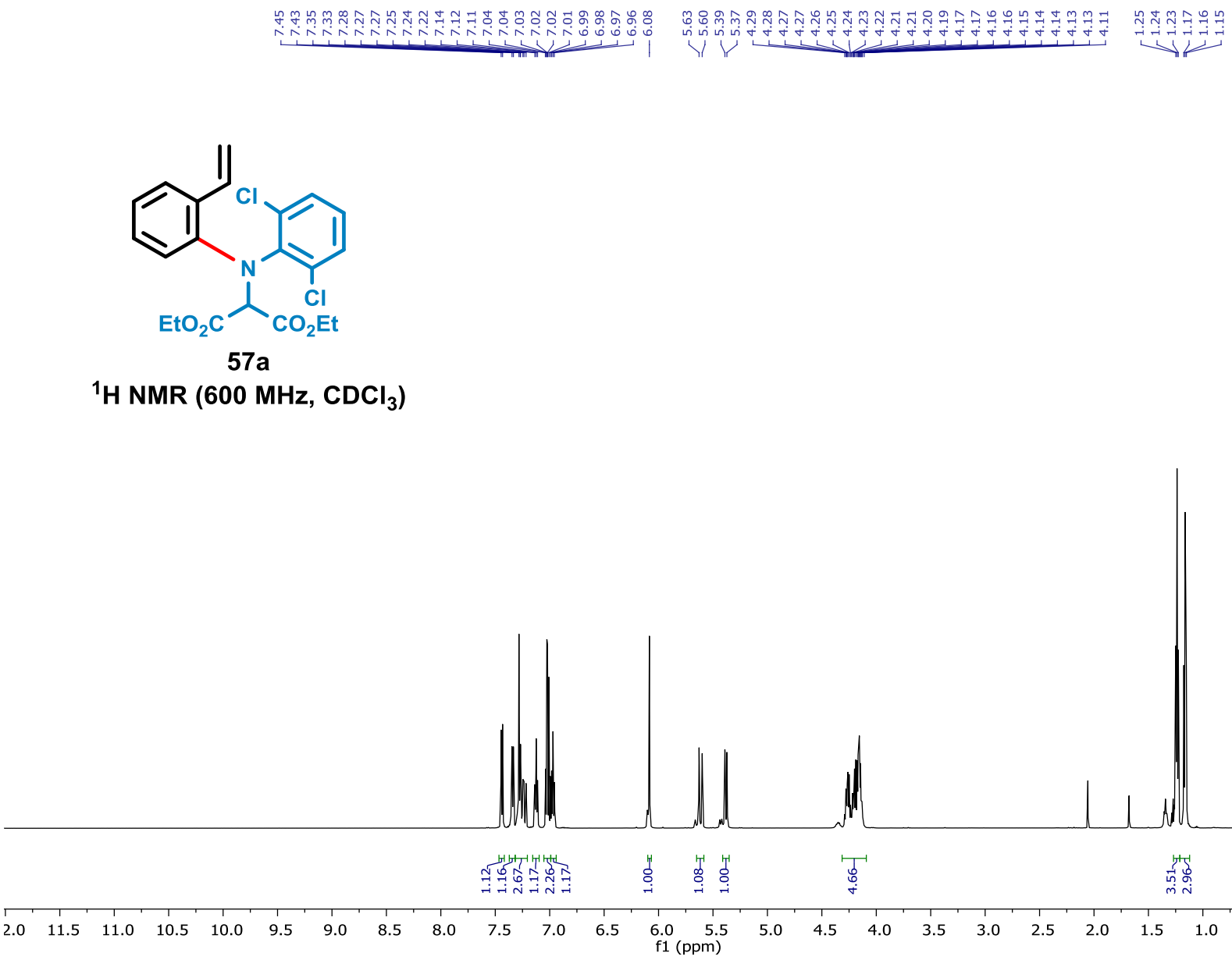
56z

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



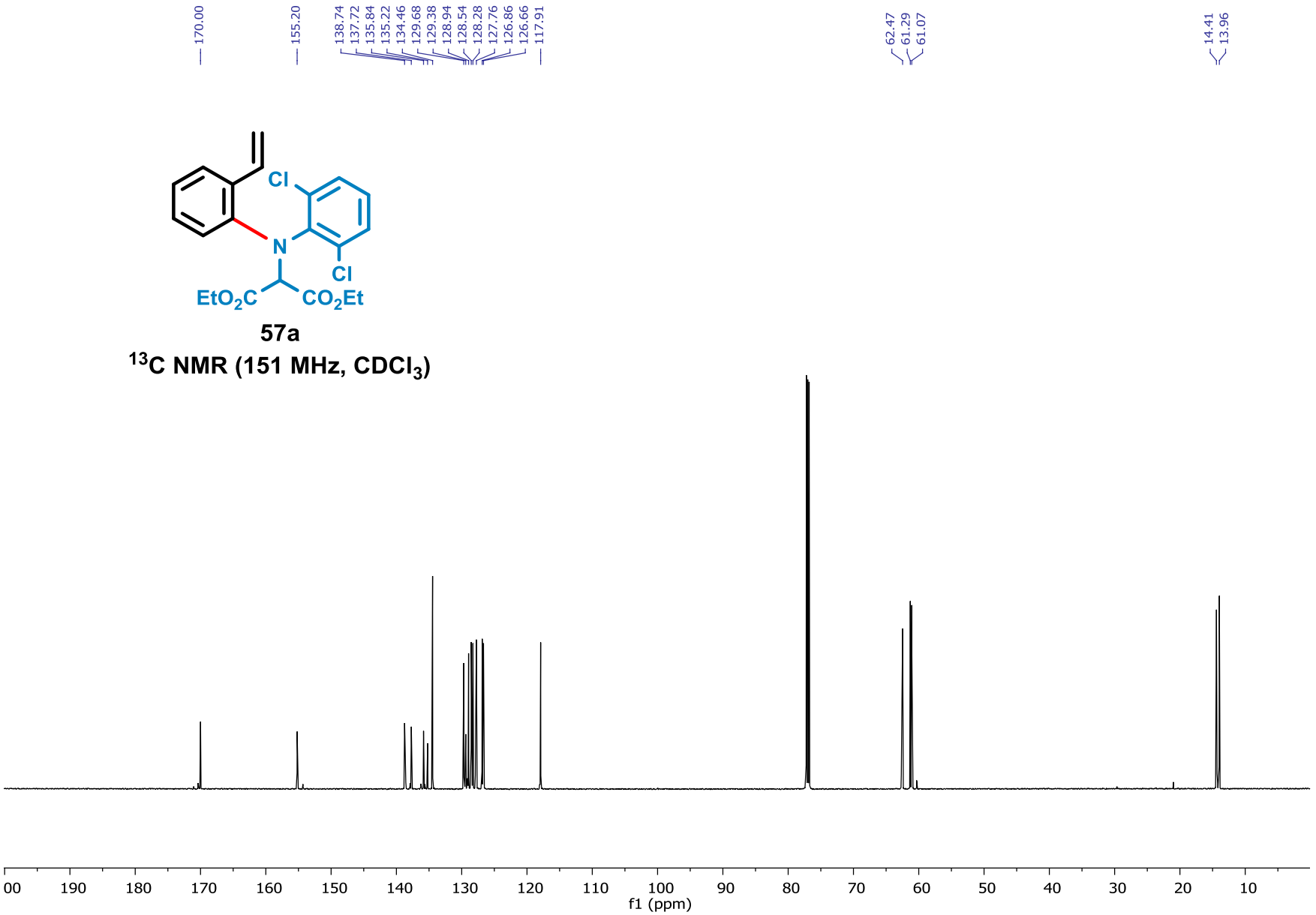
56z

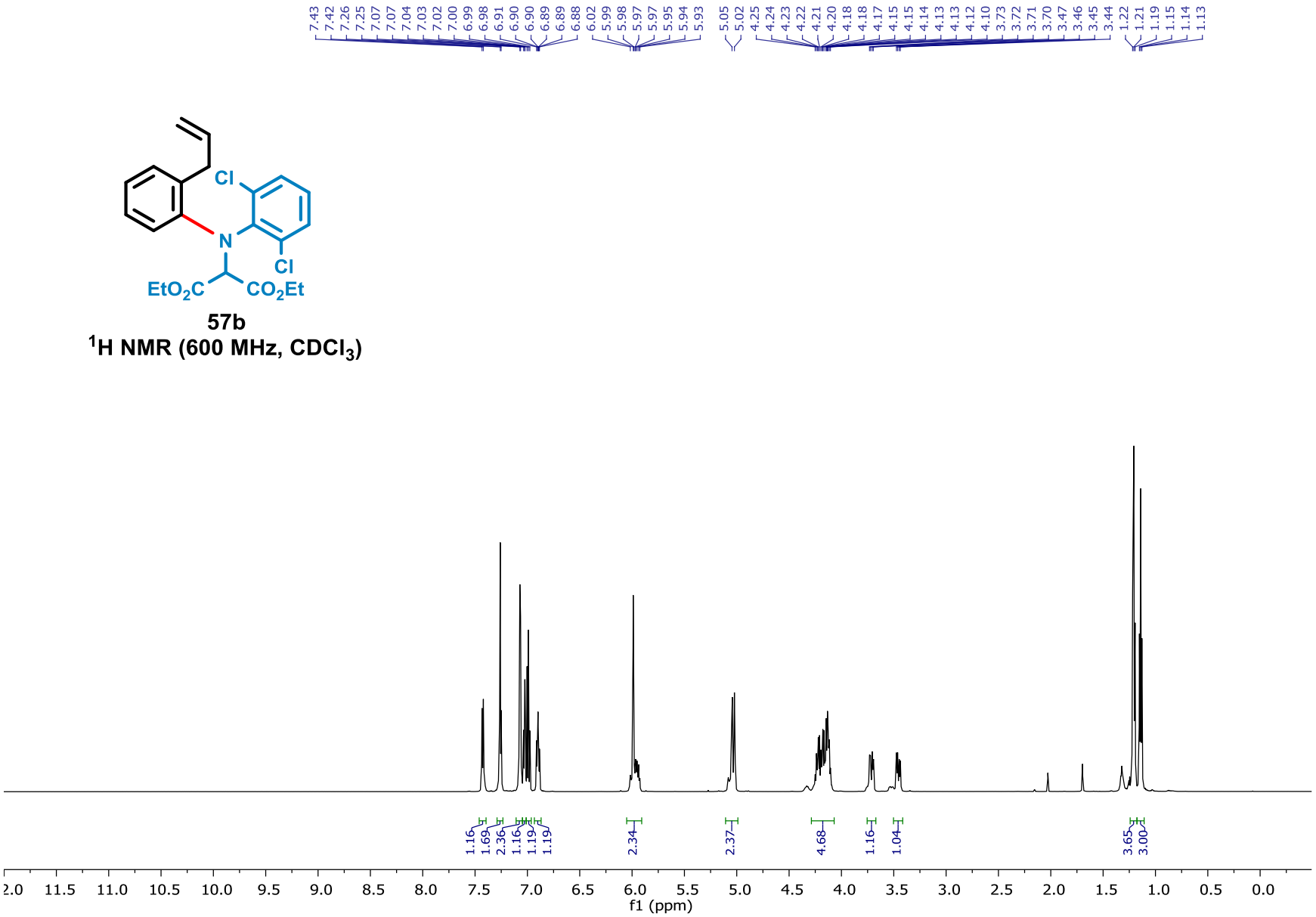
^{13}C NMR (151 MHz, $CDCl_3$)



57a

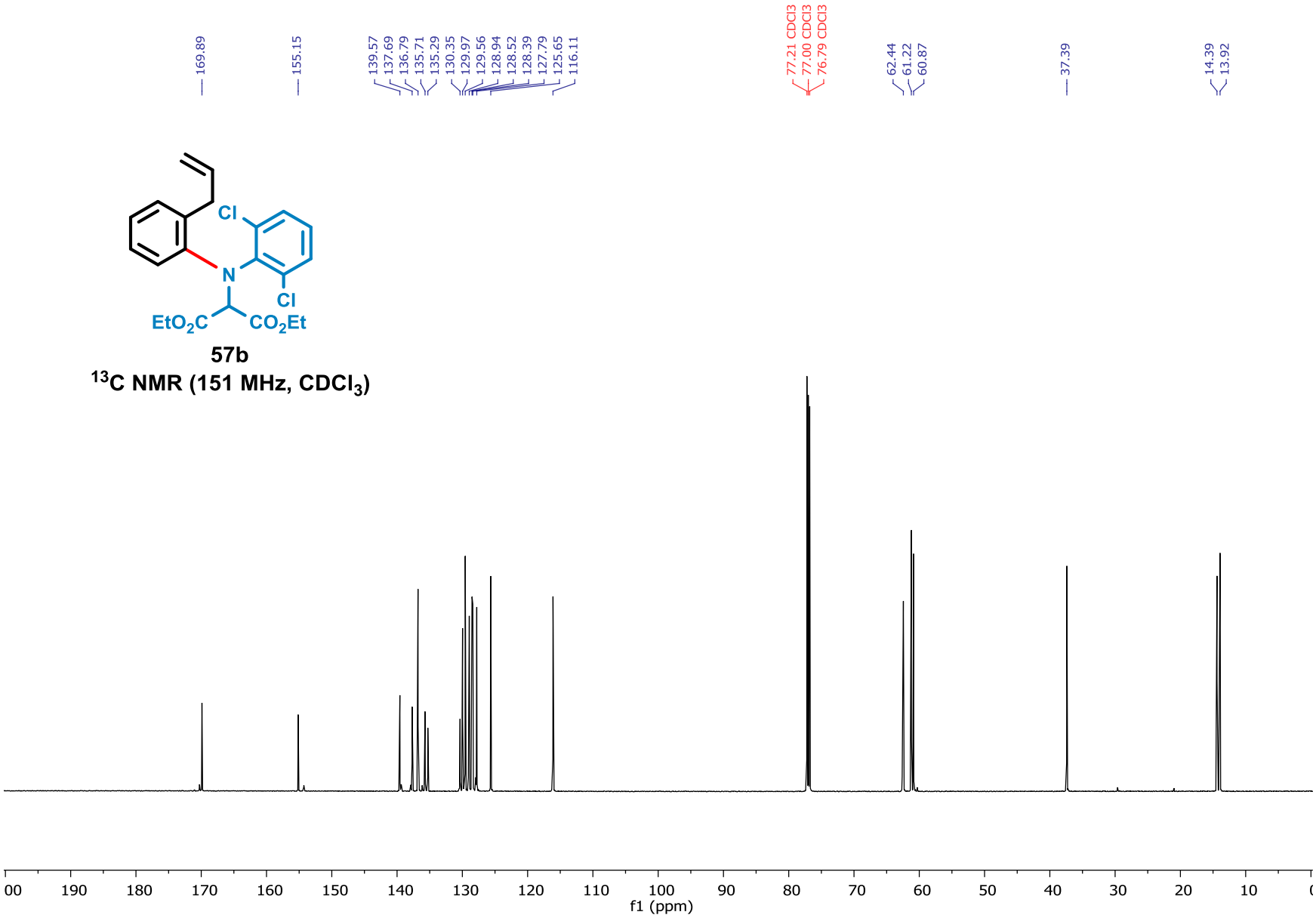
^{1}H NMR (600 MHz, $CDCl_3$)


170.00
155.20
138.74
137.72
135.84
135.22
134.46
129.68
129.38
128.94
128.54
128.28
127.76
126.86
126.66
117.91
62.47
61.29
61.07
14.41
13.96
Cl
N
Cl
EtO2C
CO2Et
57a
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



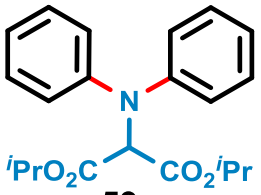
57b

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



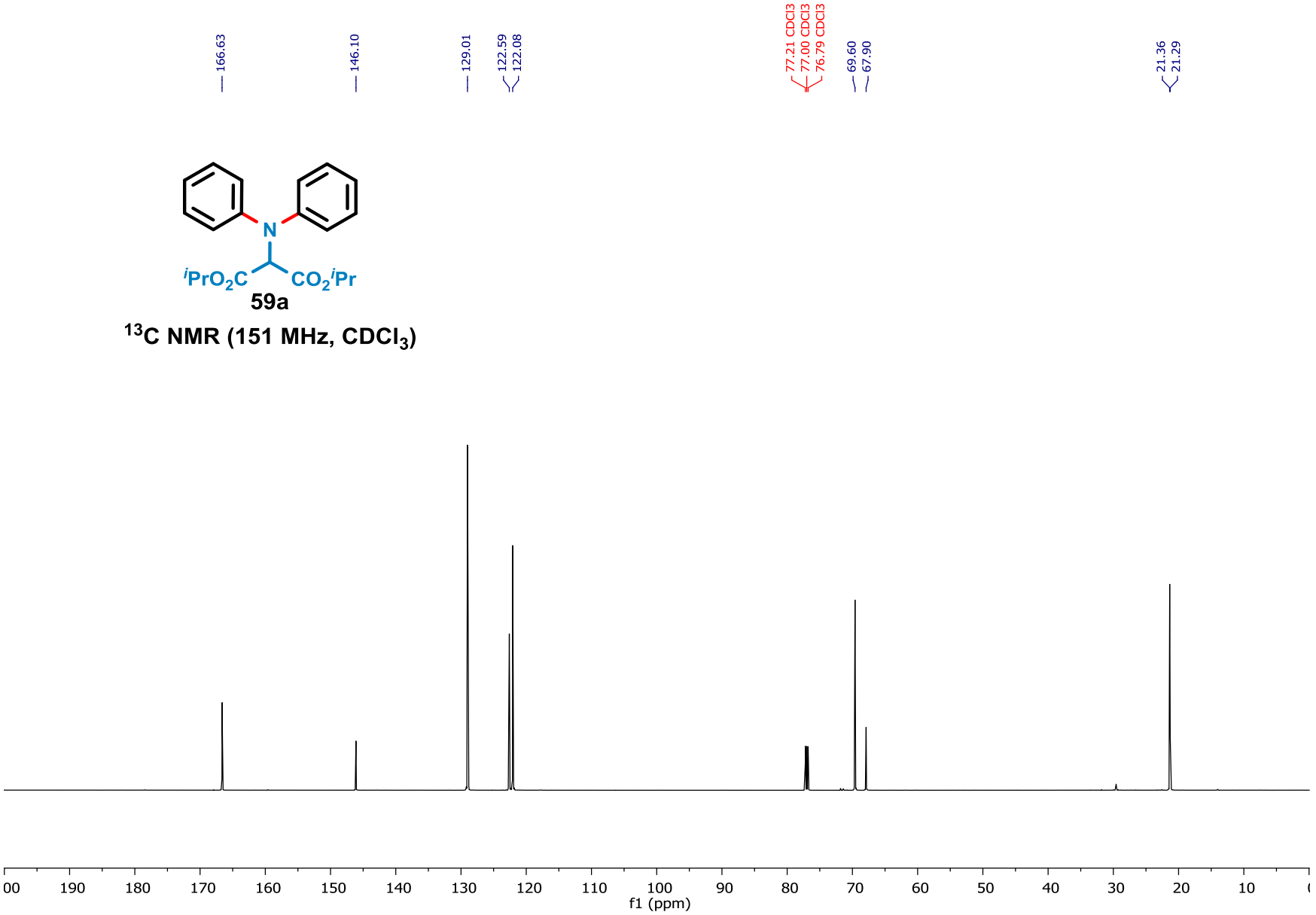
57b

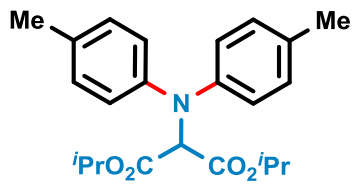
^{13}C NMR (151 MHz, $CDCl_3$)



59a

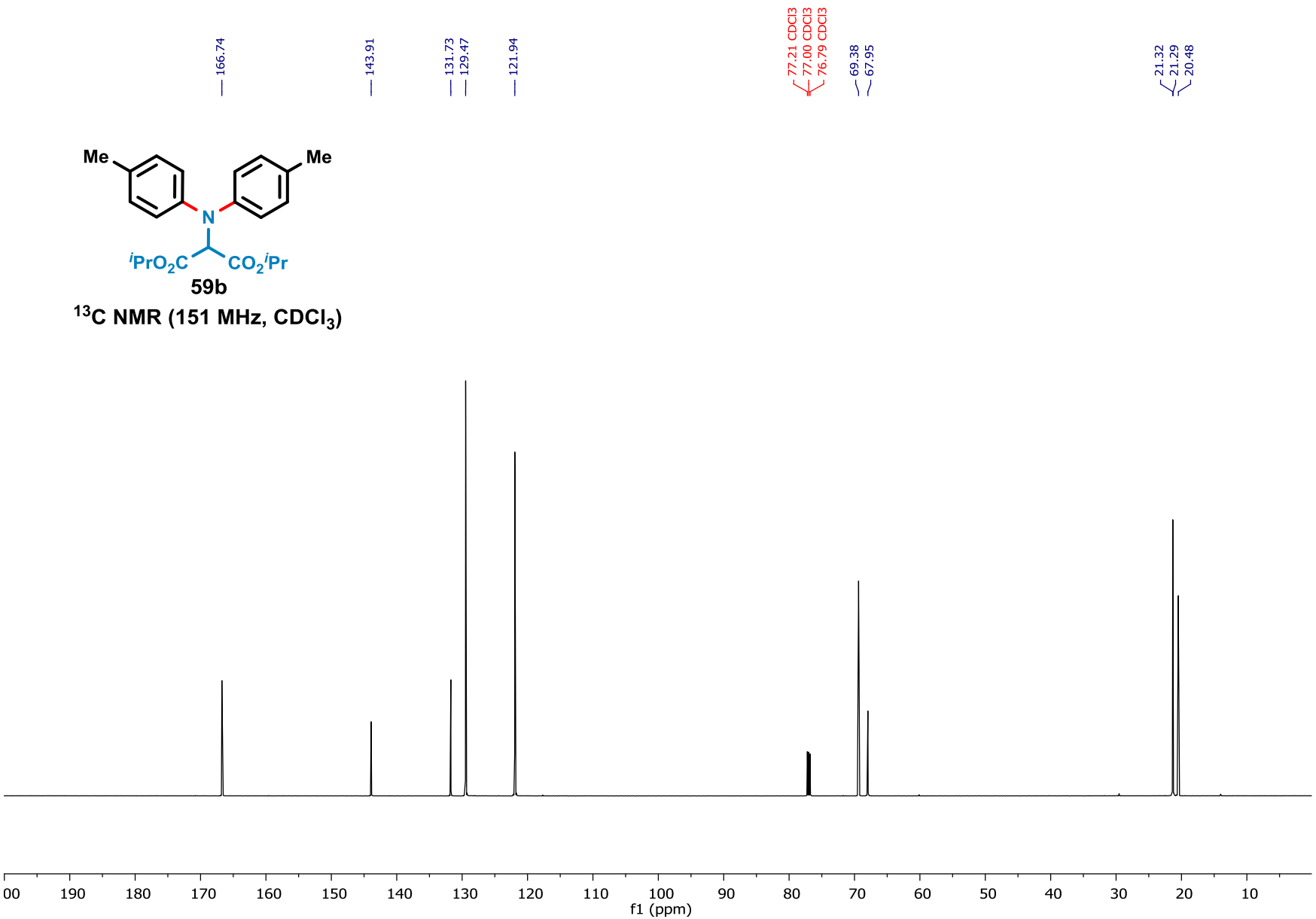
^{1}H NMR (600 MHz, $CDCl_3$)

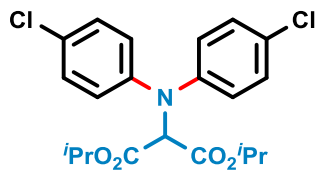

166.63
146.10
129.01
122.59
122.08
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.60
67.90
21.36
21.29
N
iPrO2C
CO2iPr
59a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



59b

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

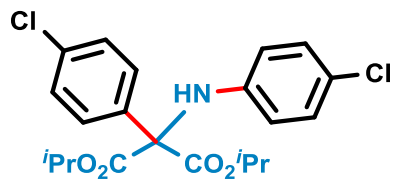

166.74
143.91
131.73
129.47
121.94
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.38
67.95
21.32
21.29
20.48
Me
Me
N
iPrO2C
CO2iPr
59b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



59c

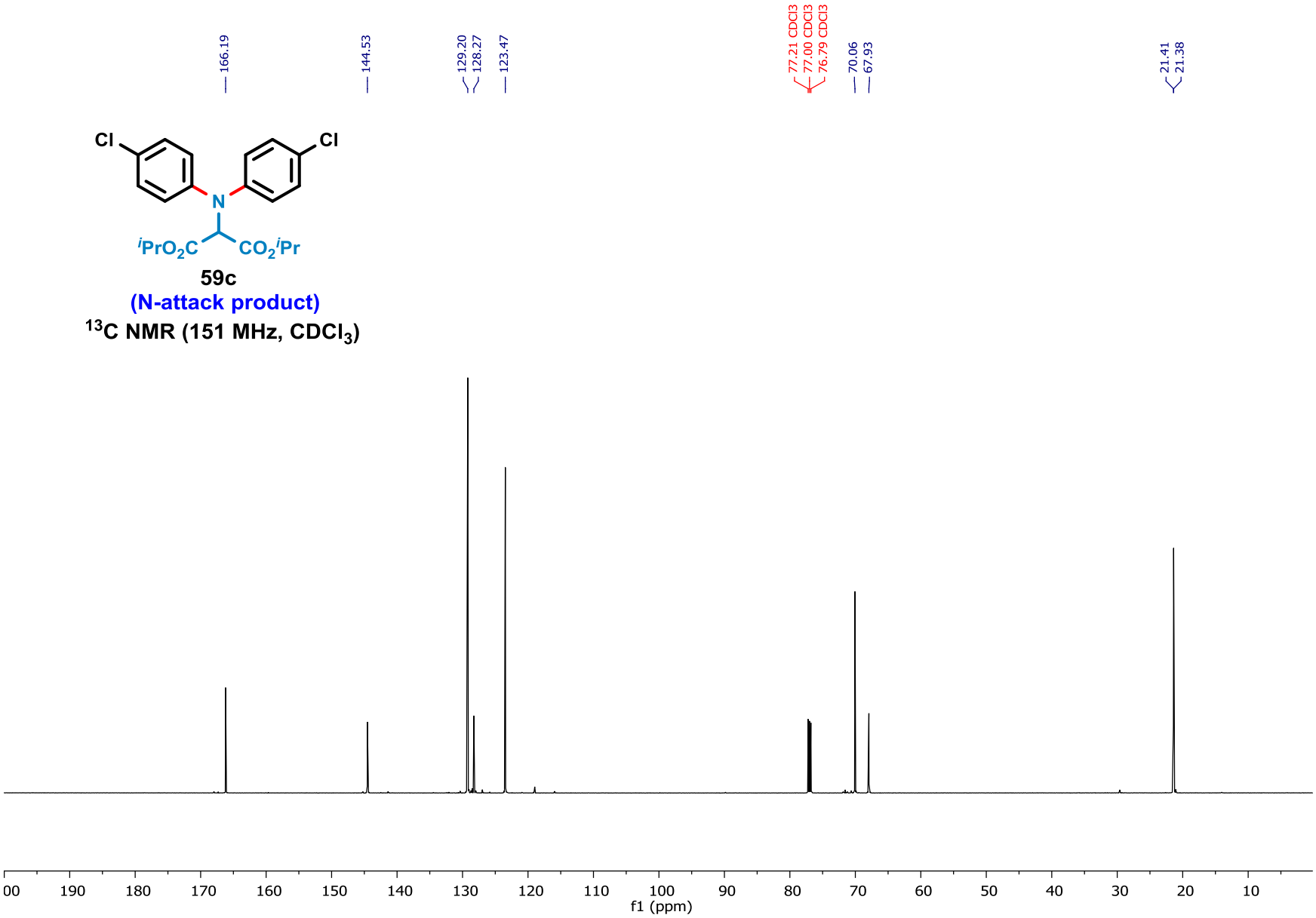
(N-attack product)

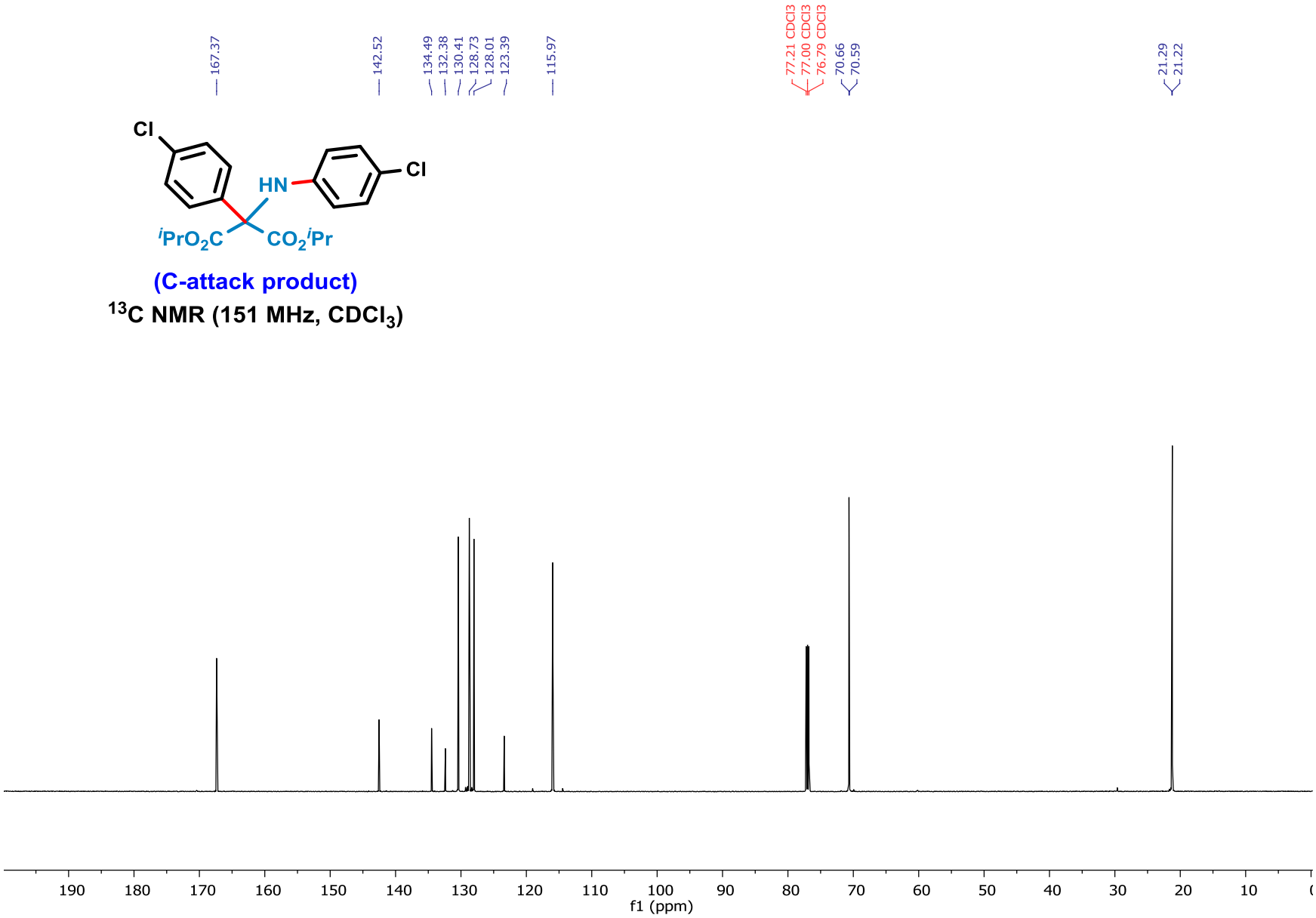
^{1}H NMR (600 MHz, $CDCl_3$)

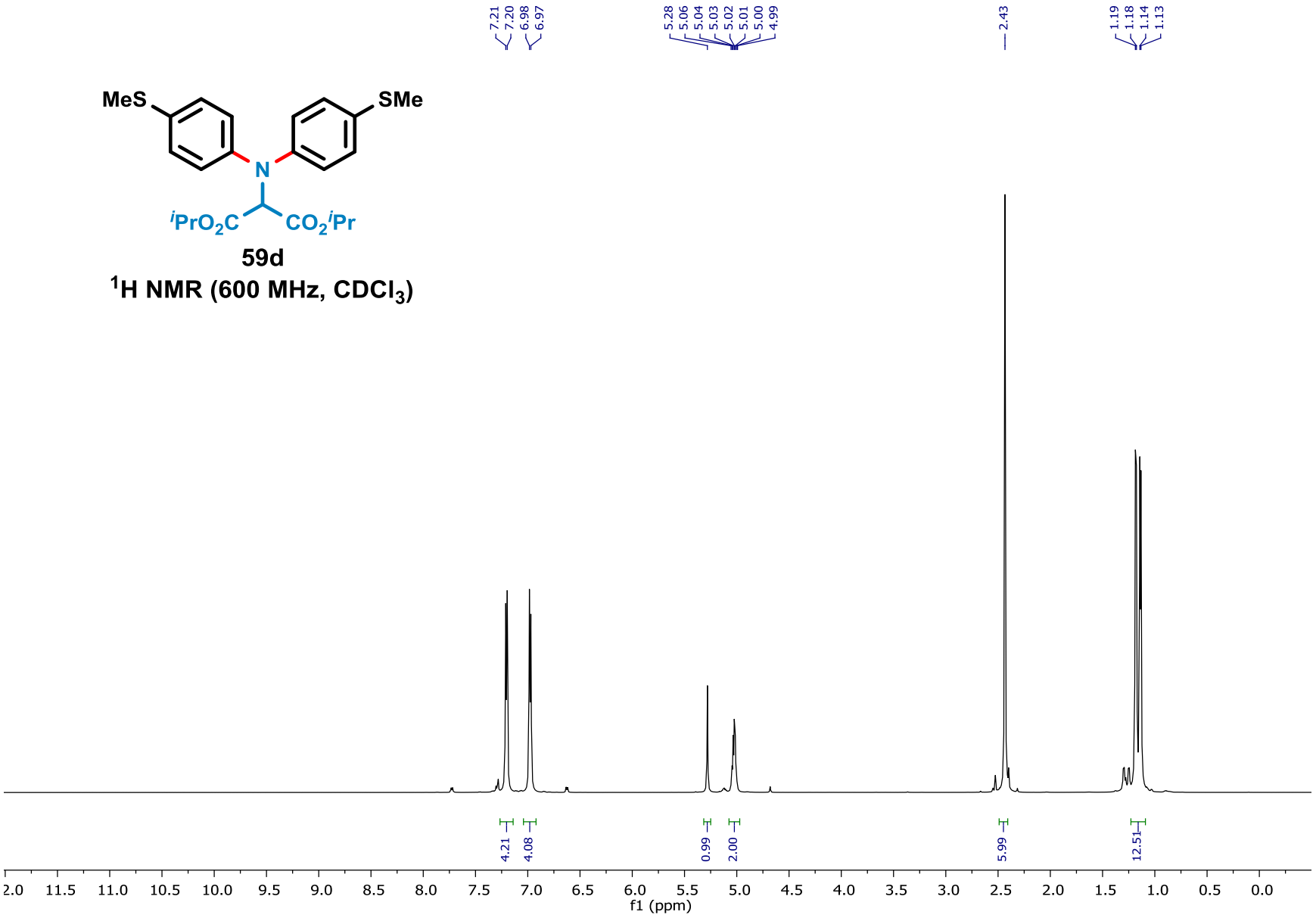


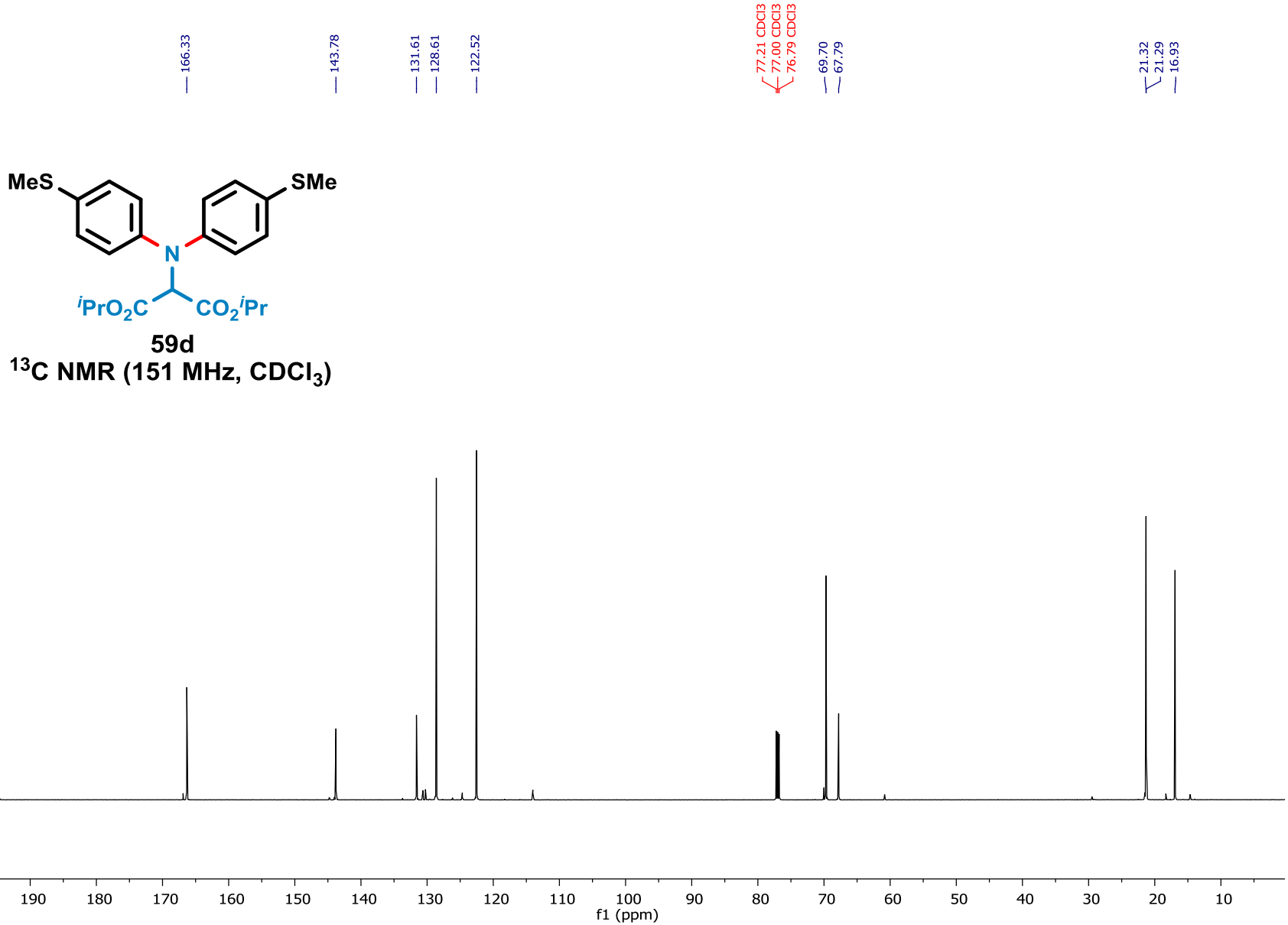
(C-attack product)

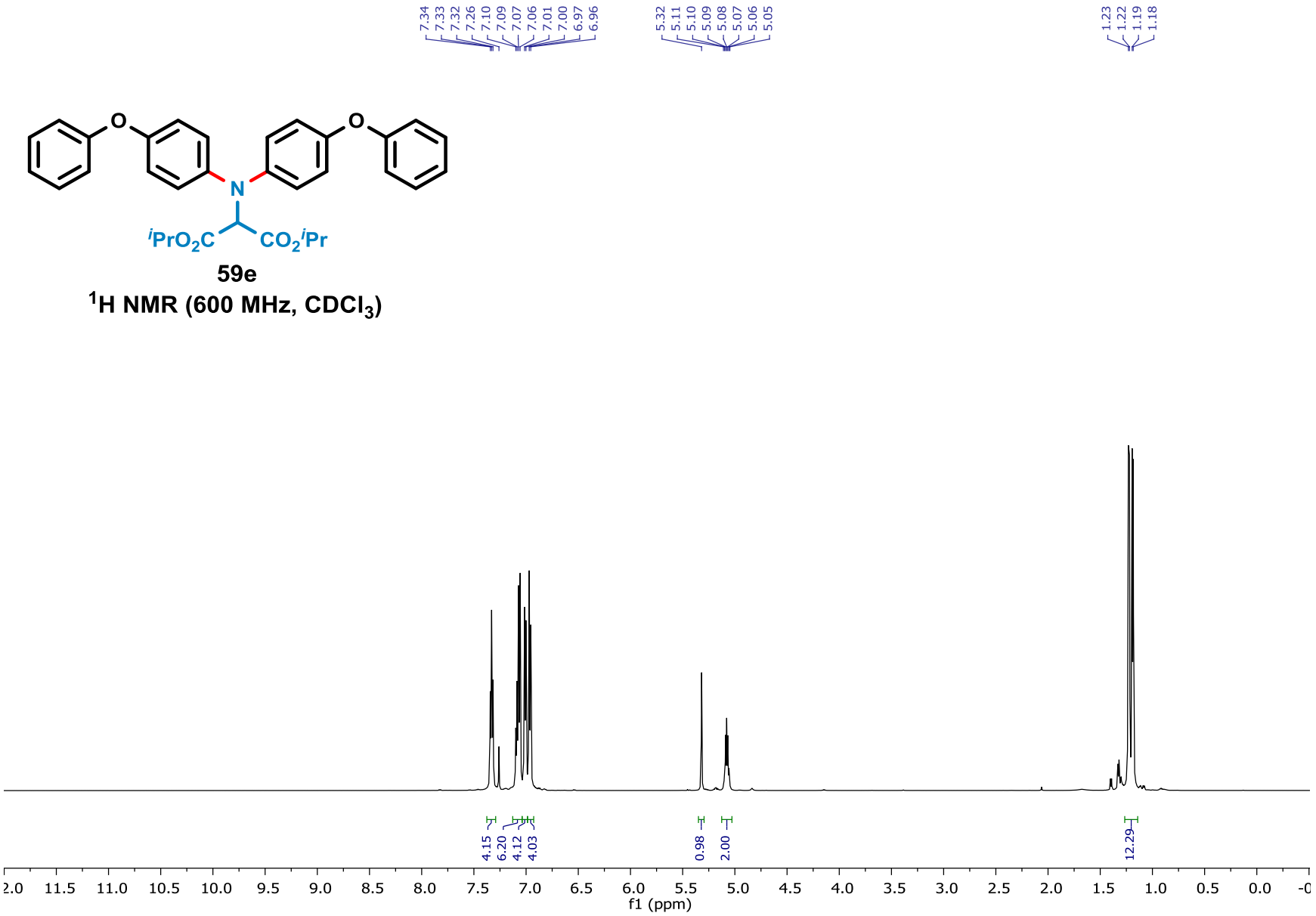
^{1}H NMR (600 MHz, $CDCl_3$)


166.19
144.53
129.20
128.27
123.47
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.06
67.93
21.41
21.38
Cl
Cl
N
iPrO2C
CO2iPr
59c
(N-attack product)
13C NMR (151 MHz, CDCl3)
f1 (ppm)


167.37
142.52
134.49
132.38
130.41
128.73
128.01
123.39
115.97
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.66
70.59
21.29
21.22
Cl
HN
Cl
iPrO2C
CO2iPr
(C-attack product)
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

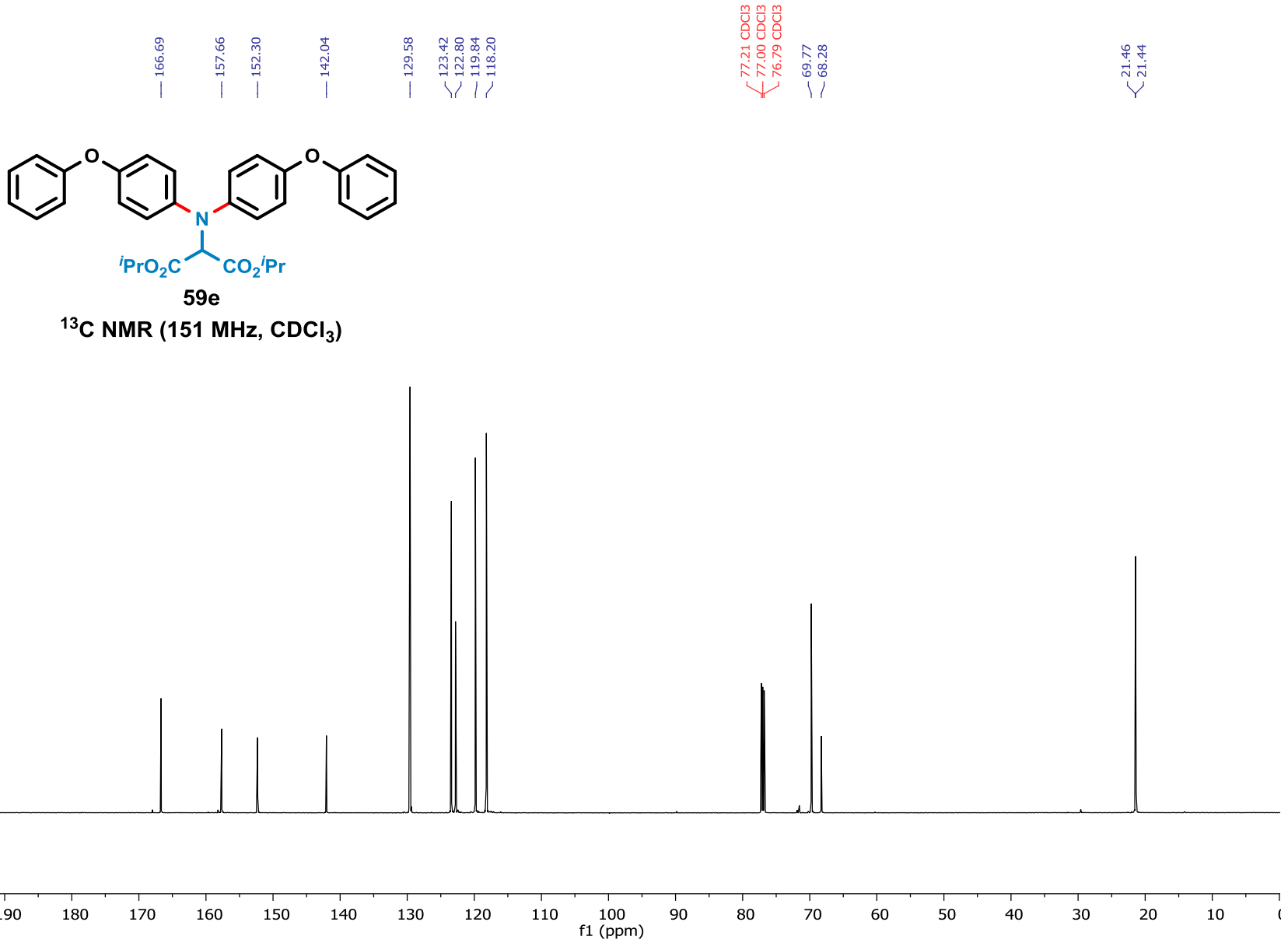

MeS
SMe
N
iPrO2C
CO2iPr
59d
1H NMR (600 MHz, CDCl3)
7.21
7.20
6.98
6.97
5.28
5.06
5.04
5.03
5.02
5.01
5.00
4.99
2.43
1.19
1.18
1.14
1.13
4.21
4.08
0.99
2.00
5.99
12.51
f1 (ppm)


166.33
143.78
131.61
128.61
122.52
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.70
67.79
21.32
21.29
16.93
MeS
SMe
N
iPrO2C
CO2iPr
59d
13C NMR (151 MHz, CDCl3)
f1 (ppm)



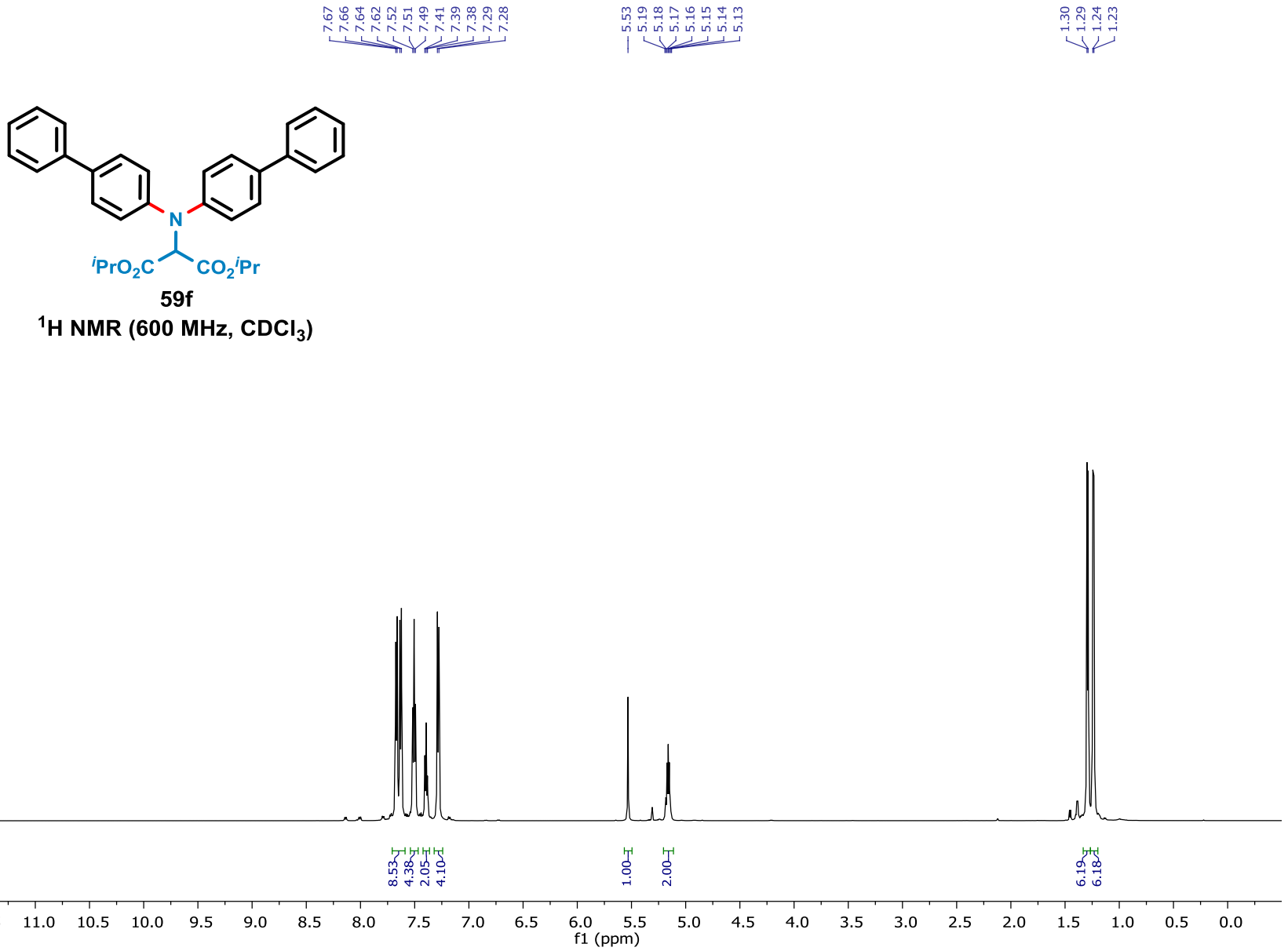
59e

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



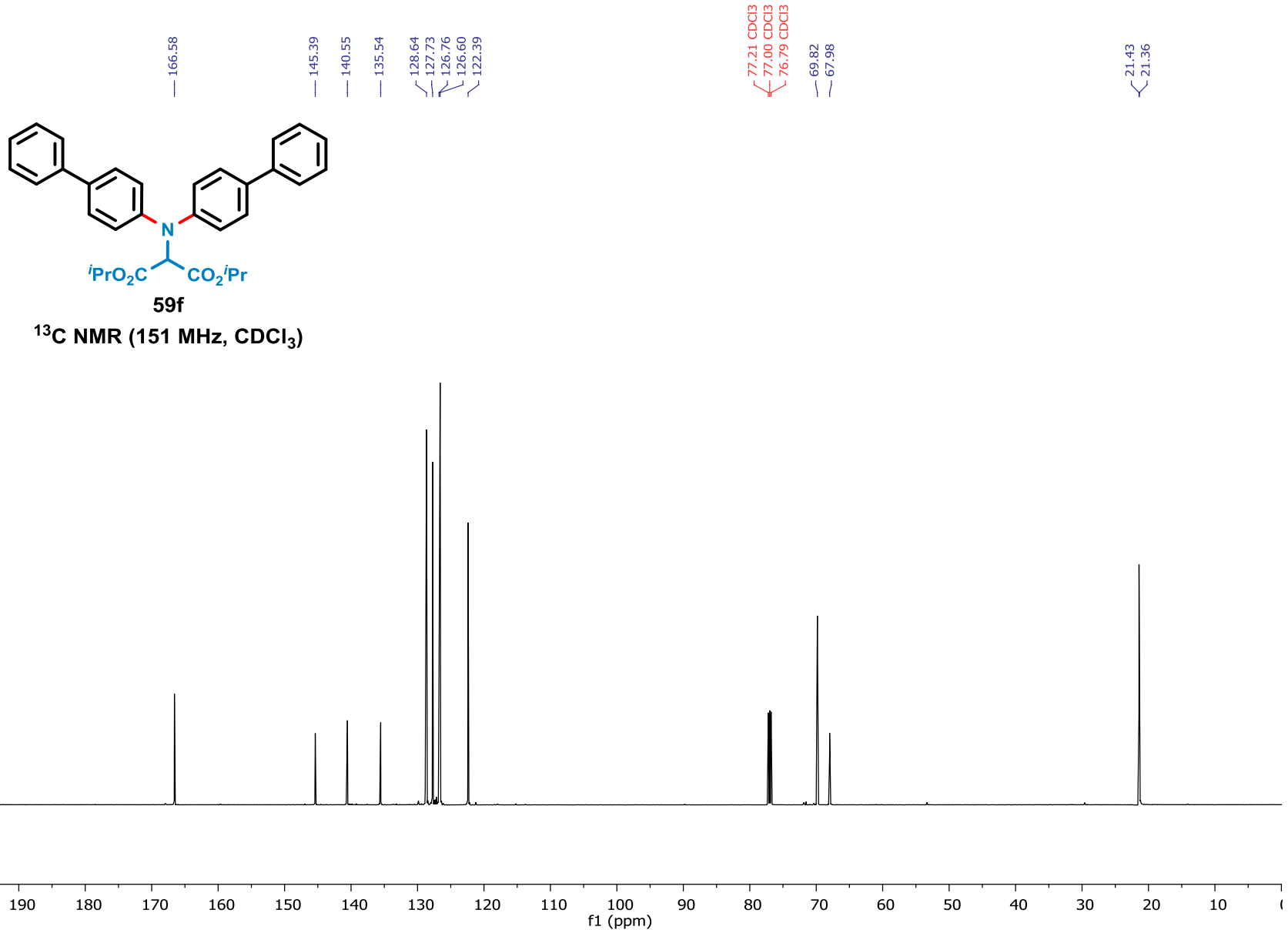
59e

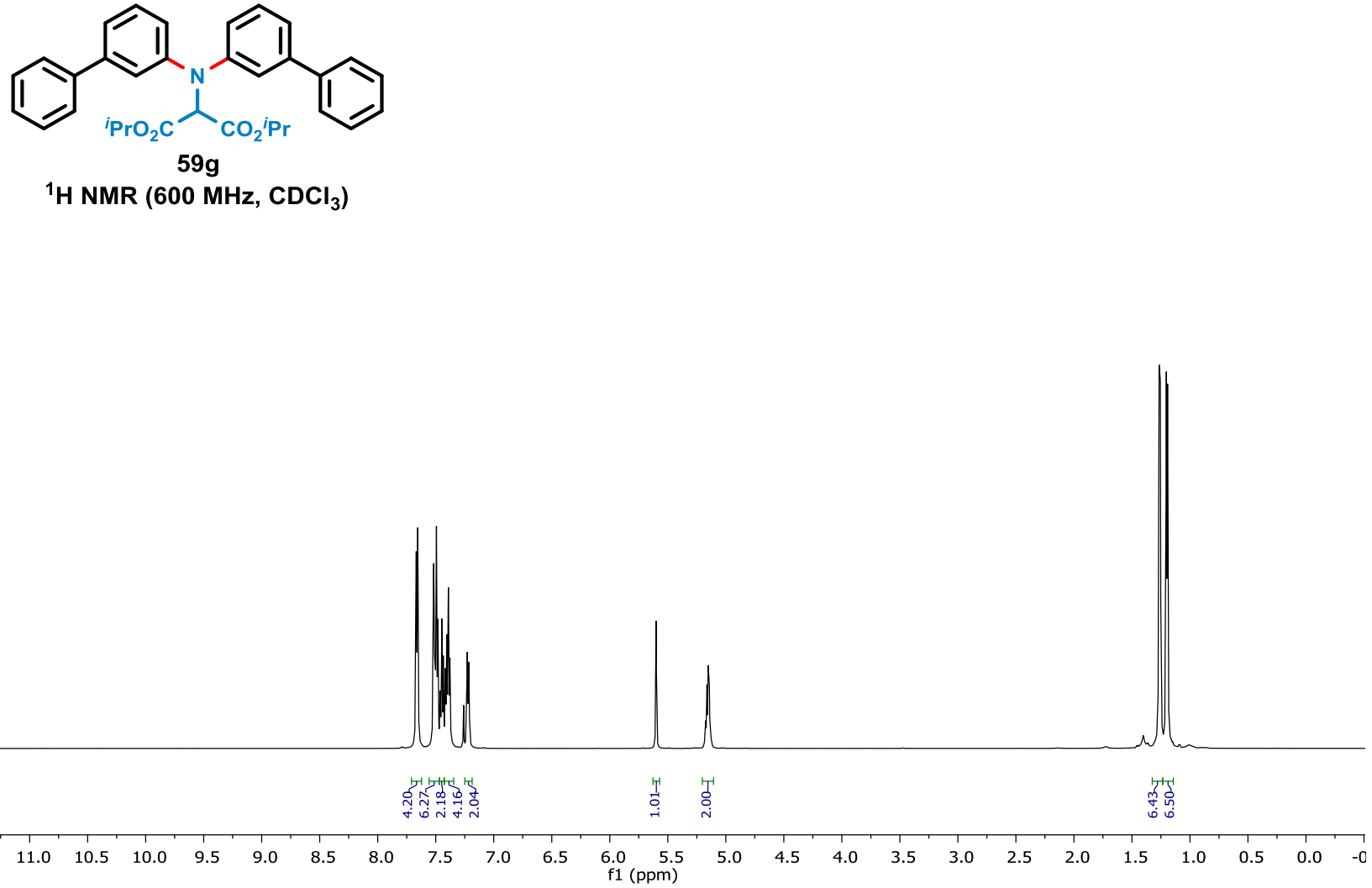
^{13}C NMR (151 MHz, $CDCl_3$)



59f

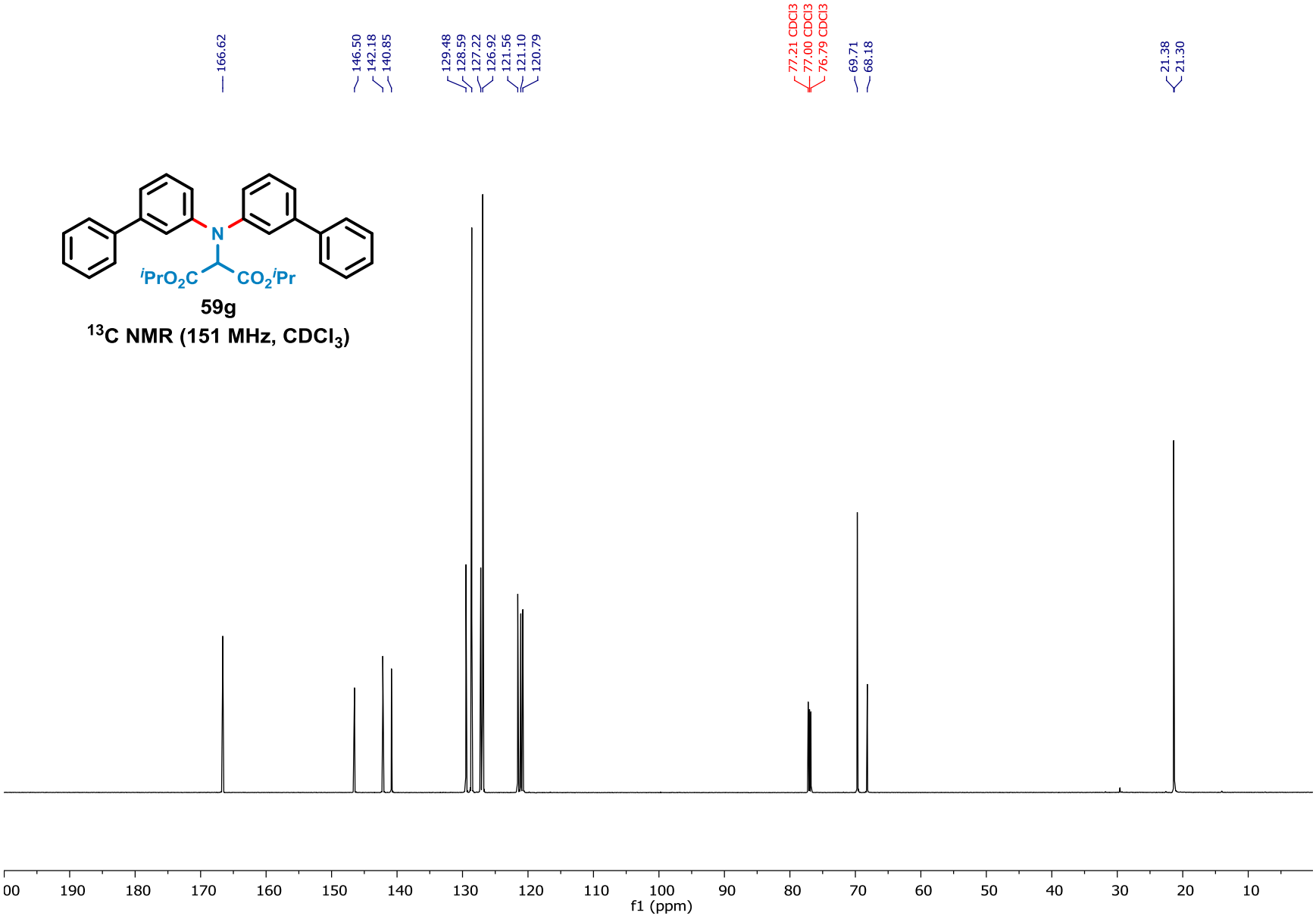
^{1}H NMR (600 MHz, $CDCl_3$)

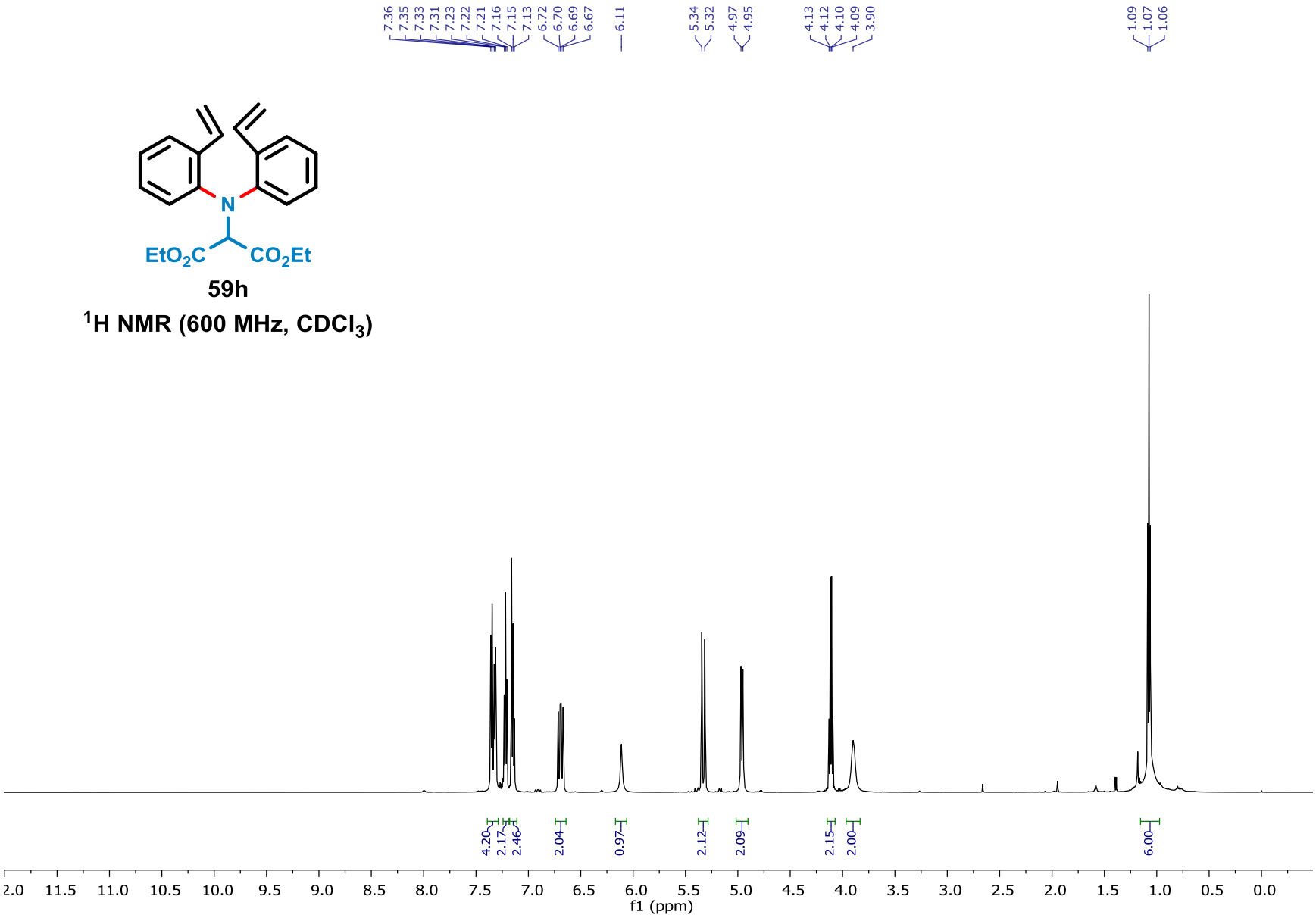

166.58
145.39
140.55
135.54
128.64
127.73
126.76
126.60
122.39
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.82
67.98
21.43
21.36
N
iPrO2C
CO2iPr
59f
13C NMR (151 MHz, CDCl3)
f1 (ppm)



59g

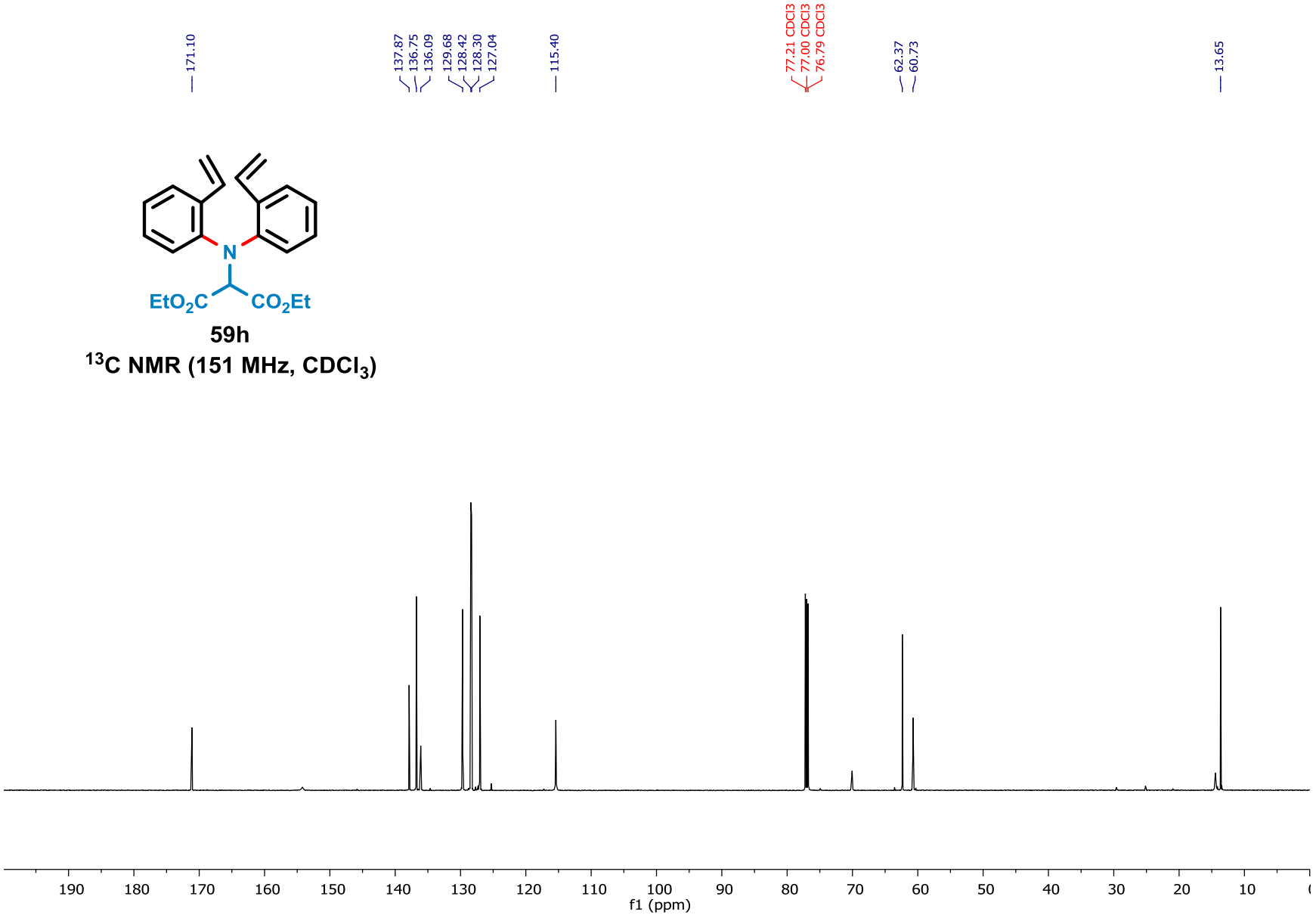
^{1}H NMR (600 MHz, $CDCl_3$)

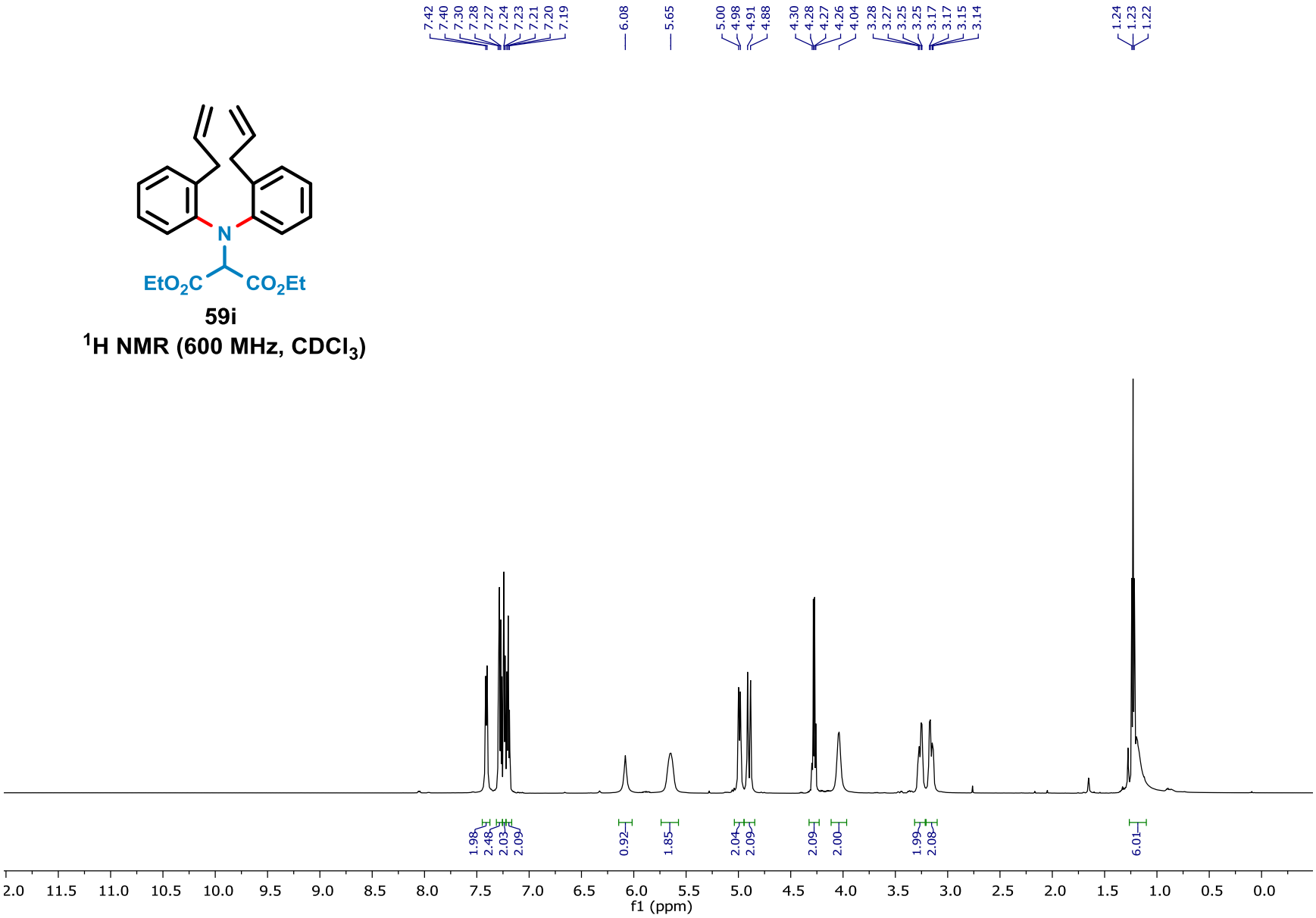

166.62
146.50
142.18
140.85
129.48
128.59
127.22
126.92
121.56
121.10
120.79
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.71
68.18
21.38
21.30
N
iPrO2C
CO2iPr
59g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

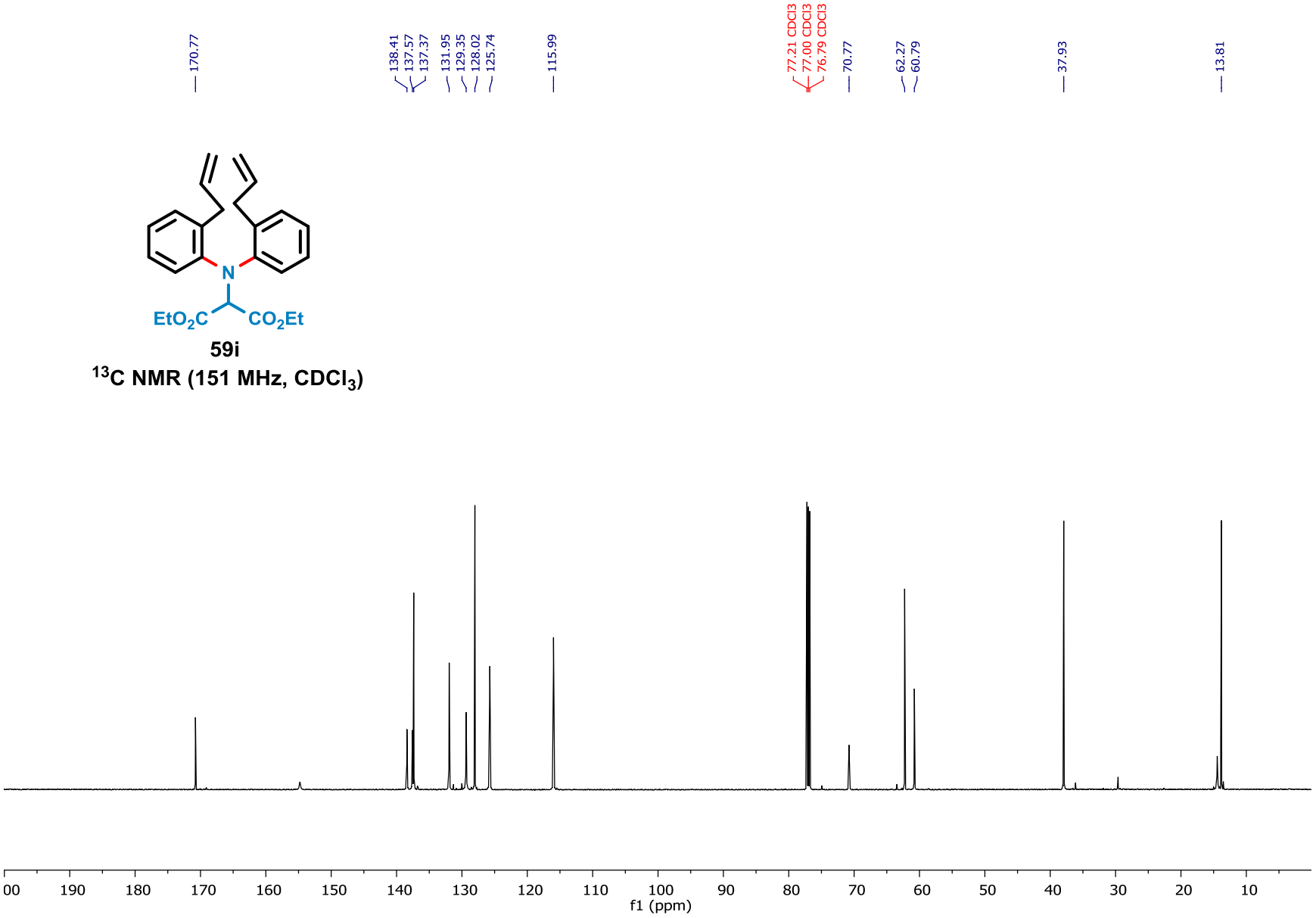


59h

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

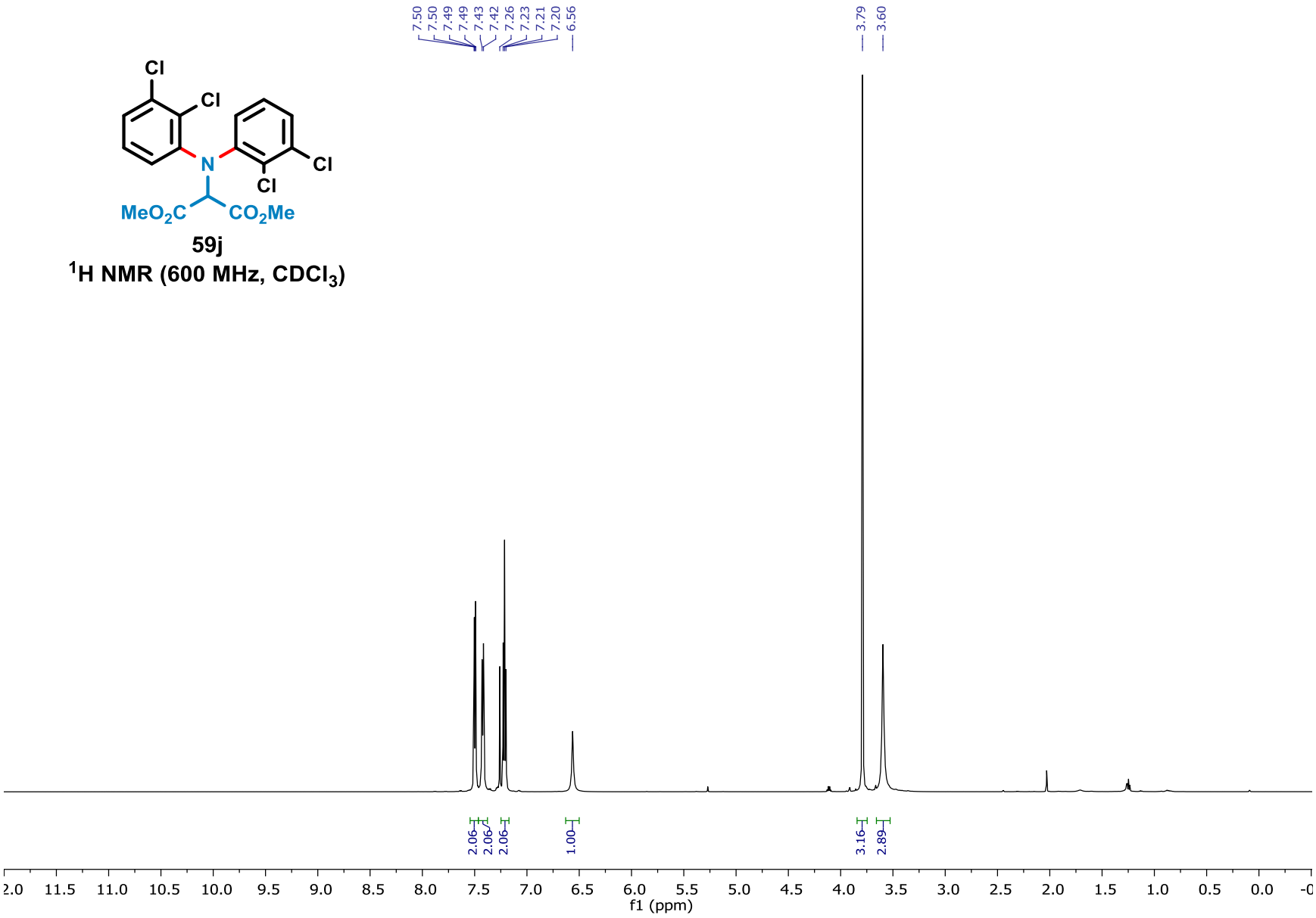

171.10
137.87
136.75
136.09
129.68
128.42
128.30
127.04
115.40
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
62.37
60.73
13.65
N
EtO2C
CO2Et
59h
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

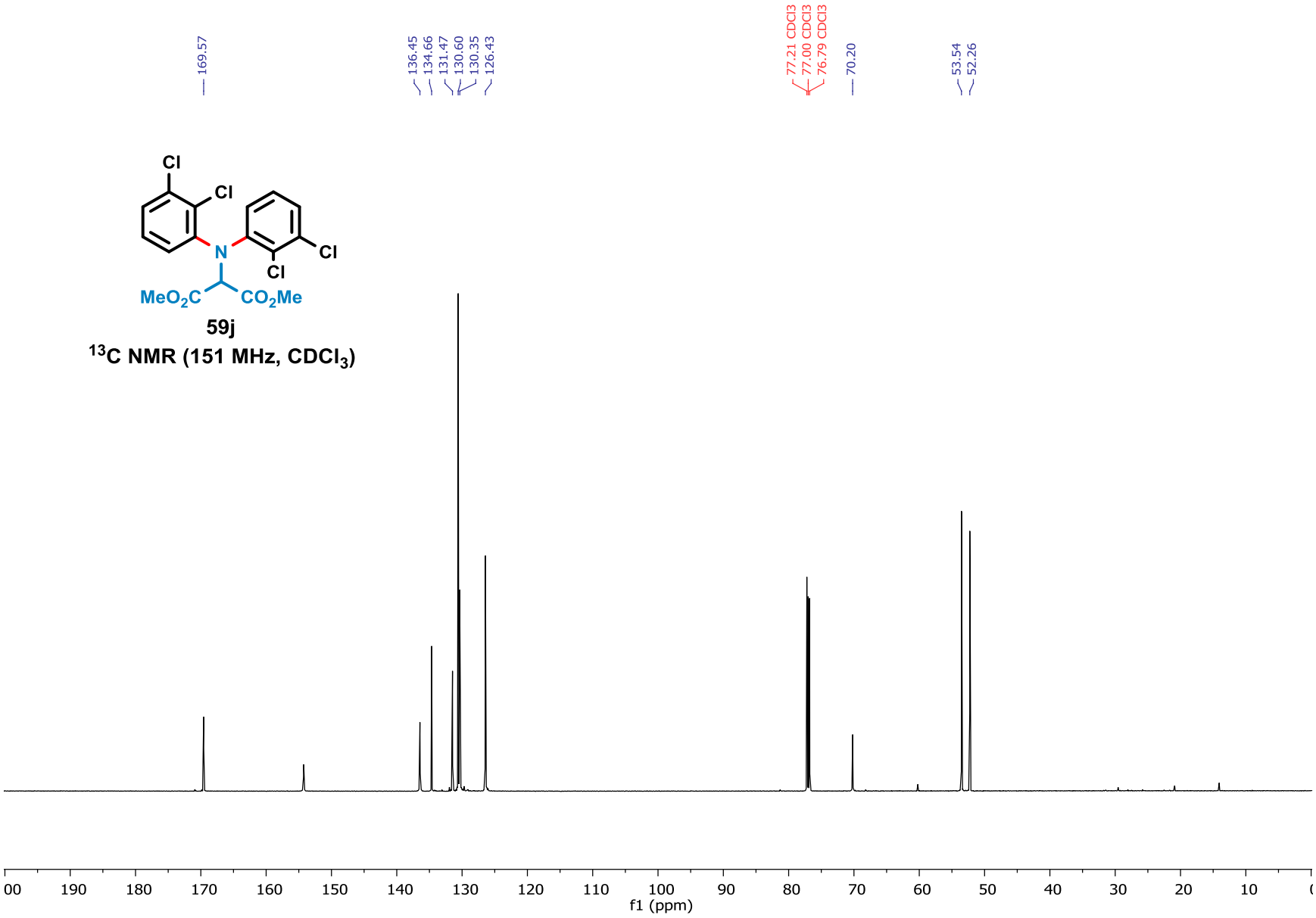

7.42
7.40
7.30
7.28
7.27
7.24
7.23
7.21
7.20
7.19
6.08
5.65
5.00
4.98
4.91
4.88
4.30
4.28
4.27
4.26
4.04
3.28
3.27
3.25
3.25
3.17
3.17
3.15
3.14
1.24
1.23
1.22
N
EtO2C
CO2Et
59i
1H NMR (600 MHz, CDCl3)
1.98
2.48
2.03
2.09
0.92
1.85
2.04
2.09
2.09
2.00
1.99
2.08
6.01
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

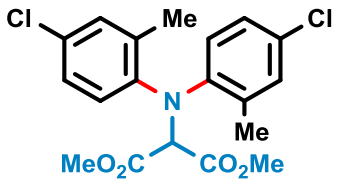


59i

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

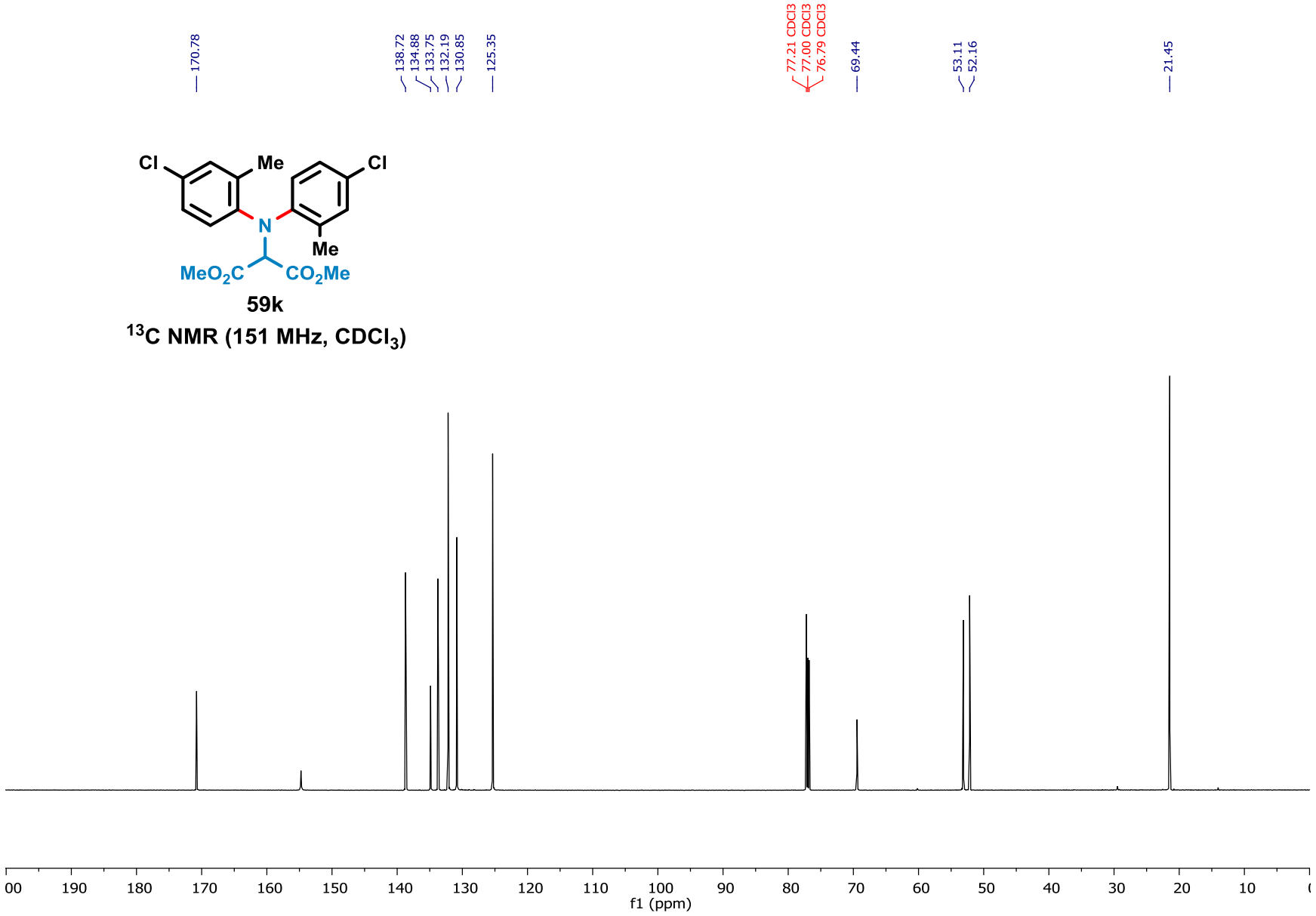

Cl
Cl
N
Cl
Cl
MeO2C
CO2Me
59j
1H NMR (600 MHz, CDCl3)
7.50
7.50
7.49
7.49
7.43
7.42
7.26
7.23
7.21
7.20
6.56
3.79
3.60
2.06
2.06
2.06
1.00
3.16
2.89
f1 (ppm)


169.57
136.45
134.66
131.47
130.60
130.35
126.43
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.20
53.54
52.26
Cl
Cl
Cl
Cl
N
MeO2C
CO2Me
59j
13C NMR (151 MHz, CDCl3)
f1 (ppm)



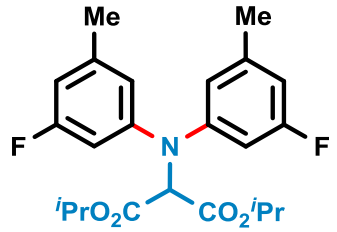
59k

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



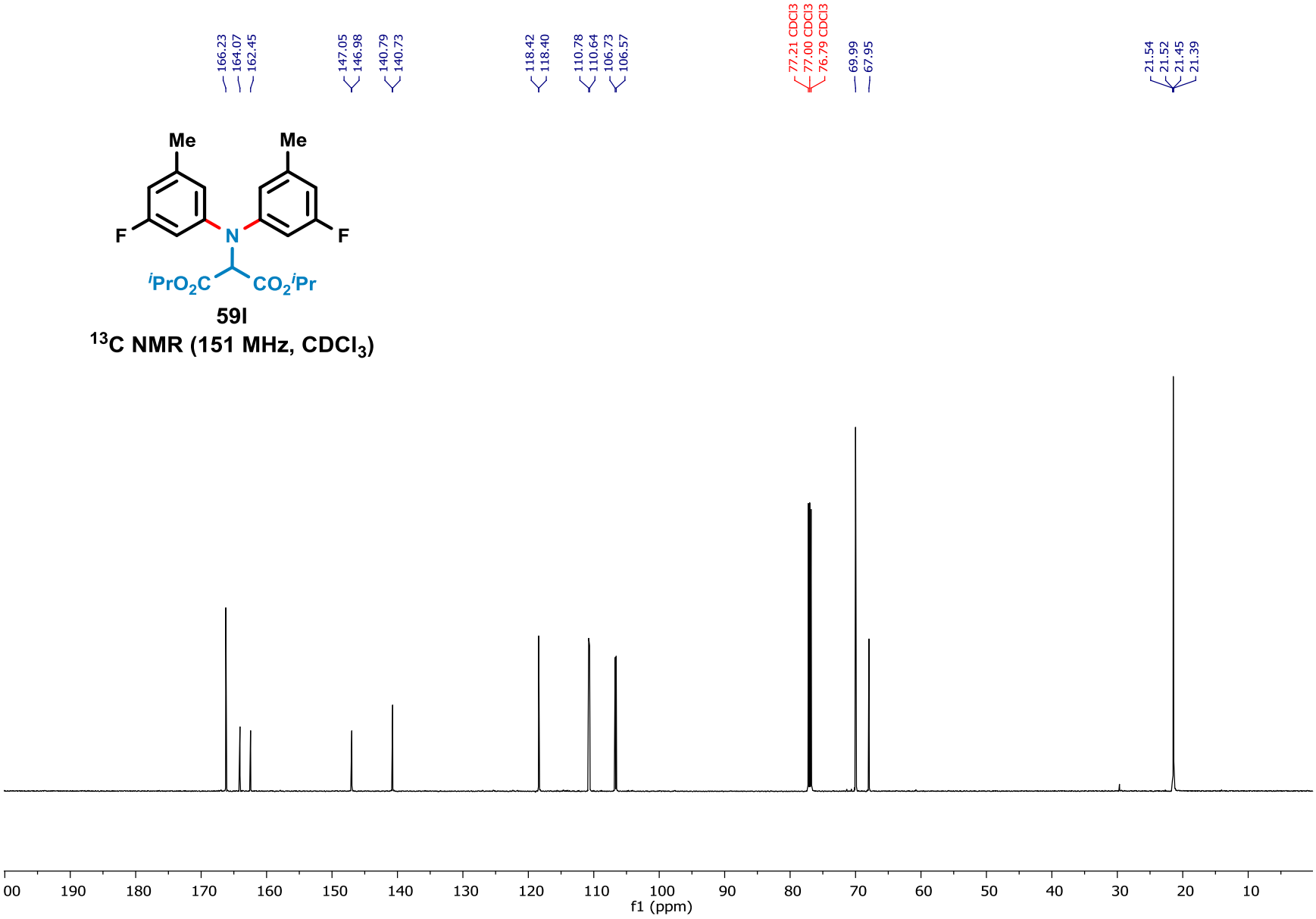
59k

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



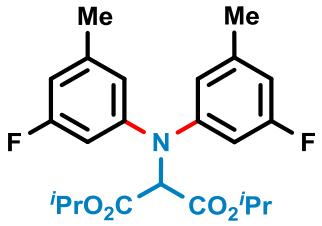
59l

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



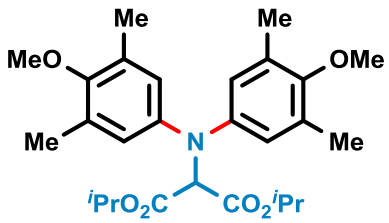
59l

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



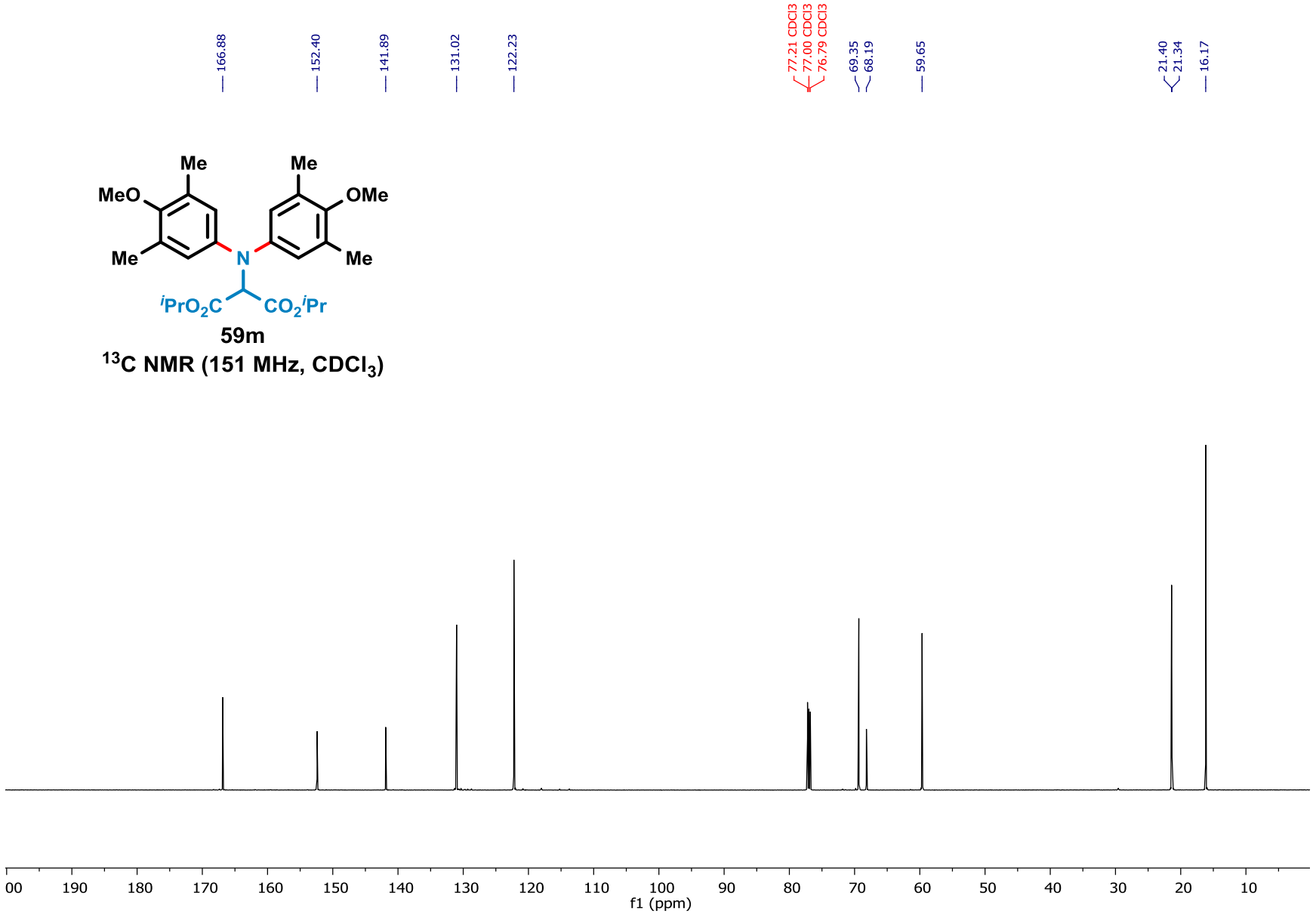
59l

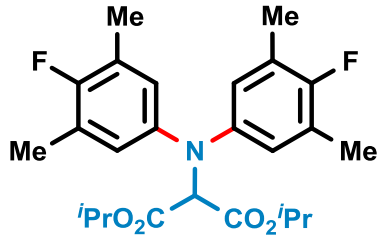
^{19}F NMR (471 MHz, $CDCl_3$)



59m

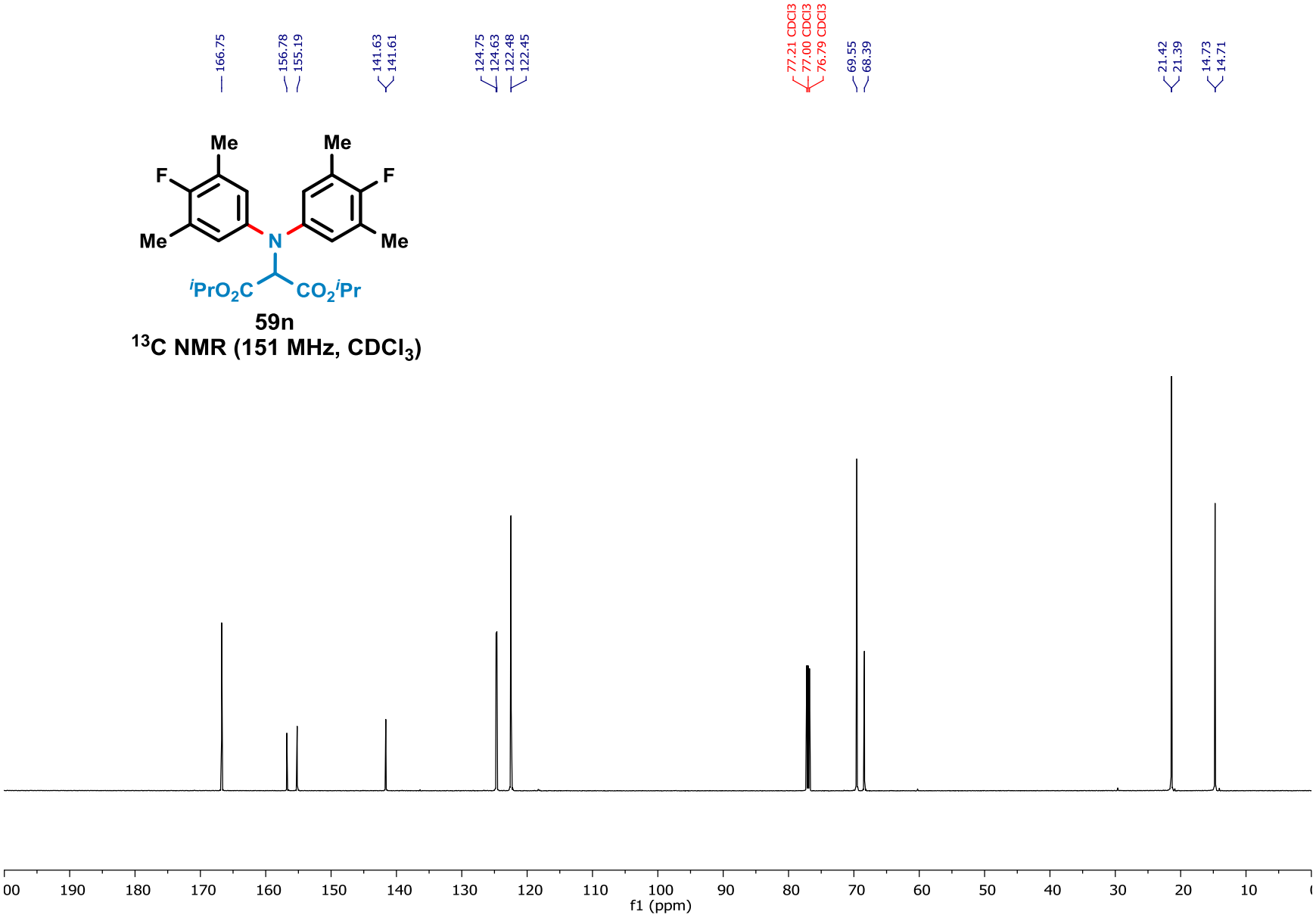
^{1}H NMR (600 MHz, $CDCl_3$)

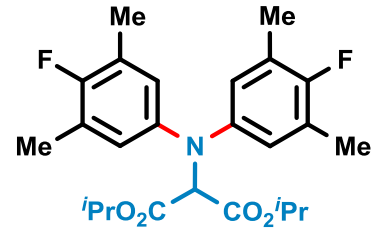

166.88
152.40
141.89
131.02
122.23
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.35
68.19
59.65
21.40
21.34
16.17
Me
MeO
Me
Me
OMe
Me
N
iPrO2C
CO2iPr
59m
13C NMR (151 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



59n

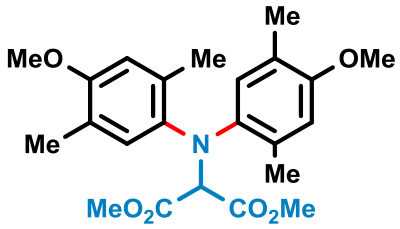
^{1}H NMR (600 MHz, $CDCl_3$)


166.75
156.78
155.19
141.63
141.61
124.75
124.63
122.48
122.45
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.55
68.39
21.42
21.39
14.73
14.71
Me
Me
F
F
Me
Me
N
iPrO2C
CO2iPr
59n
13C NMR (151 MHz, CDCl3)
f1 (ppm)



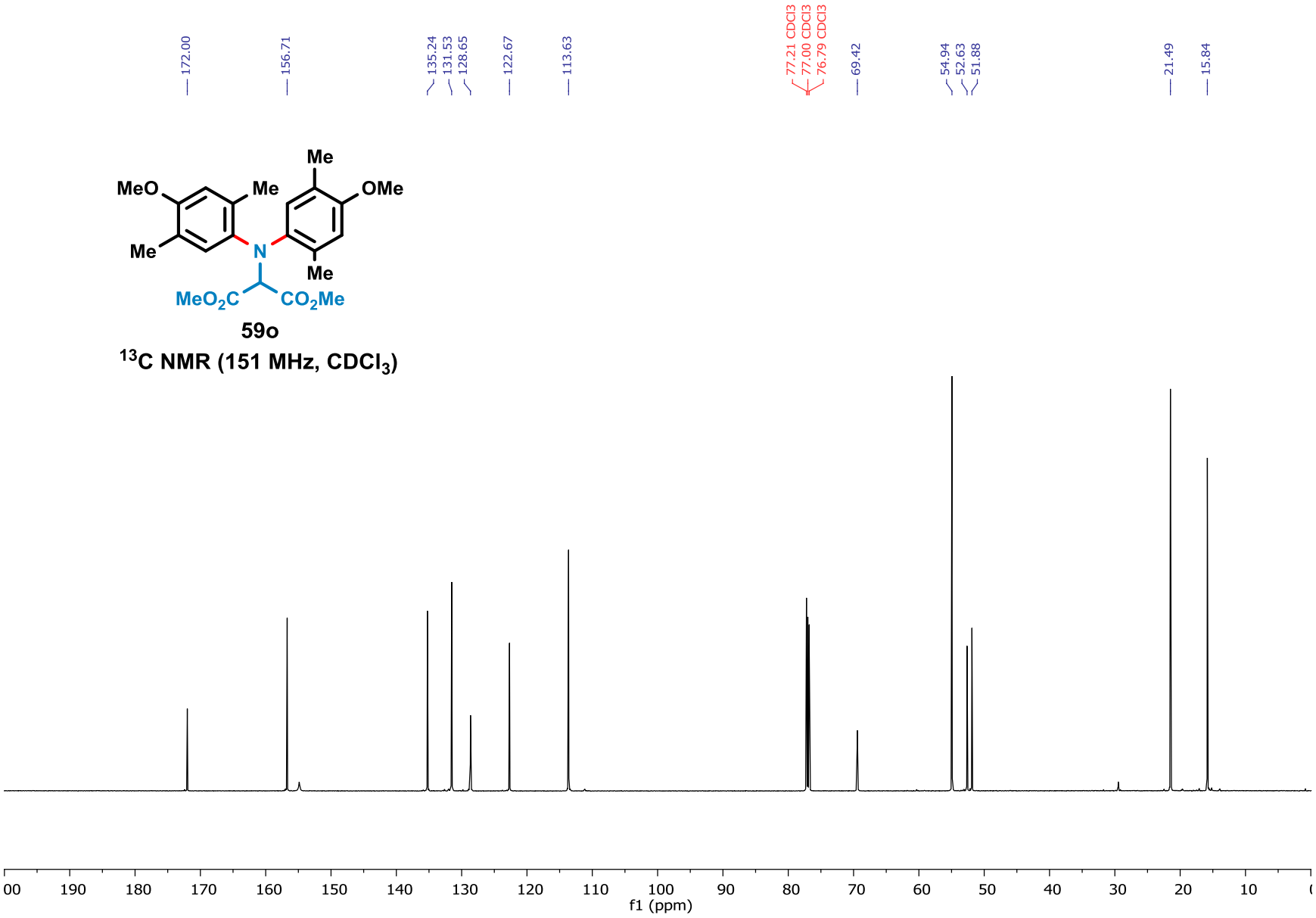
59n

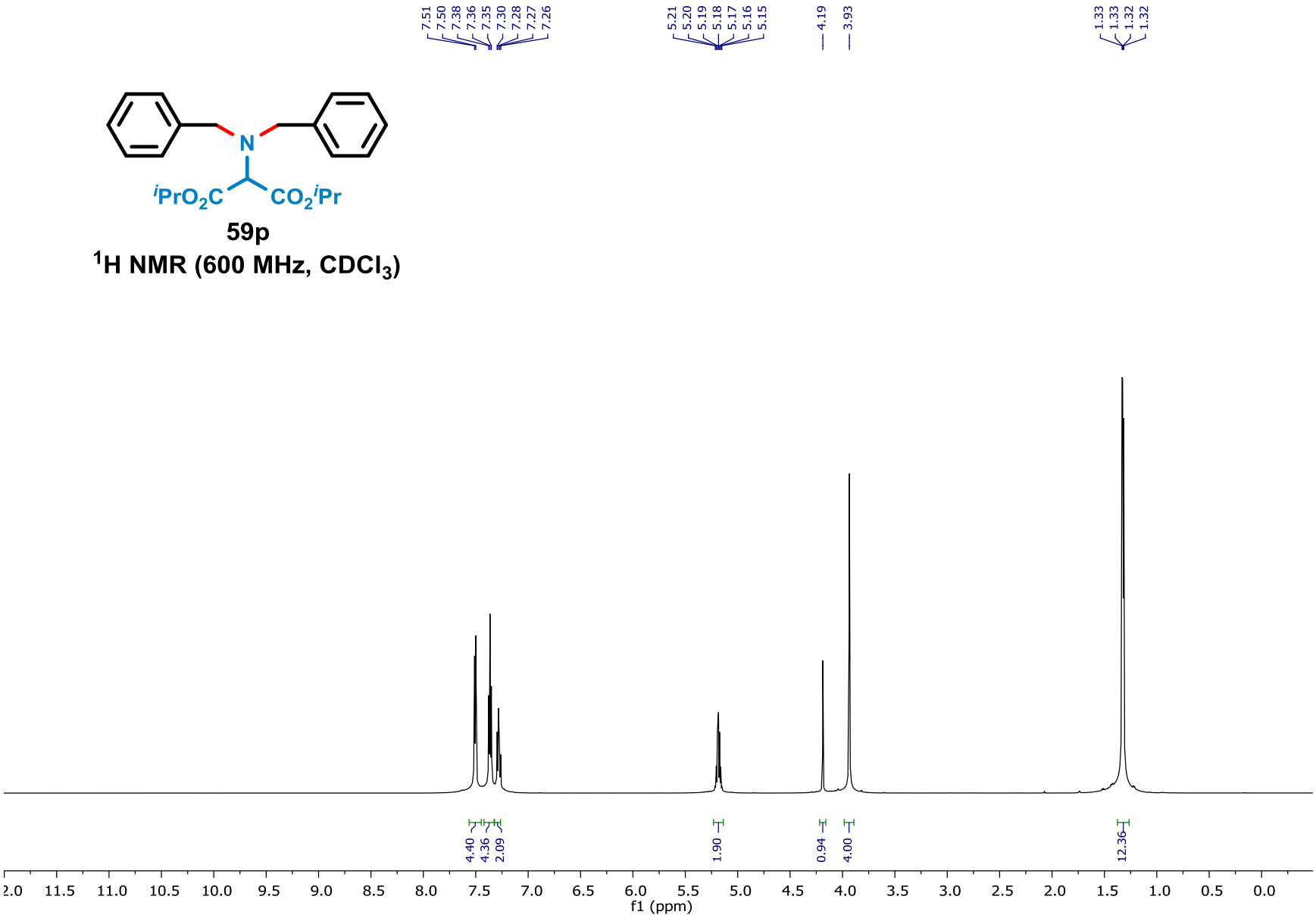
^{19}F NMR (471 MHz, $CDCl_3$)



59o

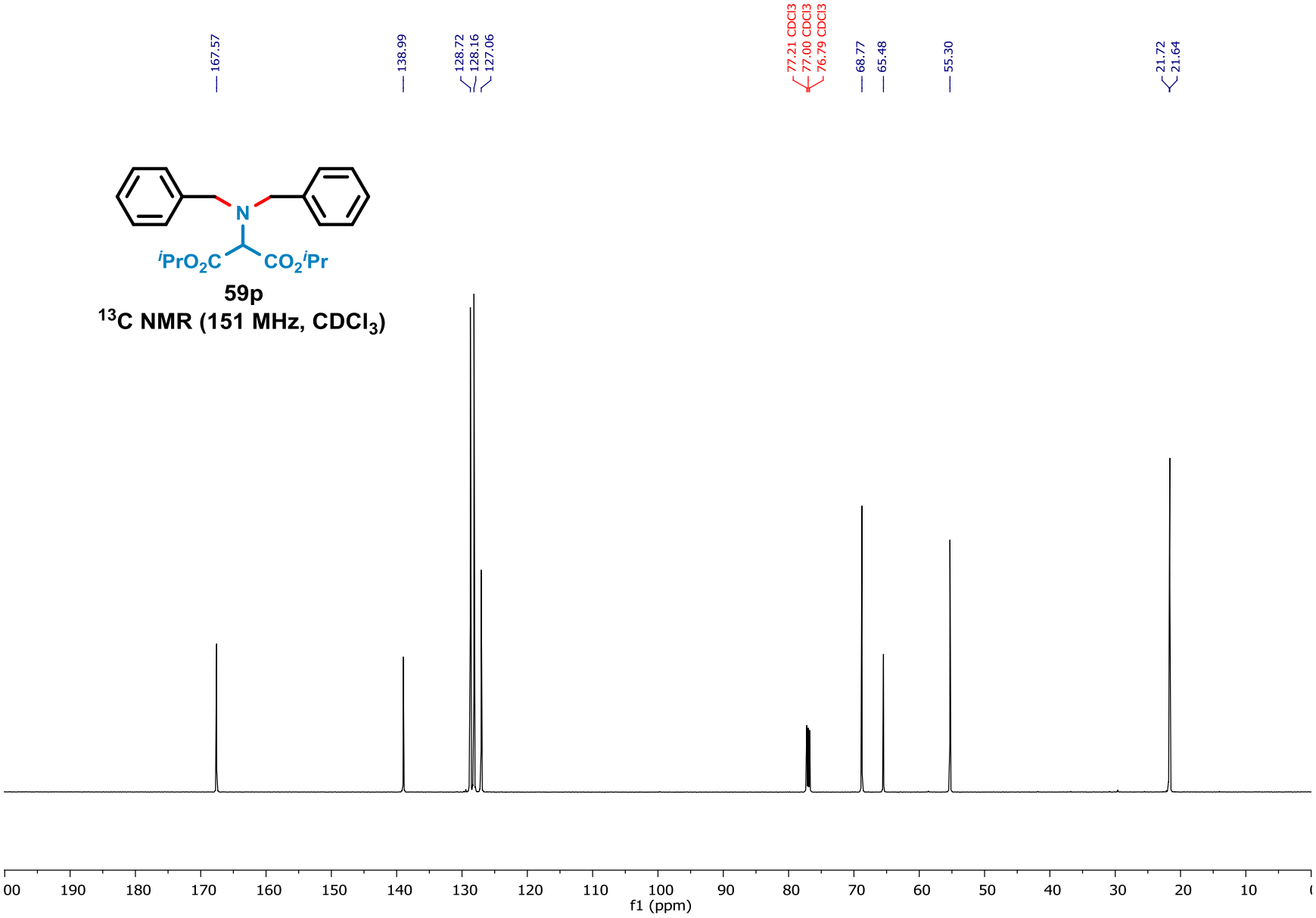
^{1}H NMR (600 MHz, $CDCl_3$)

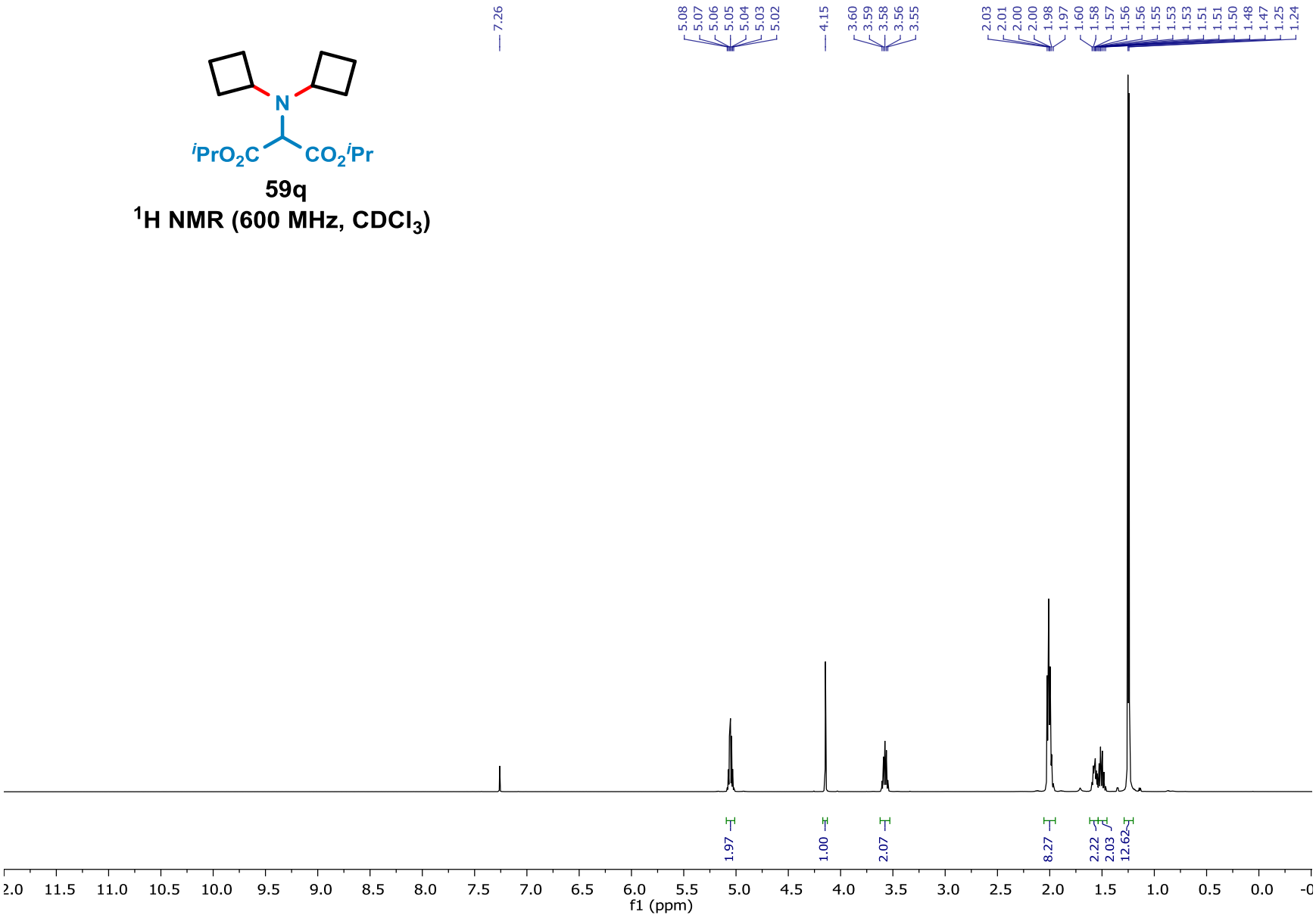

172.00
156.71
135.24
131.53
128.65
122.67
113.63
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
69.42
54.94
52.63
51.88
21.49
15.84
Me
MeO
Me
OMe
Me
N
Me
MeO2C
CO2Me
59o
13C NMR (151 MHz, CDCl3)
f1 (ppm)

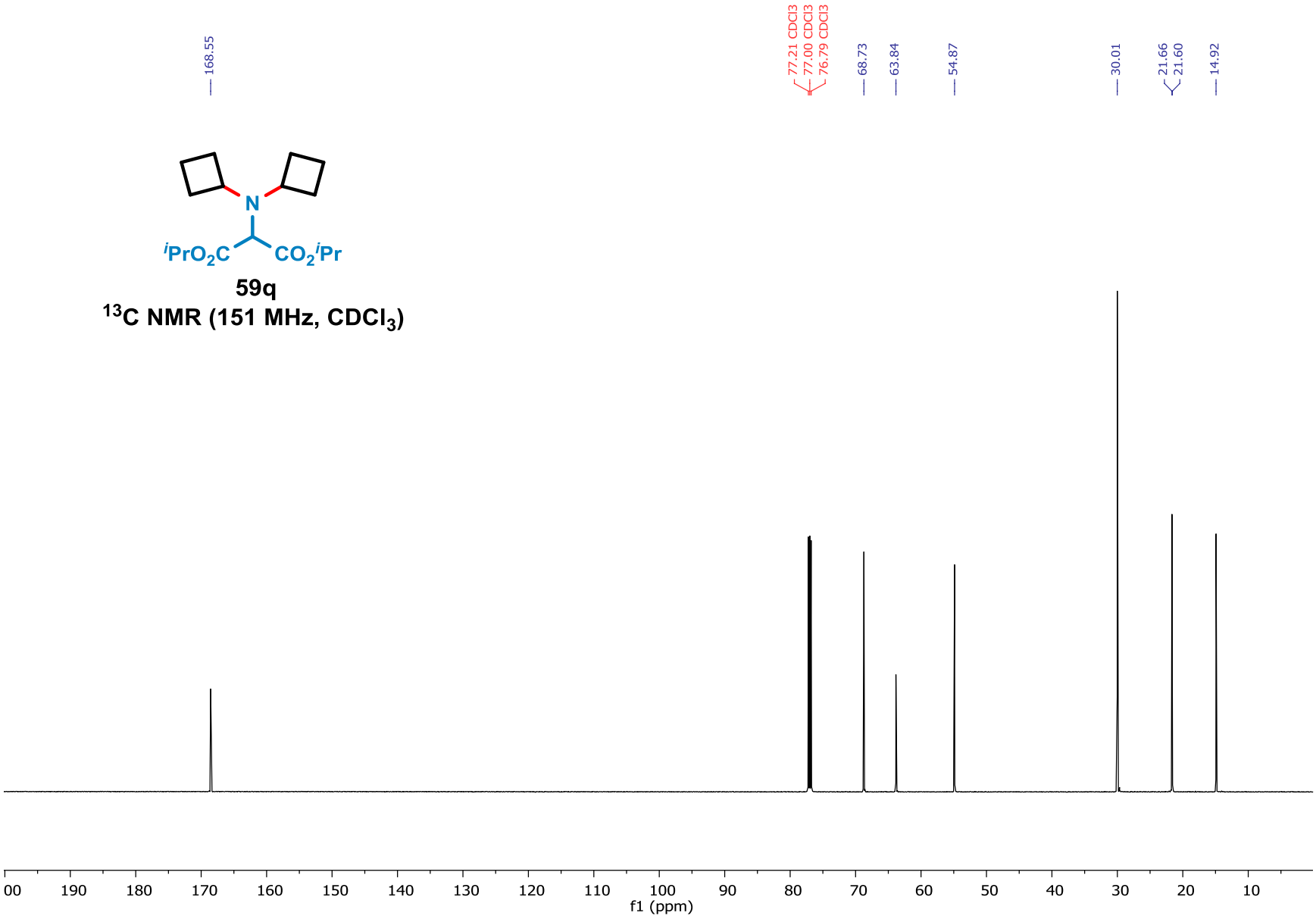


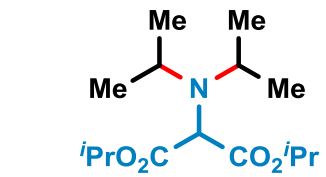
59p

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


167.57
138.99
128.72
128.16
127.06
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.77
65.48
55.30
21.72
21.64
N
iPrO2C
CO2iPr
59p
13C NMR (151 MHz, CDCl3)
f1 (ppm)

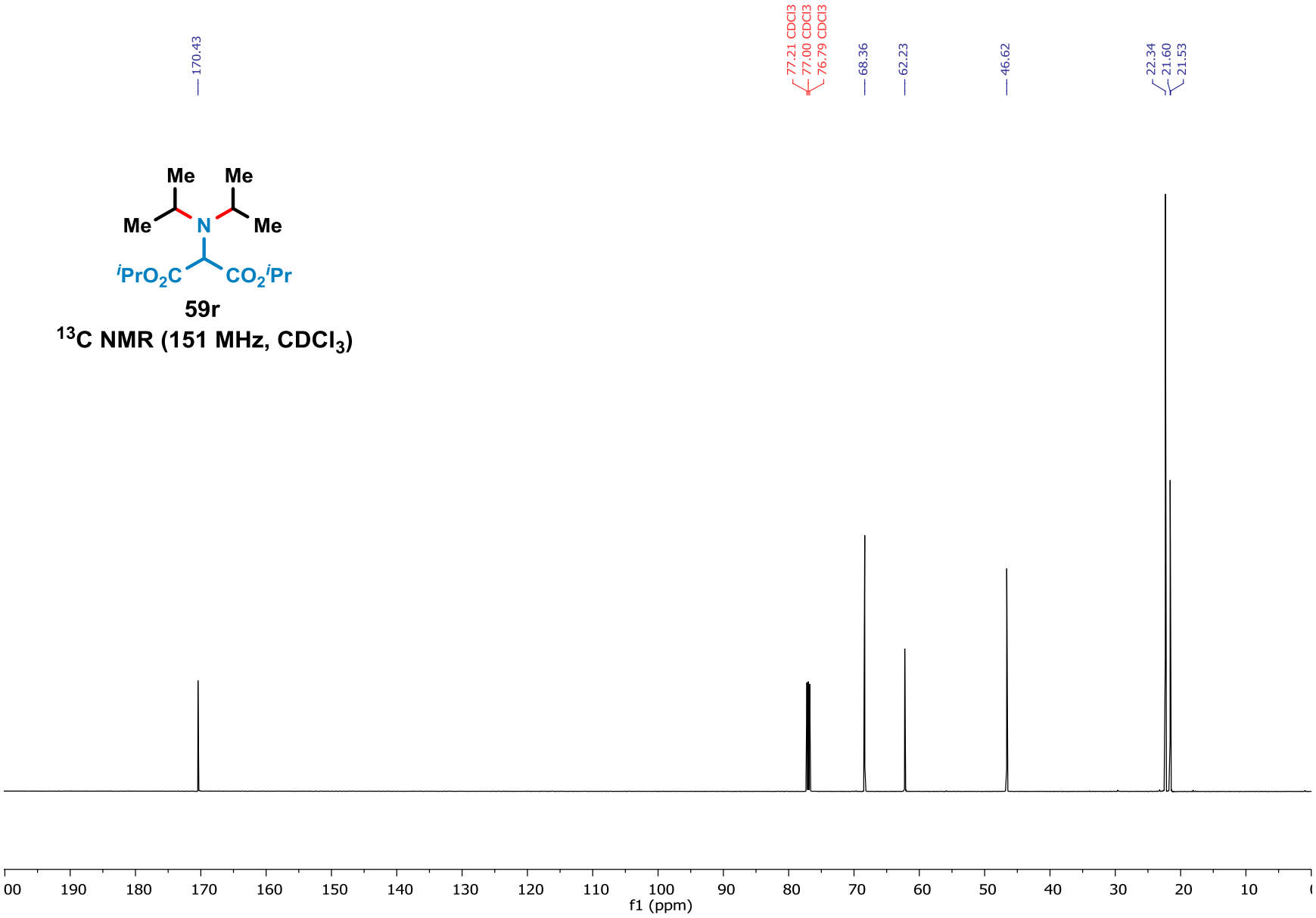

N
iPrO2C
CO2iPr
59q
1H NMR (600 MHz, CDCl3)
7.26
5.08
5.07
5.06
5.05
5.04
5.03
5.02
4.15
3.60
3.59
3.58
3.56
3.55
2.03
2.01
2.00
2.00
1.98
1.97
1.60
1.58
1.57
1.56
1.56
1.55
1.53
1.53
1.51
1.51
1.50
1.48
1.47
1.25
1.24
1.97
1.00
2.07
8.27
2.22
2.03
12.62
f1 (ppm)

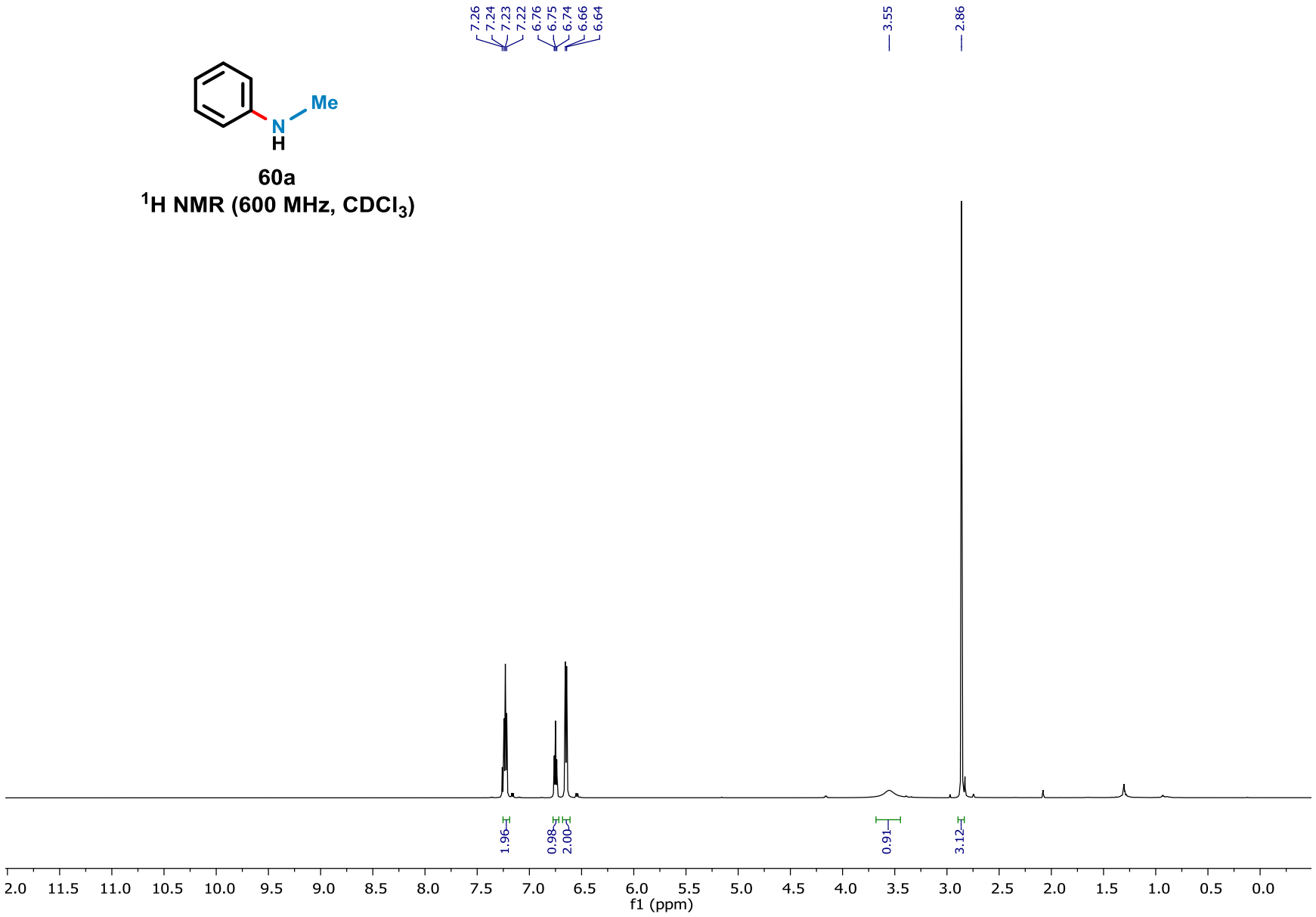

168.55
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.73
63.84
54.87
30.01
21.66
21.60
14.92
N
iPrO2C
CO2iPr
59q
13C NMR (151 MHz, CDCl3)
f1 (ppm)



59r

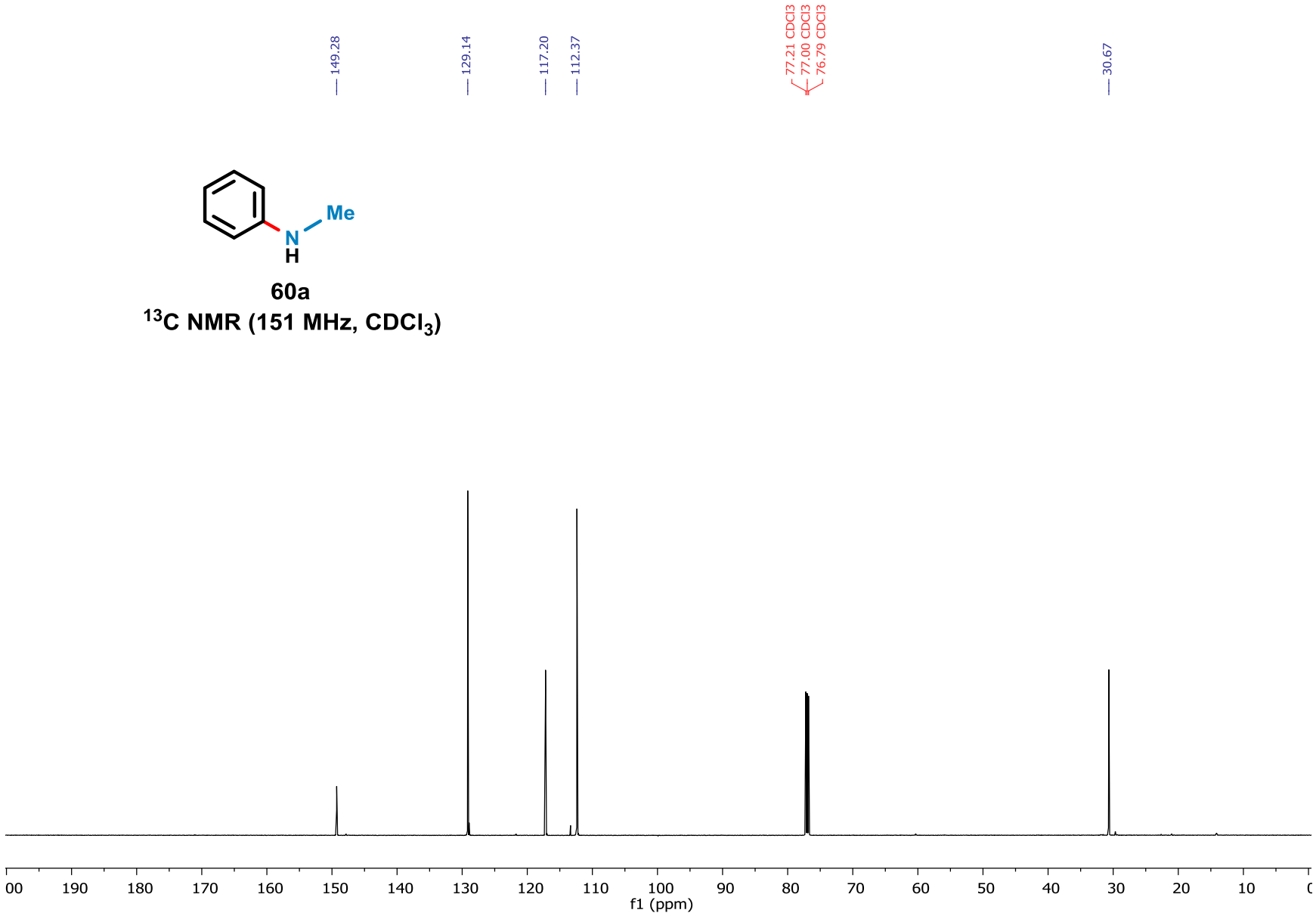
^{1}H NMR (600 MHz, $CDCl_3$)


170.43
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
68.36
62.23
46.62
22.34
21.60
21.53
Me
Me
Me
Me
N
iPrO2C
CO2iPr
59r
13C NMR (151 MHz, CDCl3)
f1 (ppm)



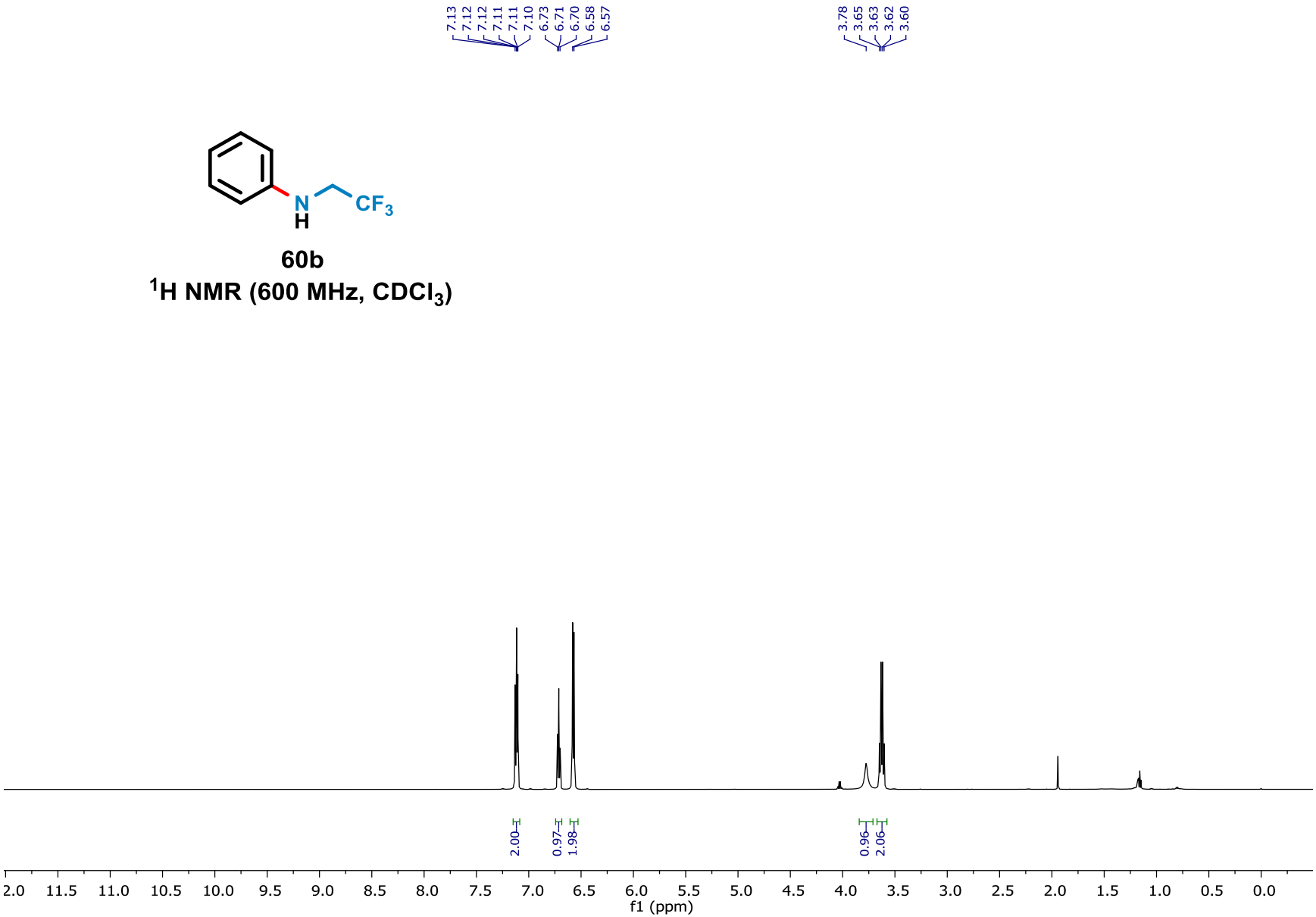
60a

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



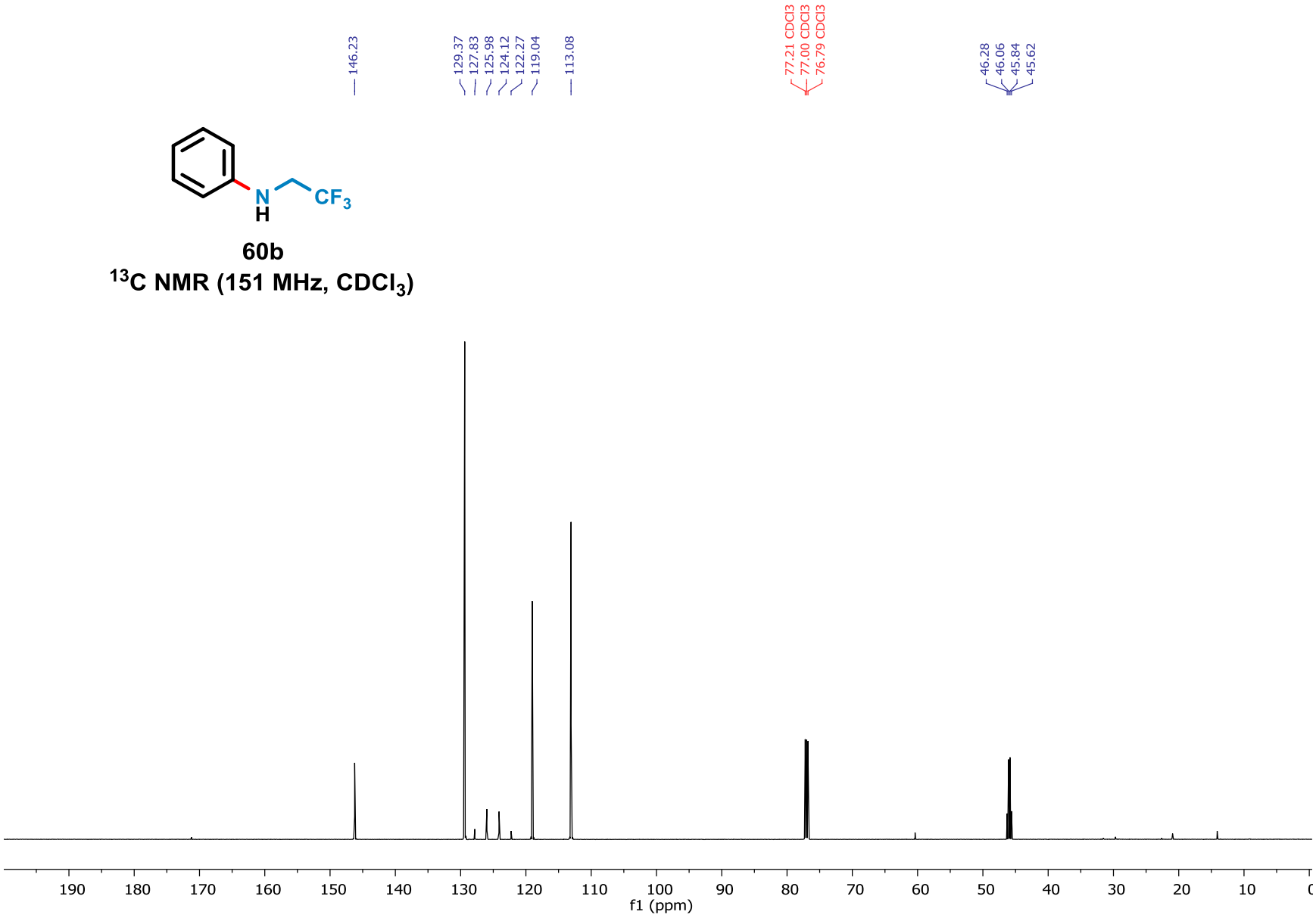
60a

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



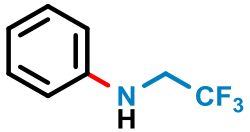
60b

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



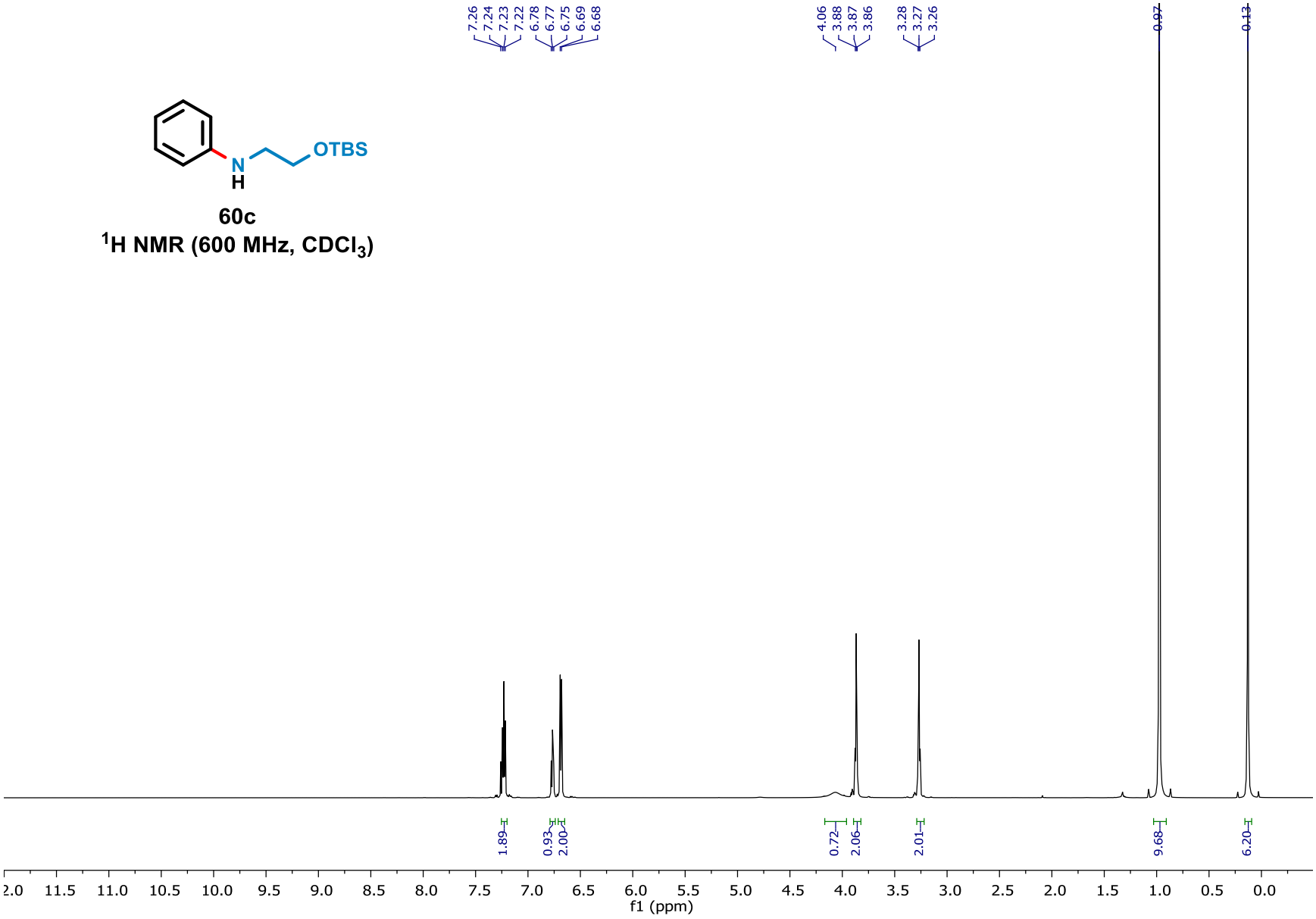
60b

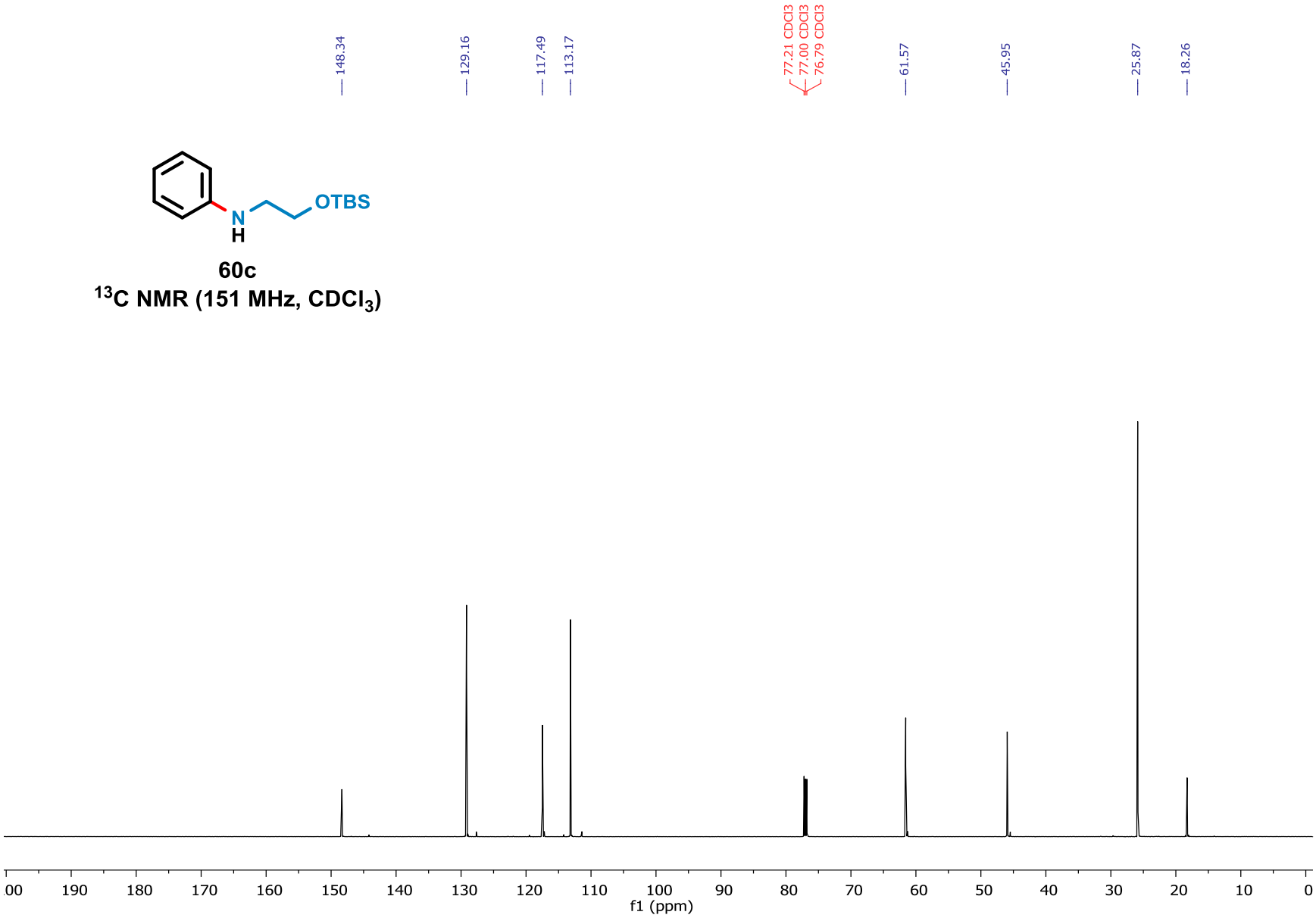
^{13}C NMR (151 MHz, $CDCl_3$)



60b

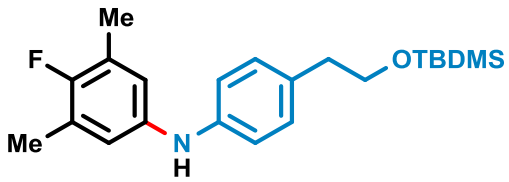
^{19}F NMR (471 MHz, $CDCl_3$)


OTBS
N
H
60c
1H NMR (600 MHz, CDCl3)
7.26
7.24
7.23
7.22
6.78
6.77
6.75
6.69
6.68
4.06
3.88
3.87
3.86
3.28
3.27
3.26
0.97
0.13
1.89
0.93
2.00
0.72
2.06
2.01
9.68
6.20
f1 (ppm)



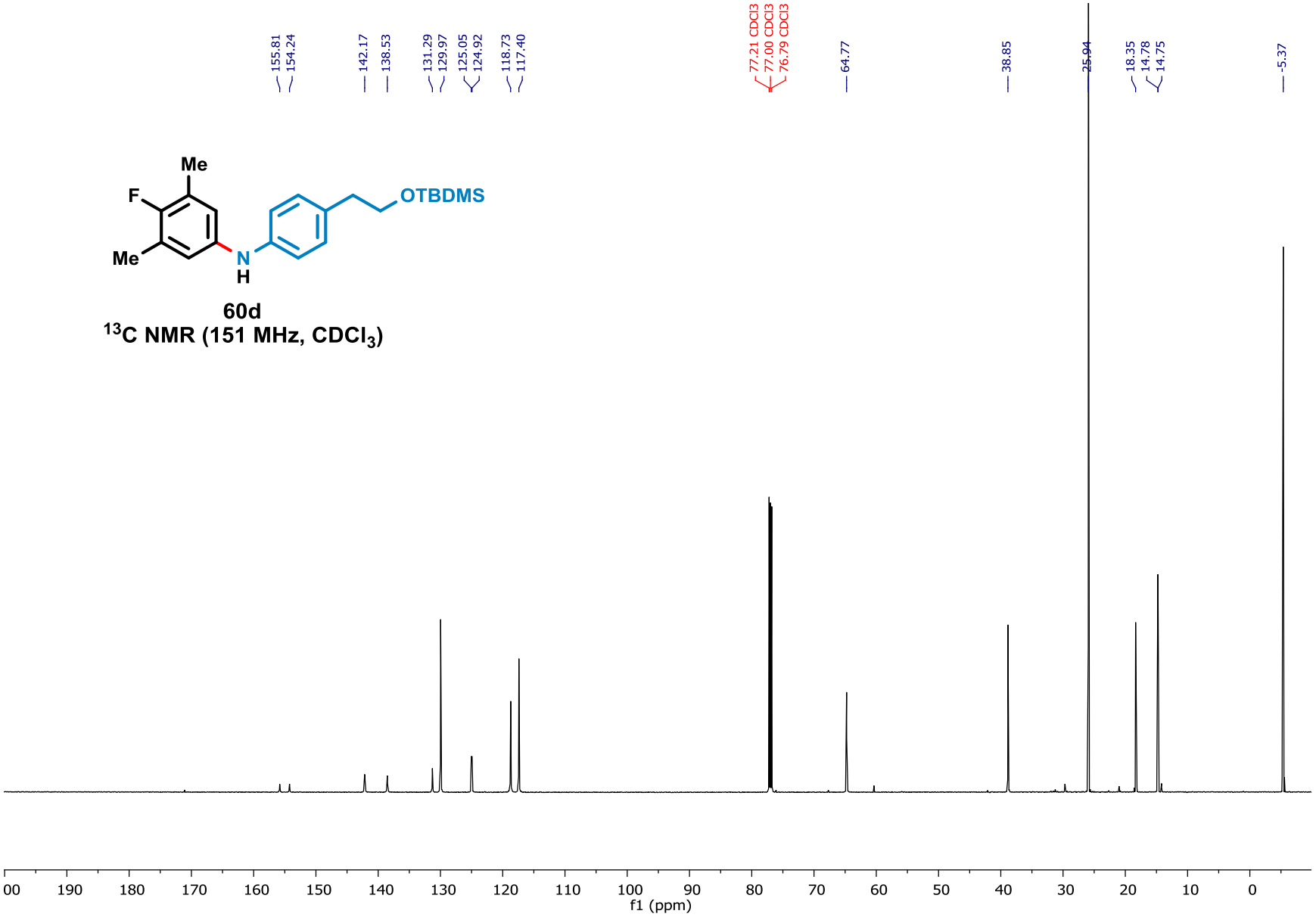
60c

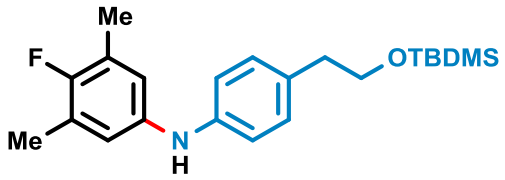
^{13}C NMR (151 MHz, $CDCl_3$)



60d

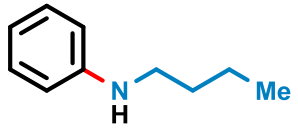
^{1}H NMR (600 MHz, $CDCl_3$)


155.81
154.24
142.17
138.53
131.29
129.97
125.05
124.92
118.73
117.40
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
64.77
38.85
25.94
18.35
14.78
14.75
-5.37
Me
F
Me
N
H
OTBDMS
60d
13C NMR (151 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



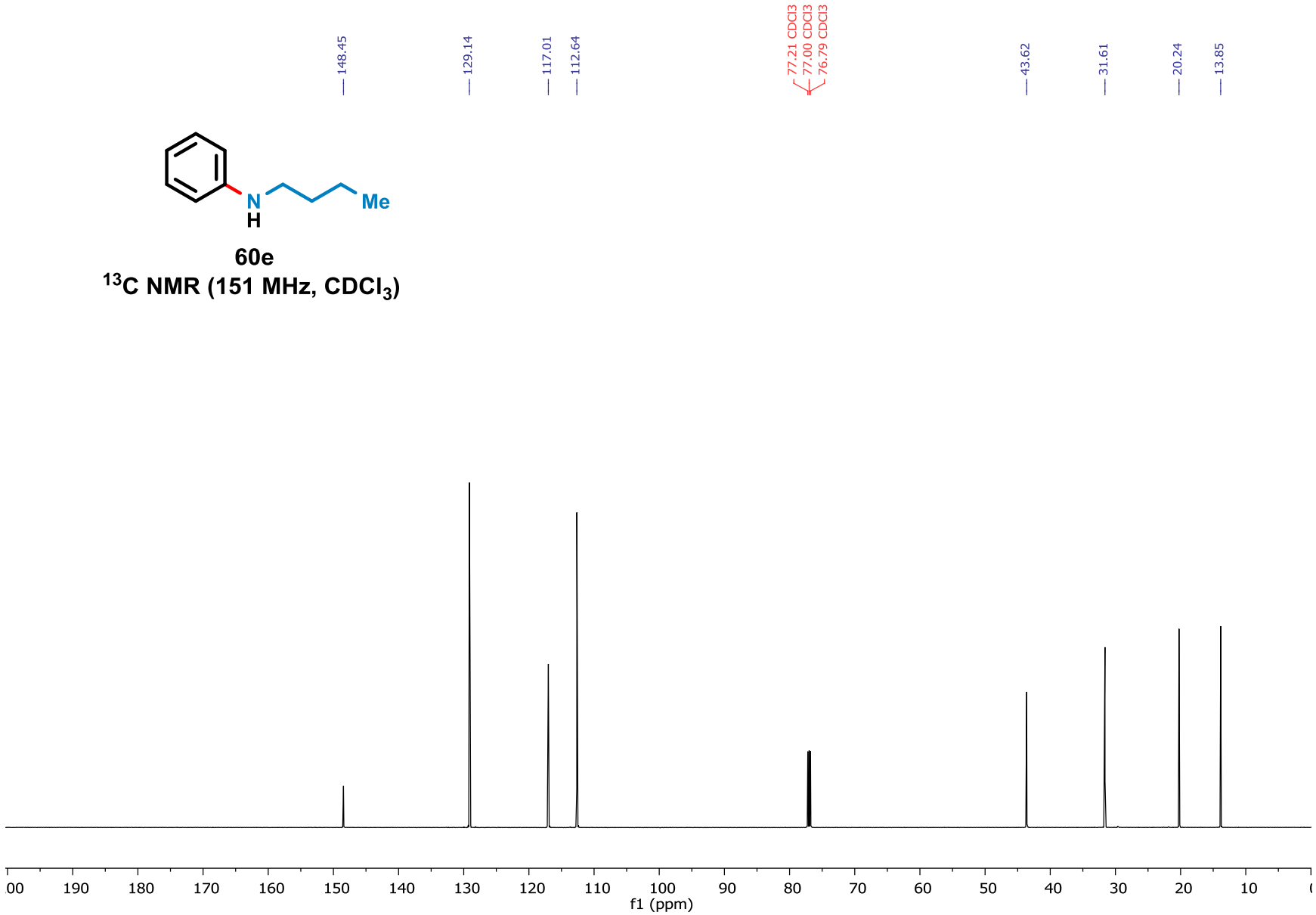
60d

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



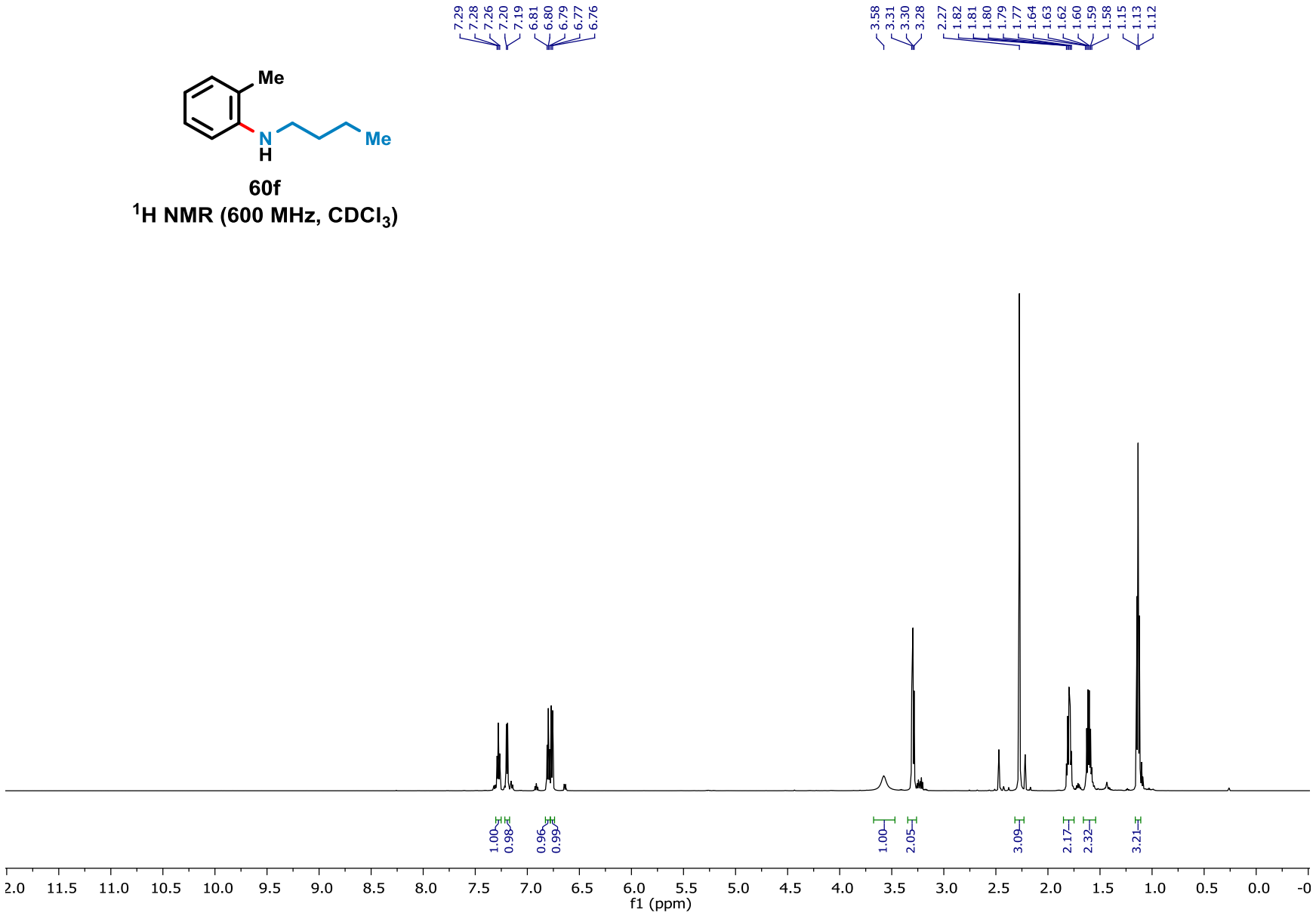
60e

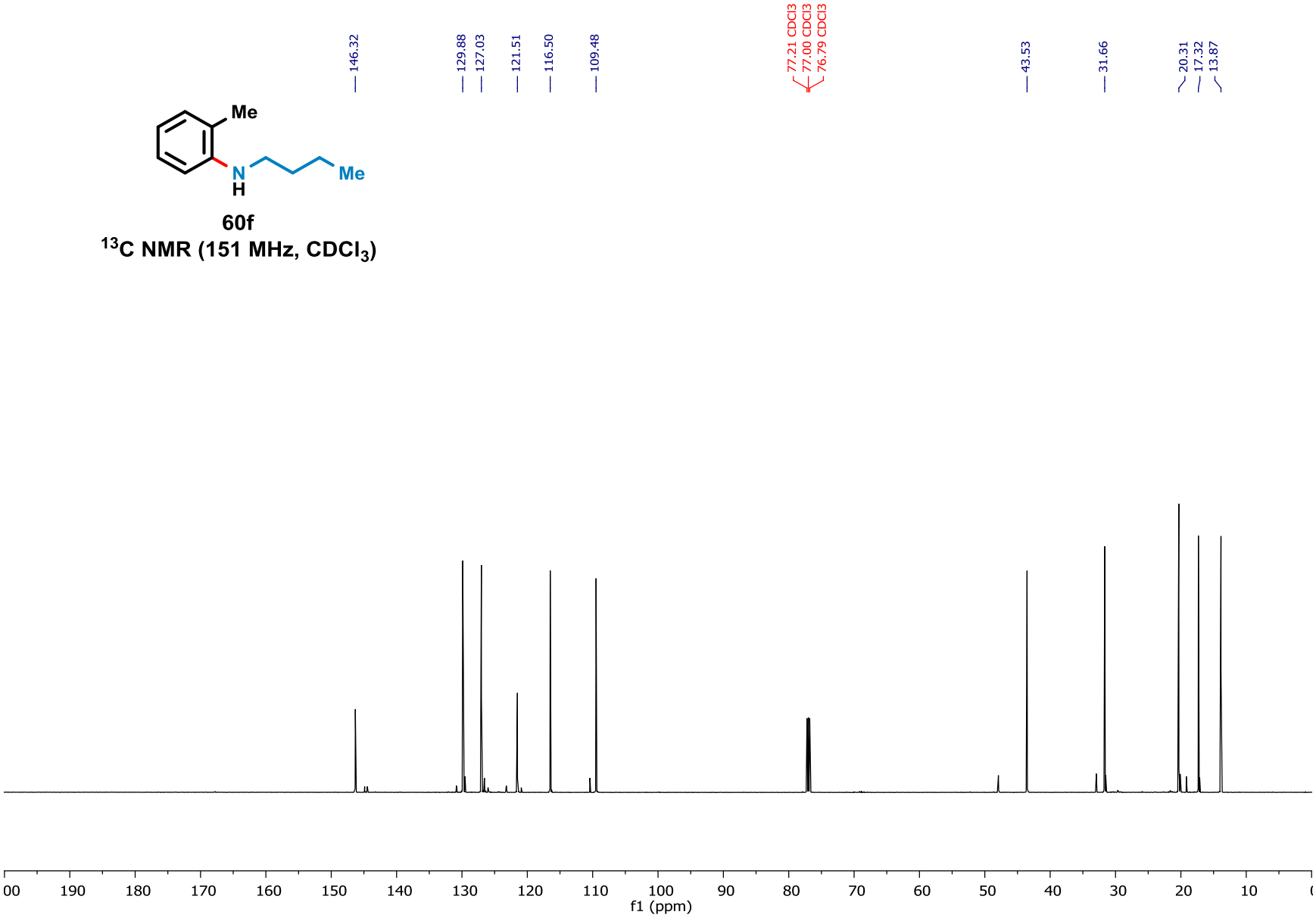
^{1}H NMR (600 MHz, $CDCl_3$)



60e

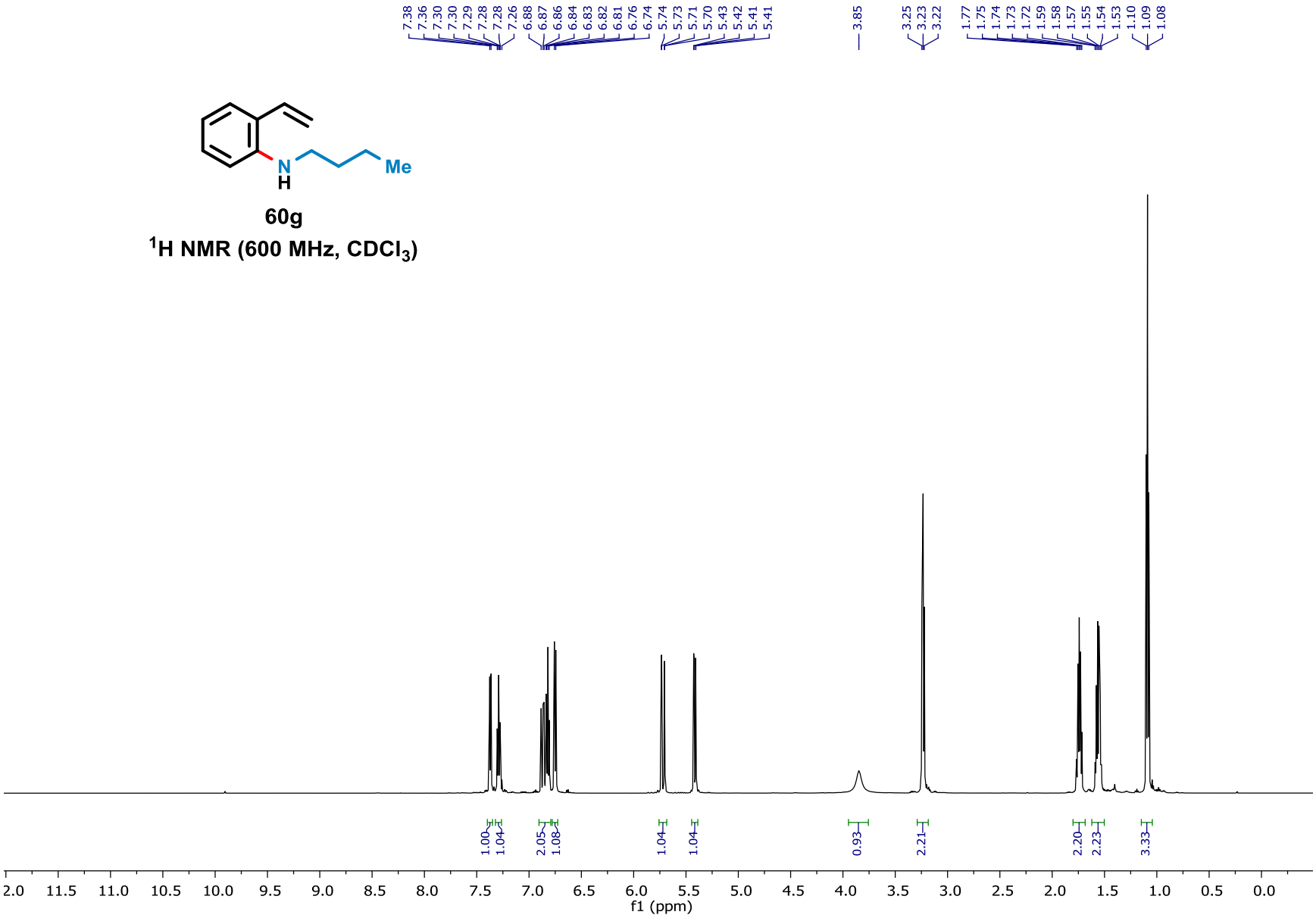
^{13}C NMR (151 MHz, $CDCl_3$)

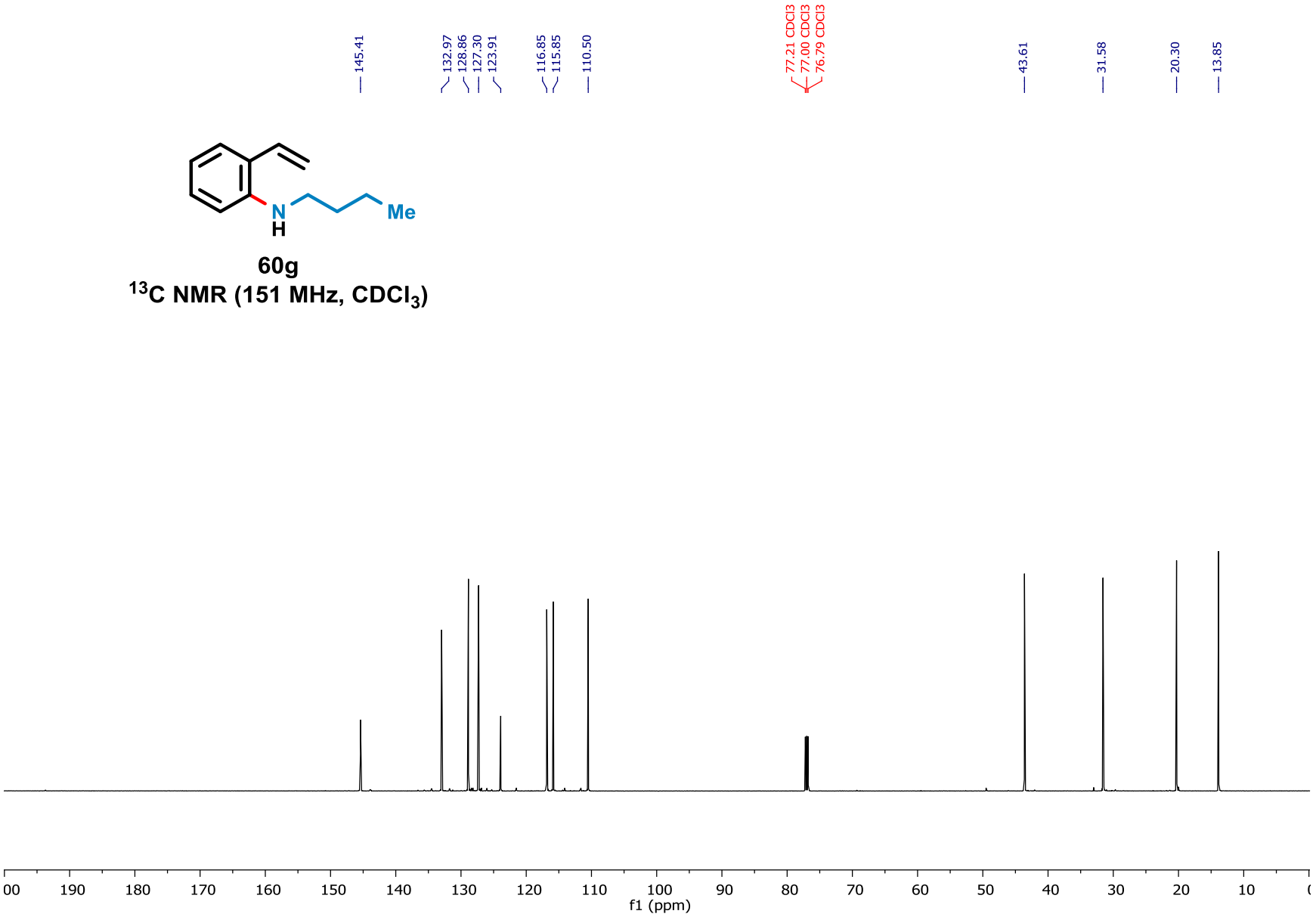

7.29
7.28
7.26
7.20
7.19
6.81
6.80
6.79
6.77
6.76
3.58
3.31
3.30
3.28
2.27
1.82
1.81
1.80
1.79
1.77
1.64
1.63
1.62
1.60
1.59
1.58
1.15
1.13
1.12
Me
N
H
Me
60f
1H NMR (600 MHz, CDCl3)
1.00
0.98
0.96
0.99
1.00
2.05
3.09
2.17
2.32
3.21
f1 (ppm)



60f

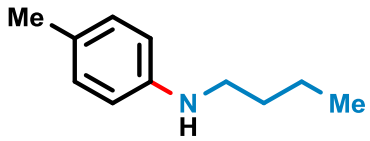
^{13}C NMR (151 MHz, $CDCl_3$)


7.38
7.36
7.30
7.30
7.29
7.28
7.28
7.26
6.88
6.87
6.86
6.84
6.83
6.82
6.81
6.76
6.74
5.74
5.73
5.71
5.70
5.43
5.42
5.41
5.41
3.85
3.25
3.23
3.22
1.77
1.75
1.74
1.73
1.72
1.59
1.58
1.57
1.55
1.54
1.53
1.10
1.09
1.08
N
H
Me
60g
1H NMR (600 MHz, CDCl3)
1.00
1.04
2.05
1.08
1.04
1.04
0.93
2.21
2.20
2.23
3.33
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



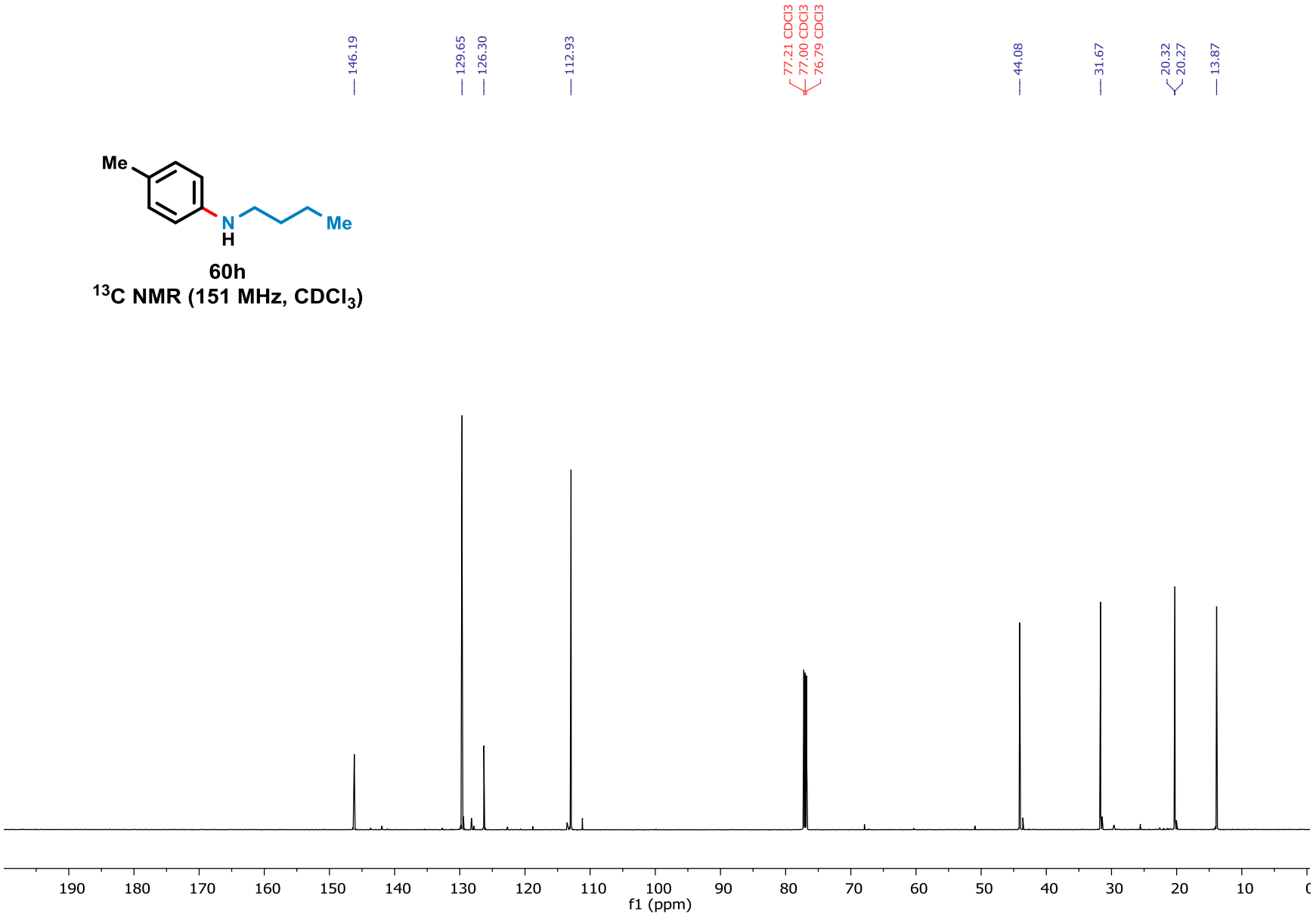
60g

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



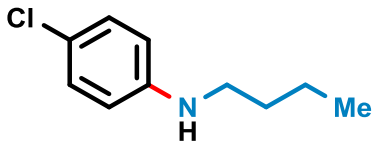
60h

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



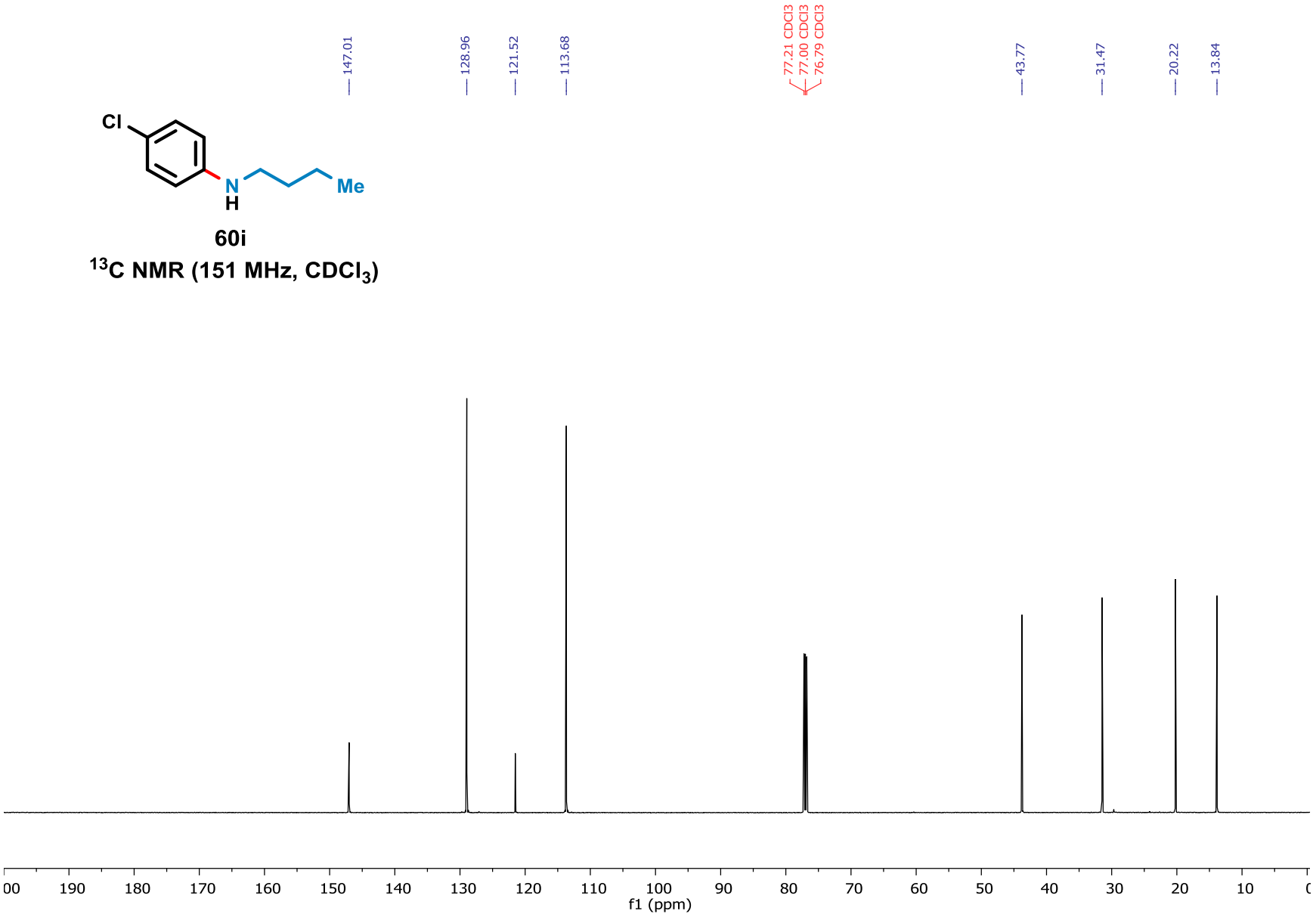
60h

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



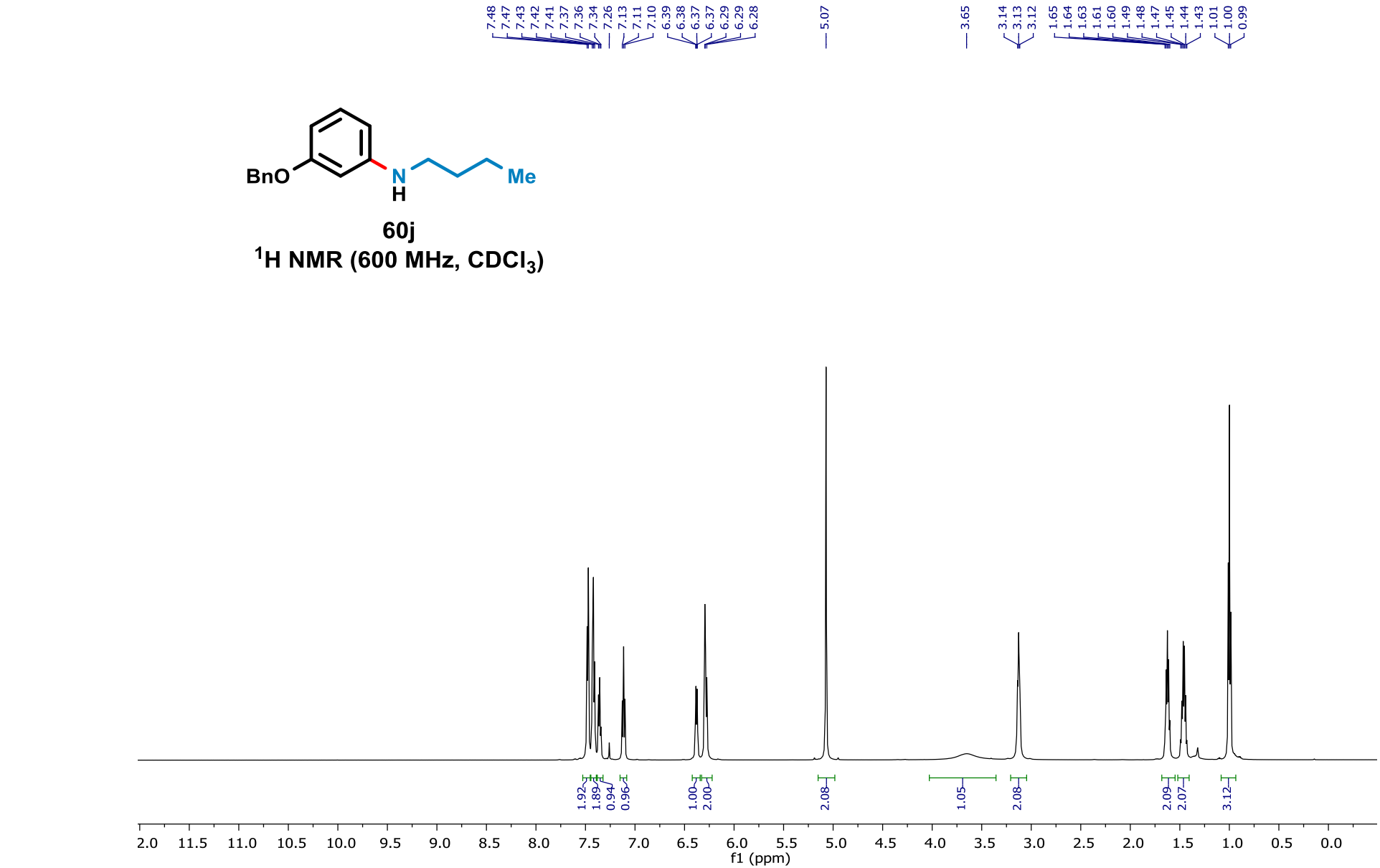
60i

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



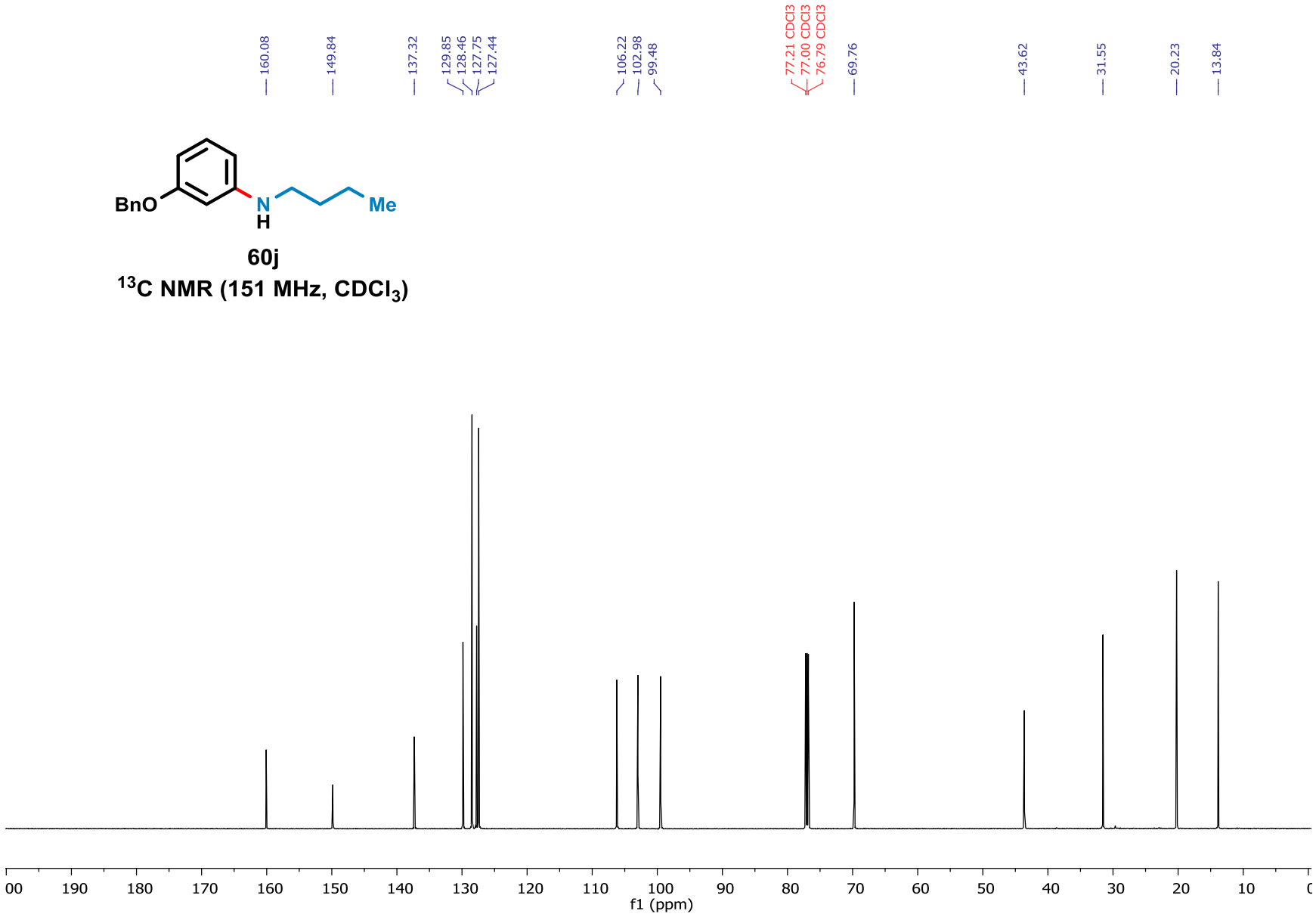
60i

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



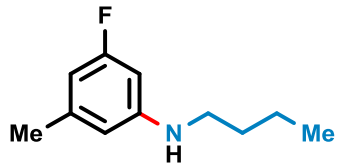
60j

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



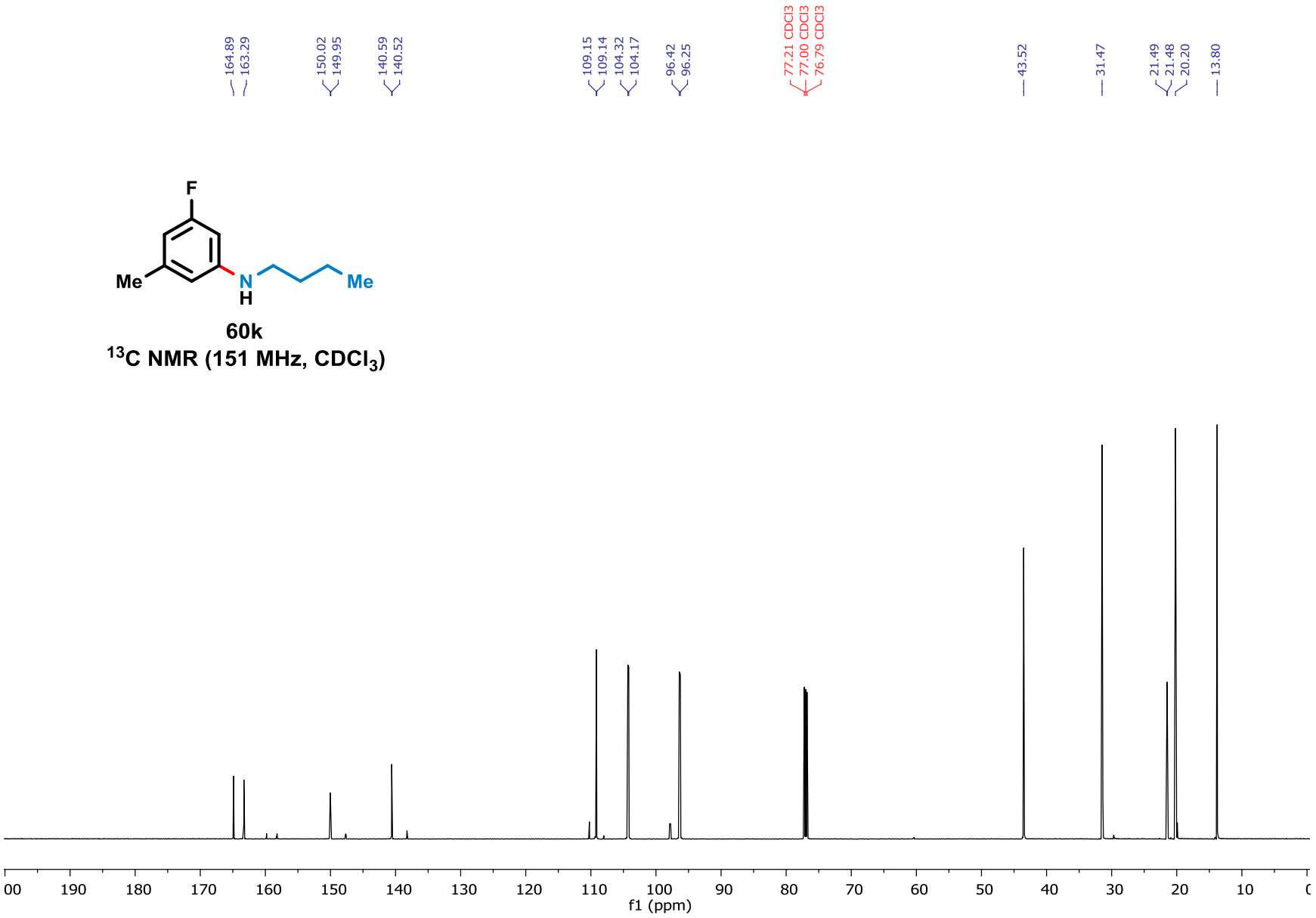
60j

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



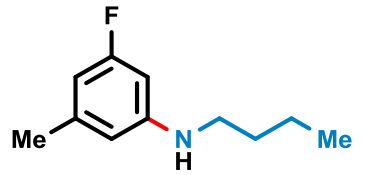
60k

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



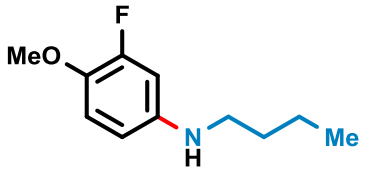
60k

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



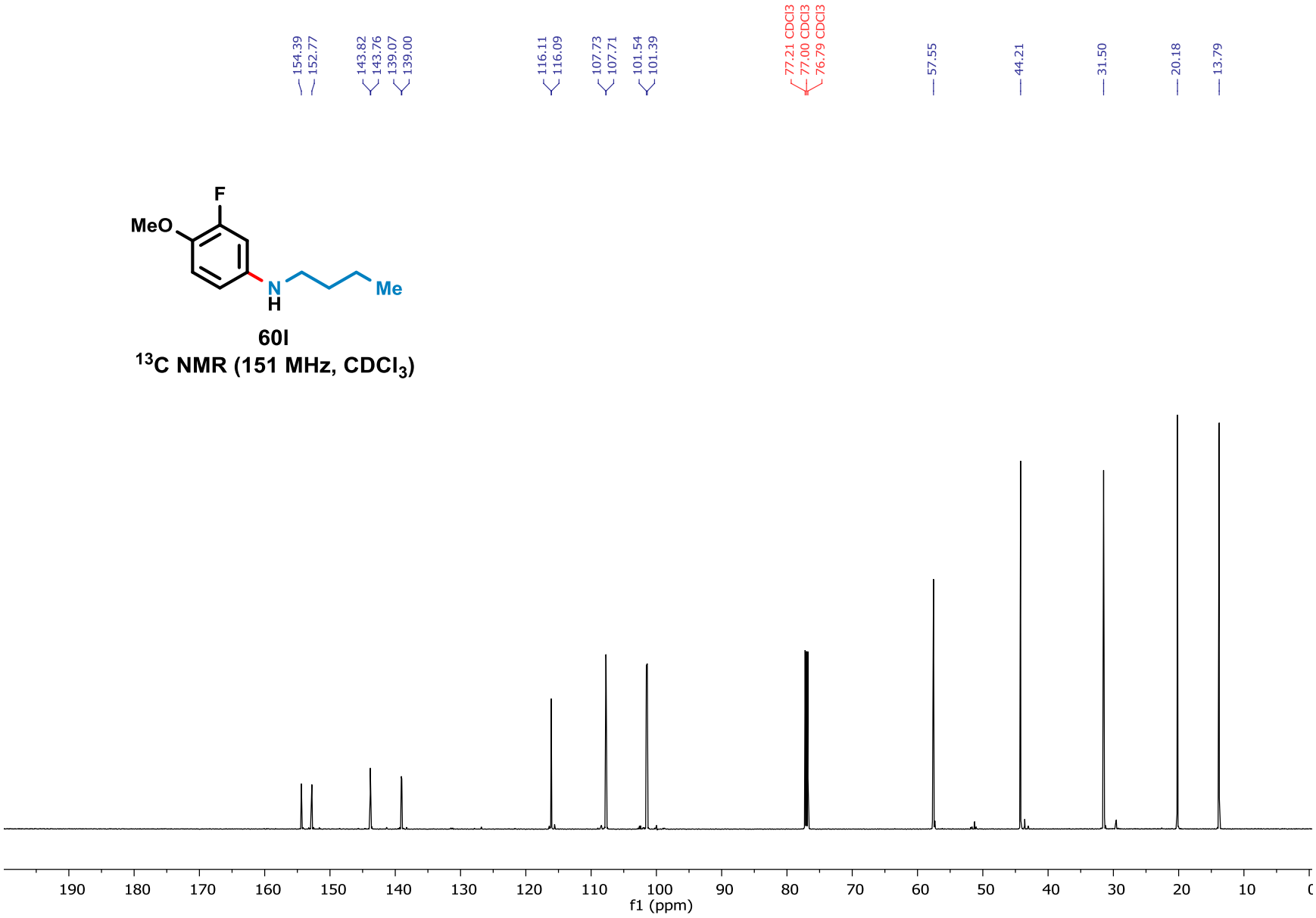
60k

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



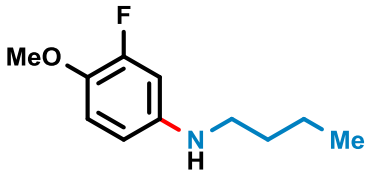
60l

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



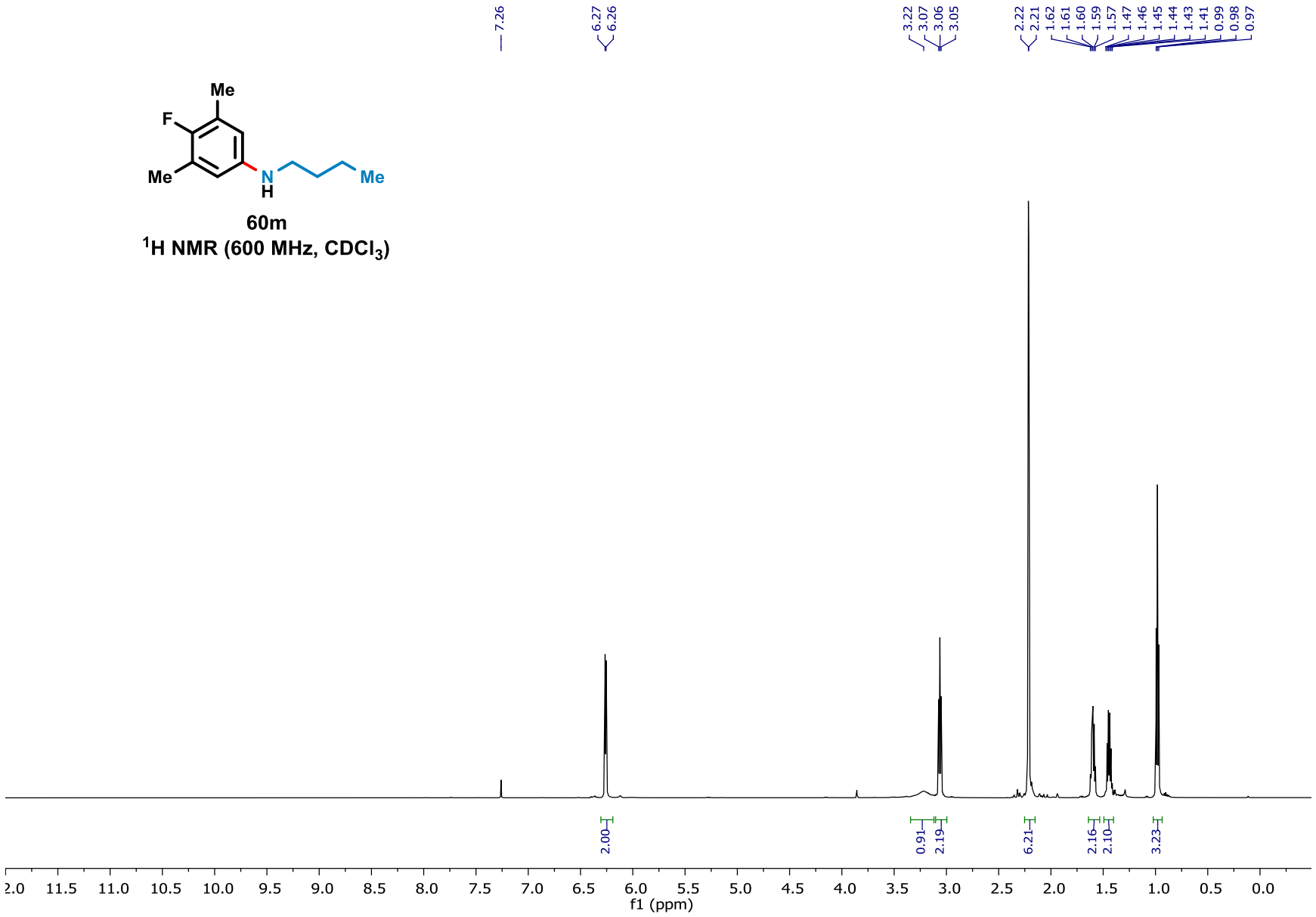
60l

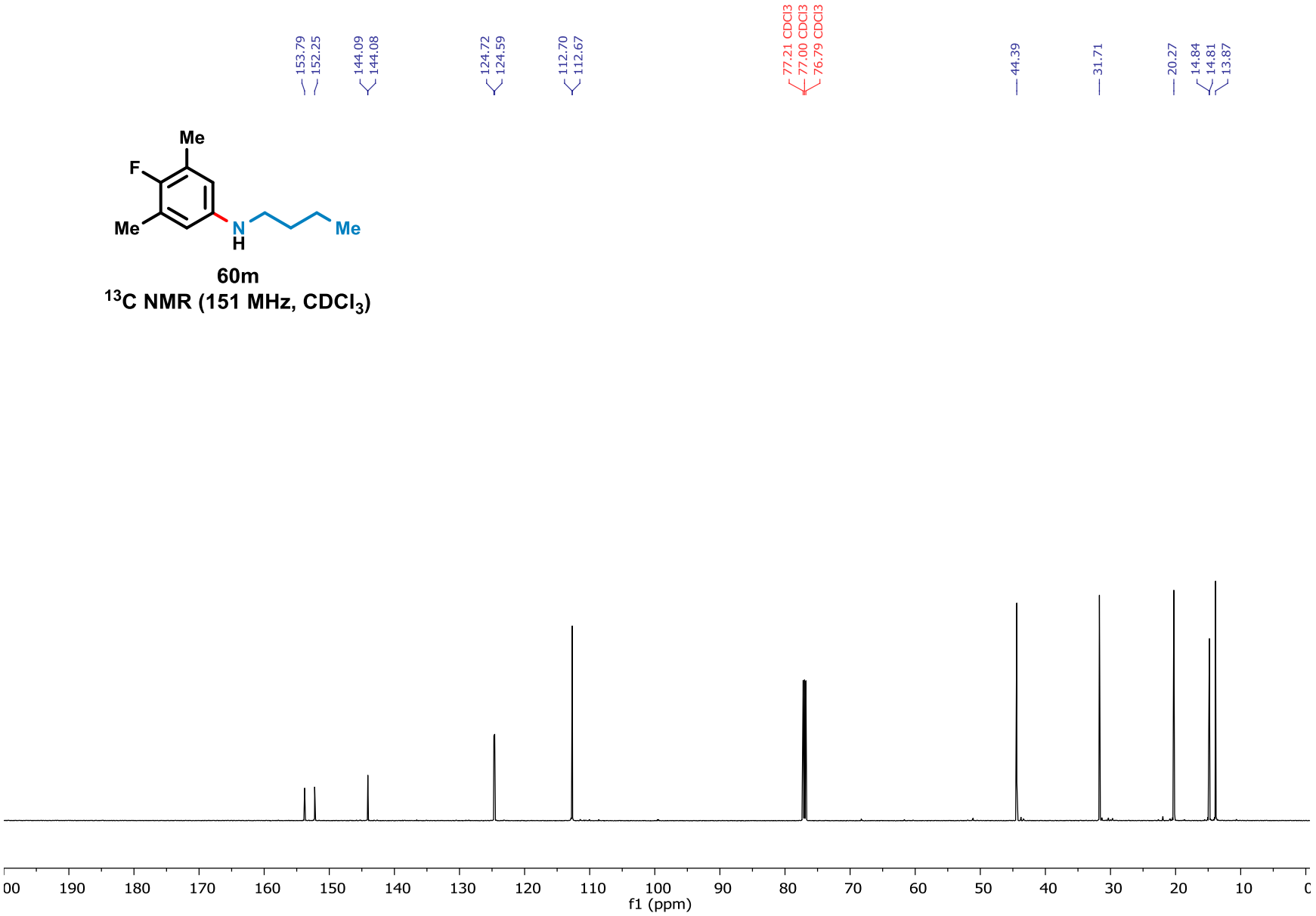
^{13}C NMR (151 MHz, $CDCl_3$)

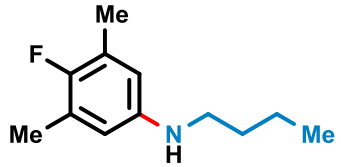


60l

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

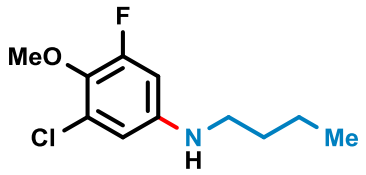

Me
F
Me
N
H
Me
60m
1H NMR (600 MHz, CDCl3)
7.26
6.27
6.26
3.22
3.07
3.06
3.05
2.22
2.21
1.62
1.61
1.60
1.59
1.57
1.47
1.46
1.45
1.44
1.43
1.41
0.99
0.98
0.97
2.00
0.91
2.19
6.21
2.16
2.10
3.23
f1 (ppm)


153.79
152.25
144.09
144.08
124.72
124.59
112.70
112.67
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
44.39
31.71
20.27
14.84
14.81
13.87
Me
F
Me
N
H
Me
60m
13C NMR (151 MHz, CDCl3)
f1 (ppm)



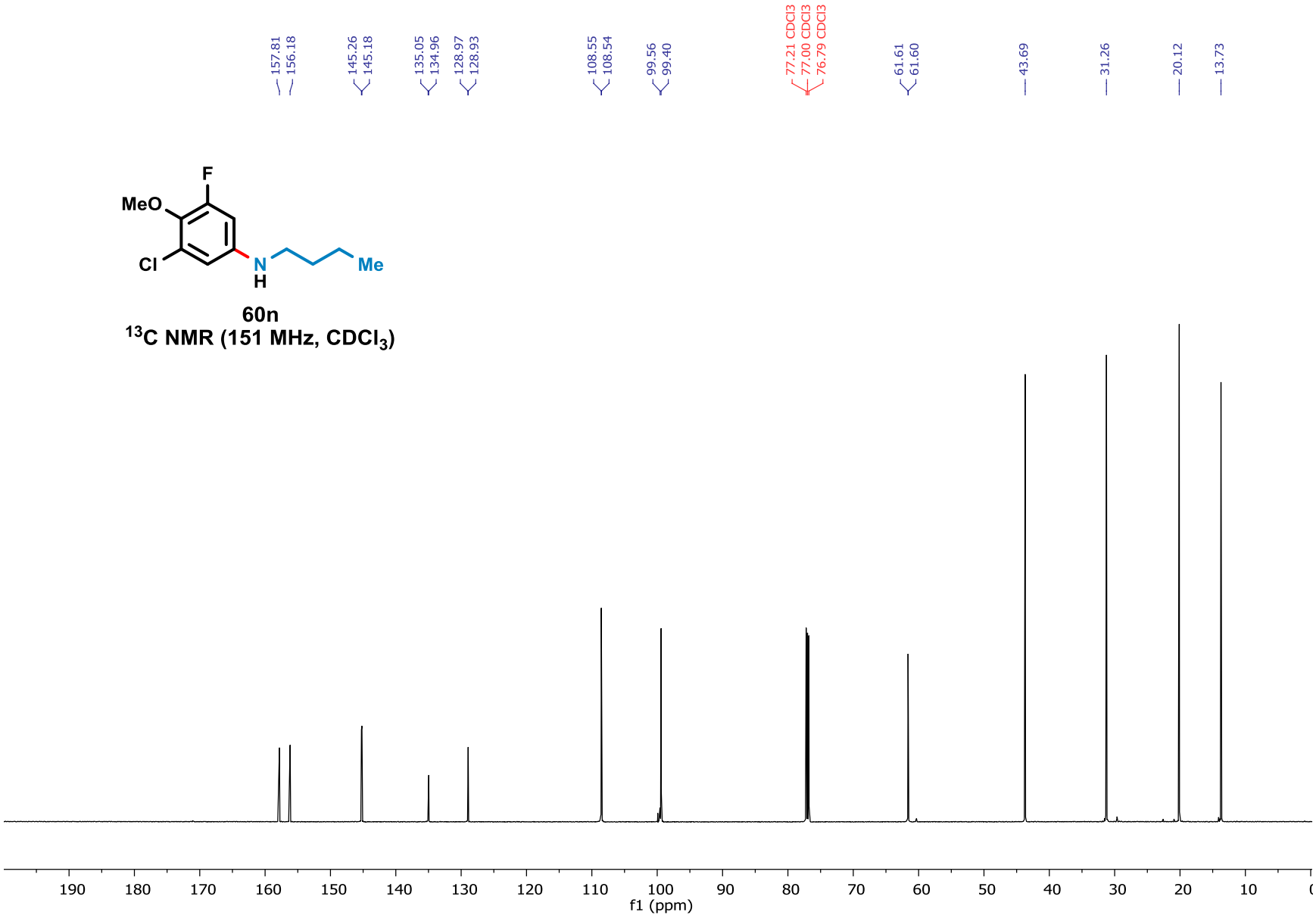
60m

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



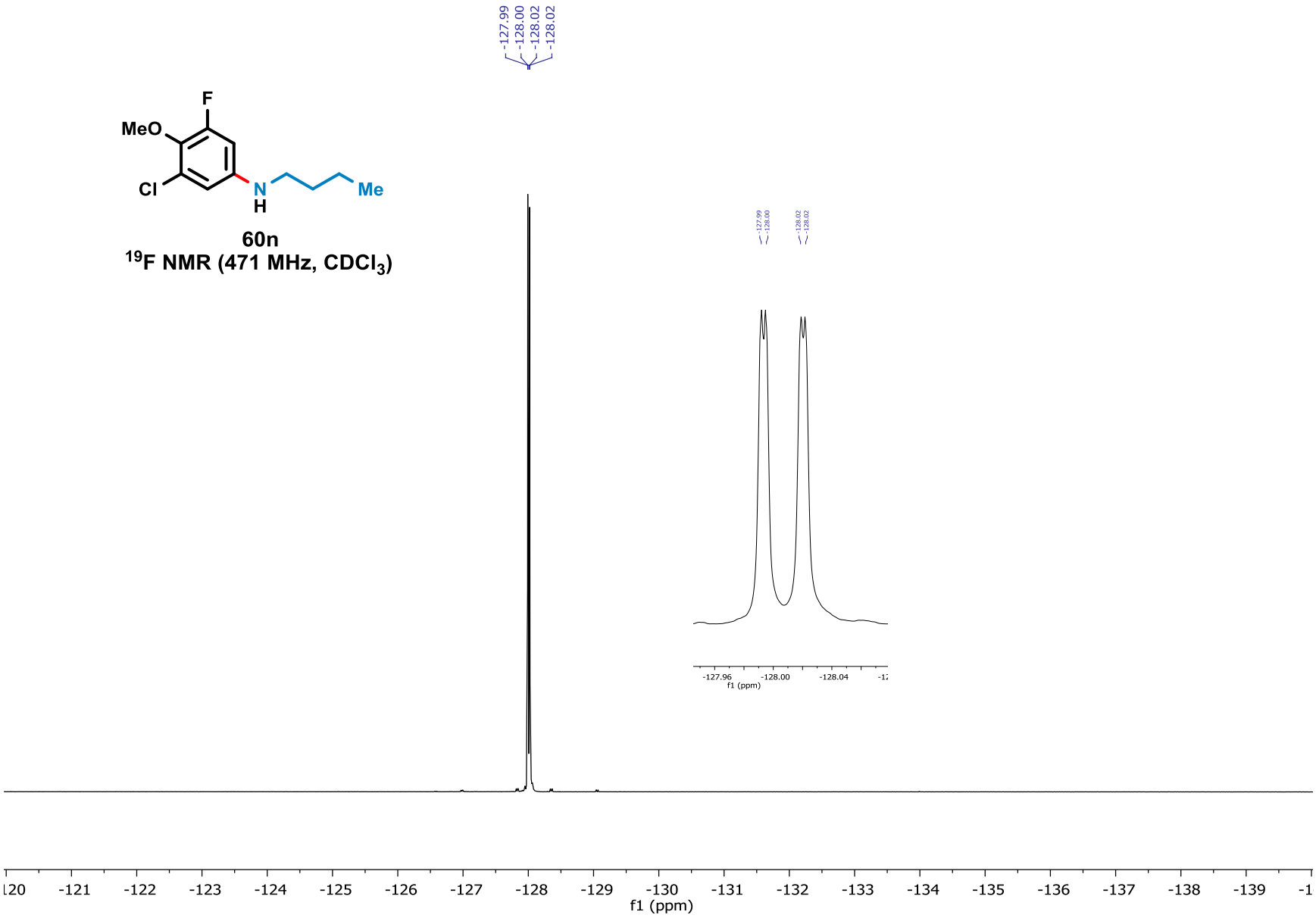
60n

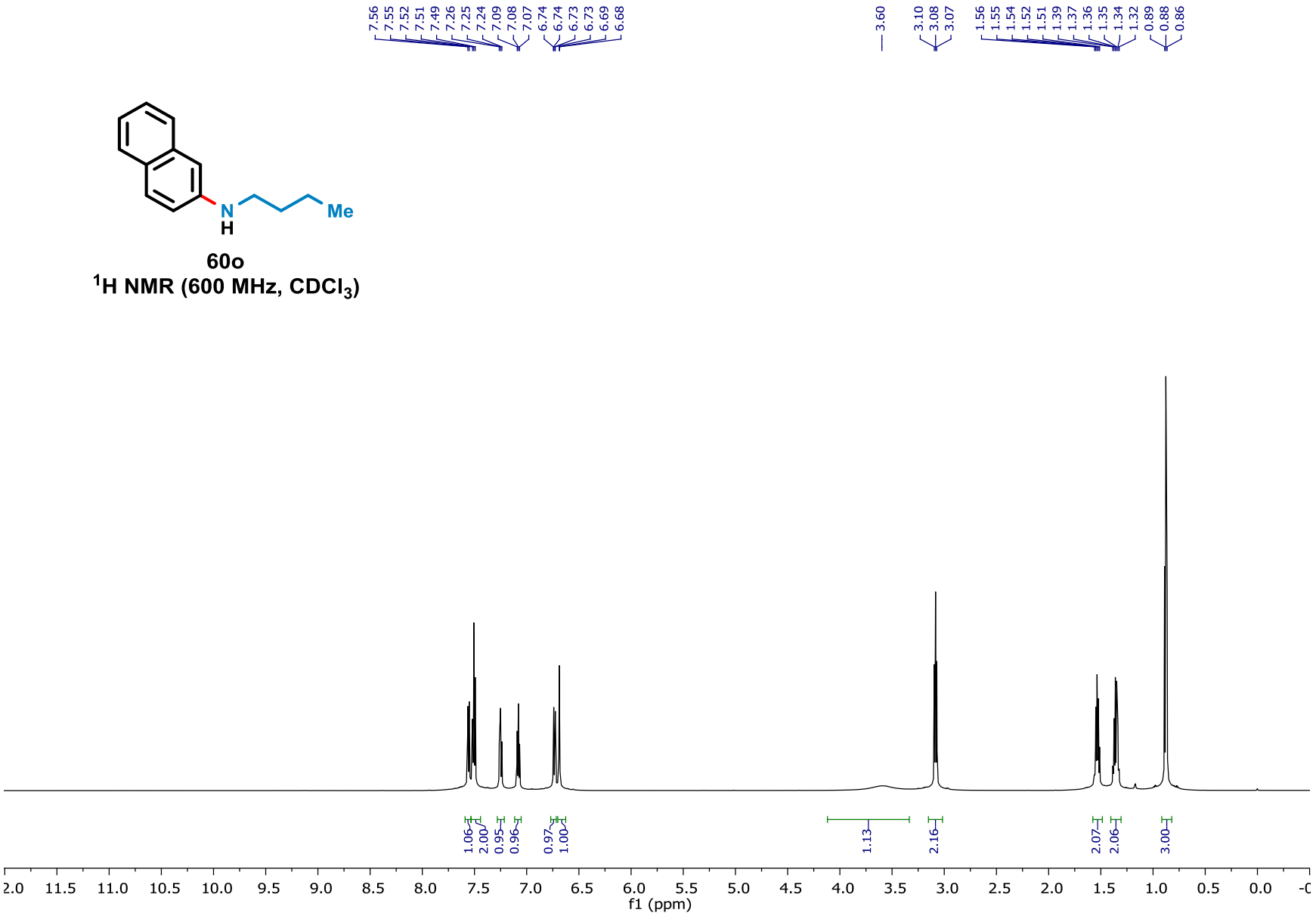
^{1}H NMR (600 MHz, $CDCl_3$)



60n

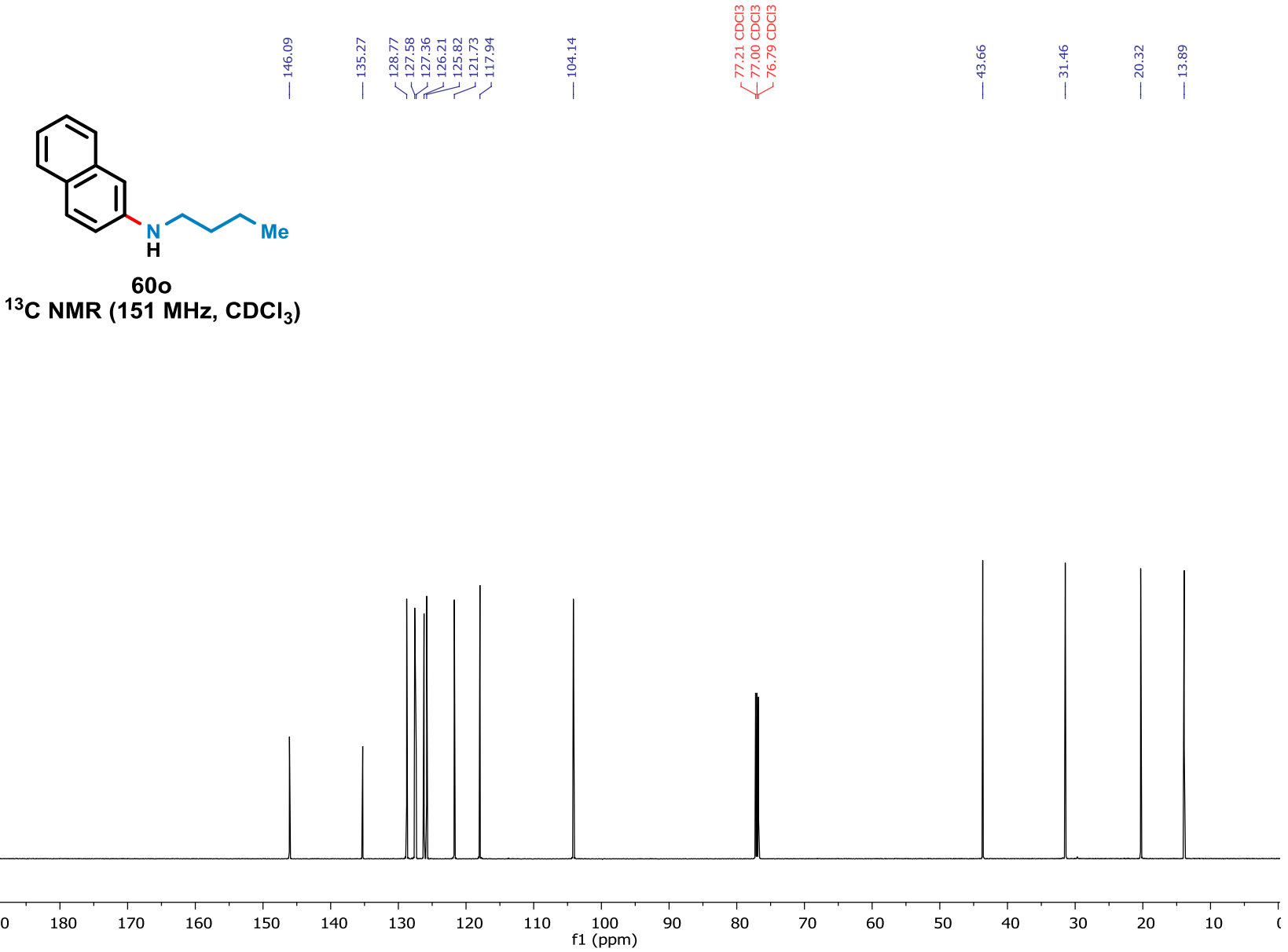
^{13}C NMR (151 MHz, $CDCl_3$)


-127.99
-128.00
-128.02
-128.02
F
MeO
Cl
N
H
Me
60n
19F NMR (471 MHz, CDCl3)
-127.96
-128.00
-128.04
f1 (ppm)
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)



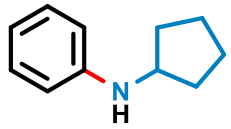
60o

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



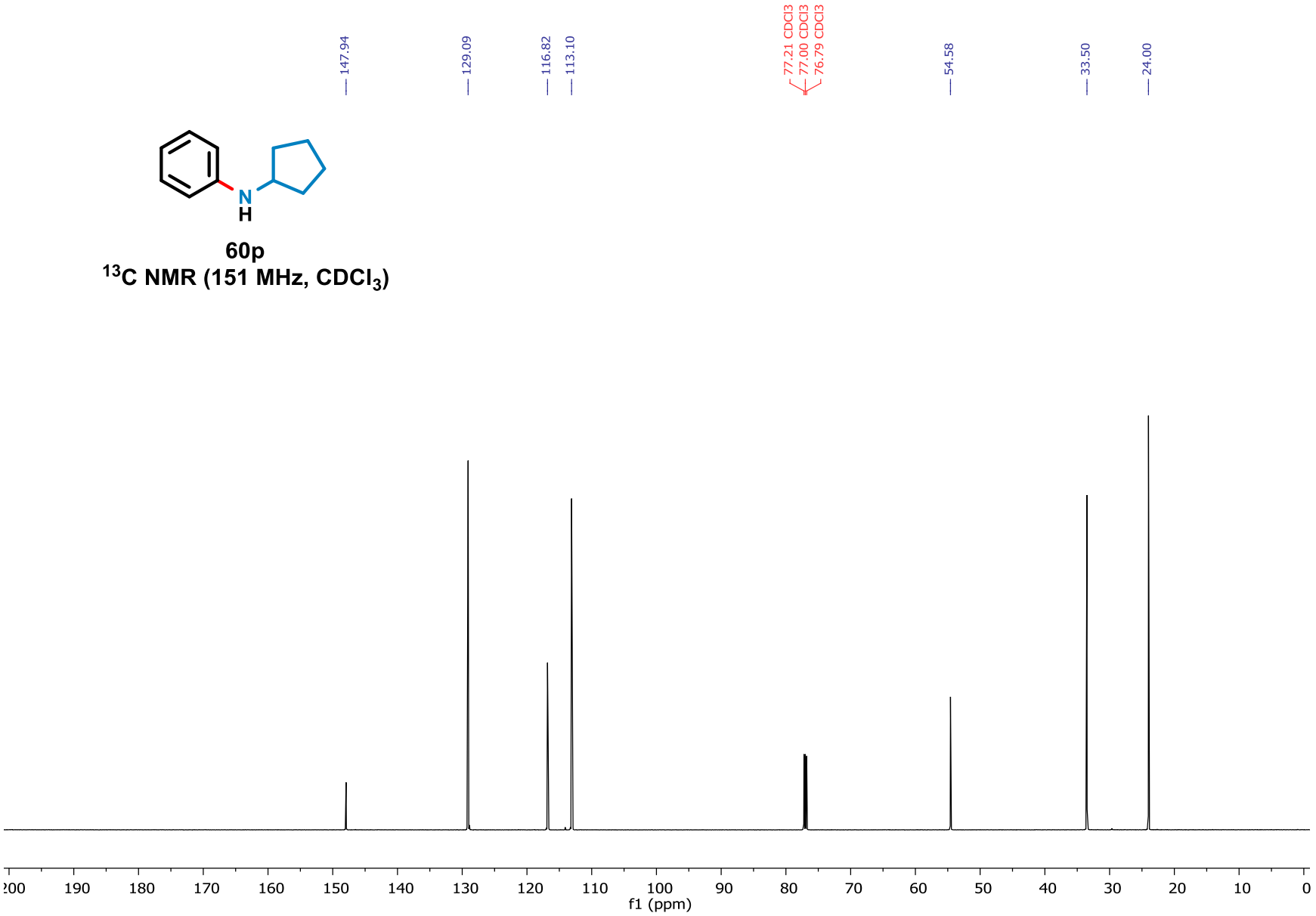
60o

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



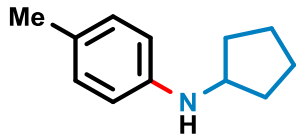
60p

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



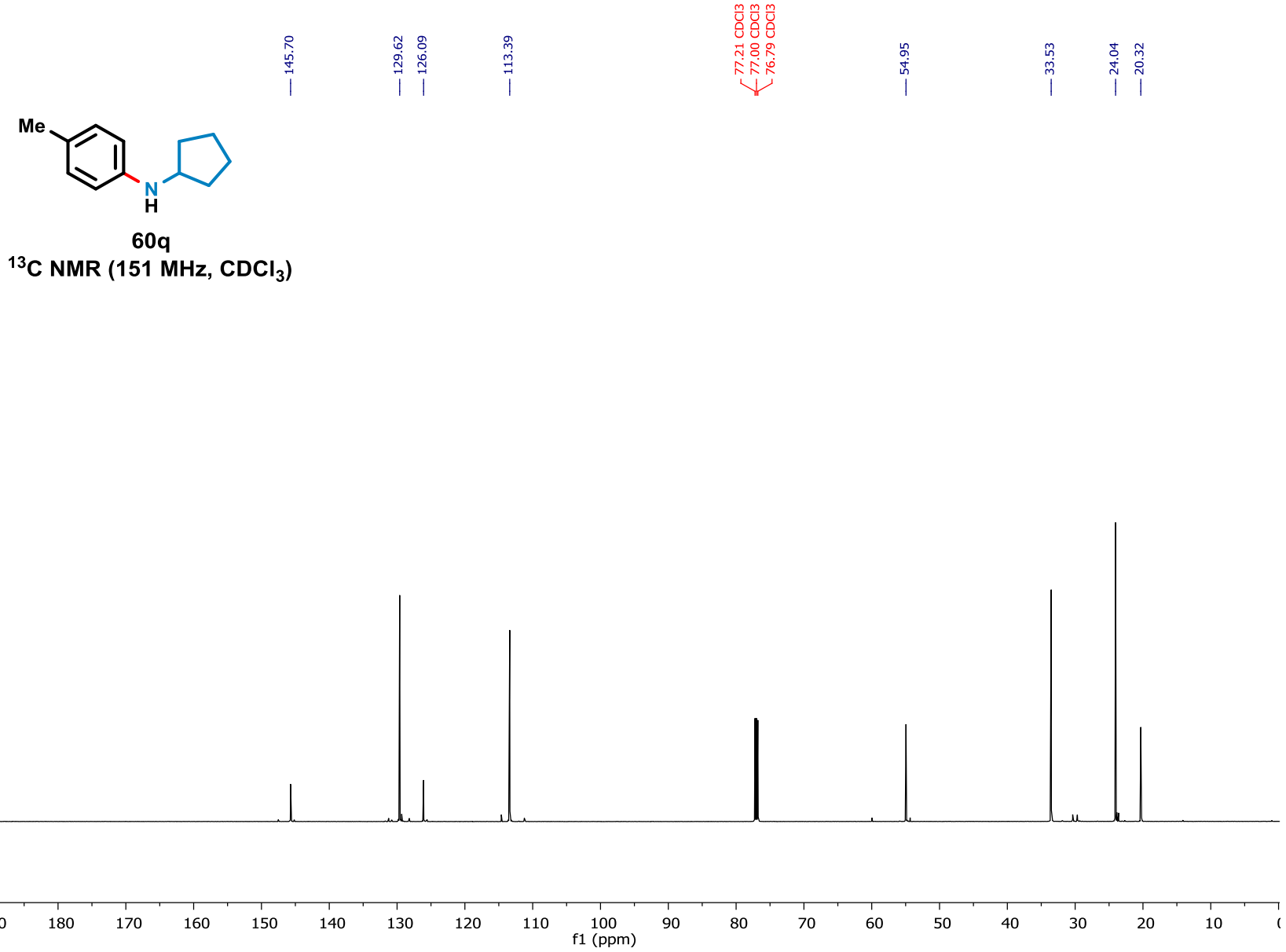
60p

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



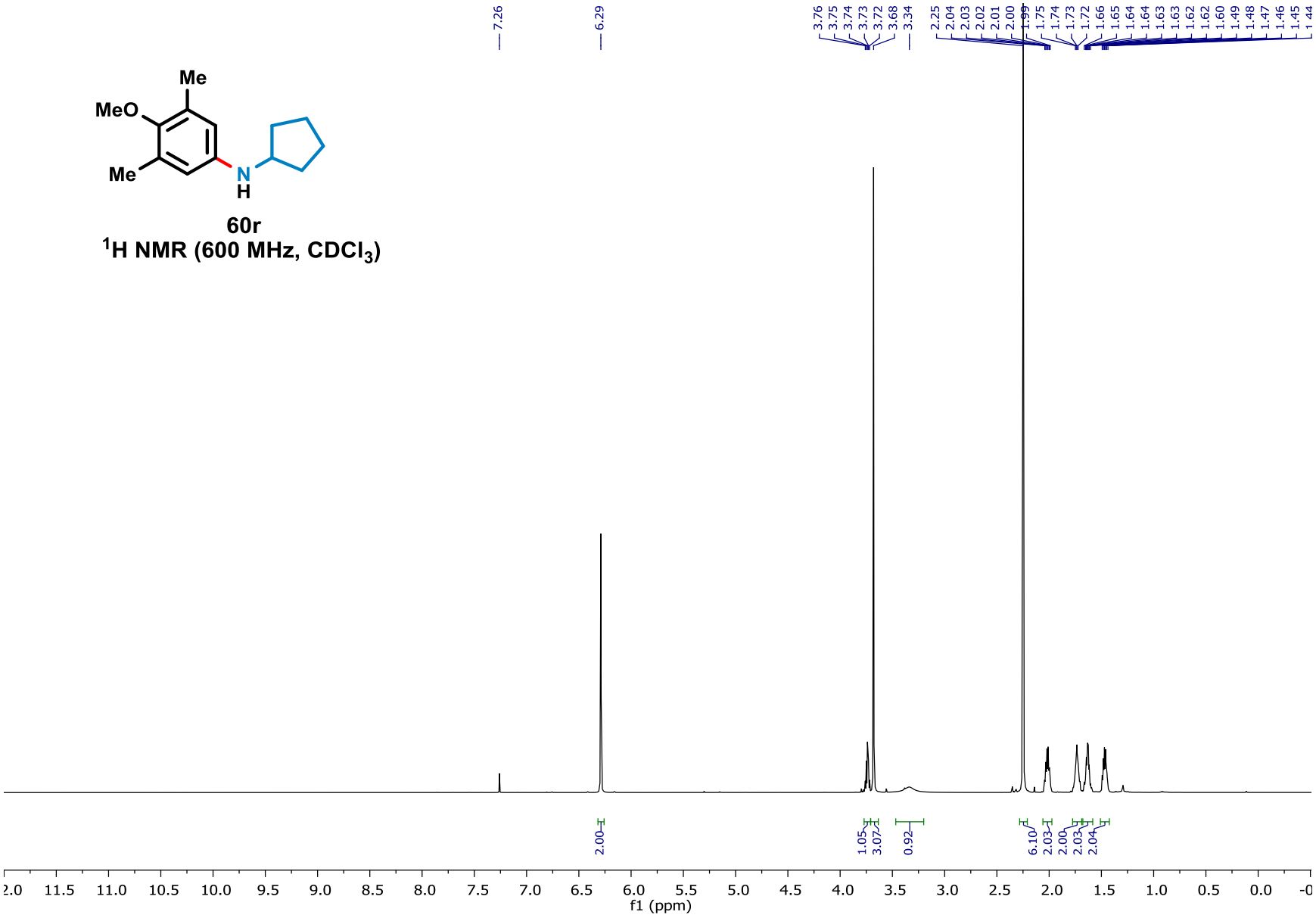
60q

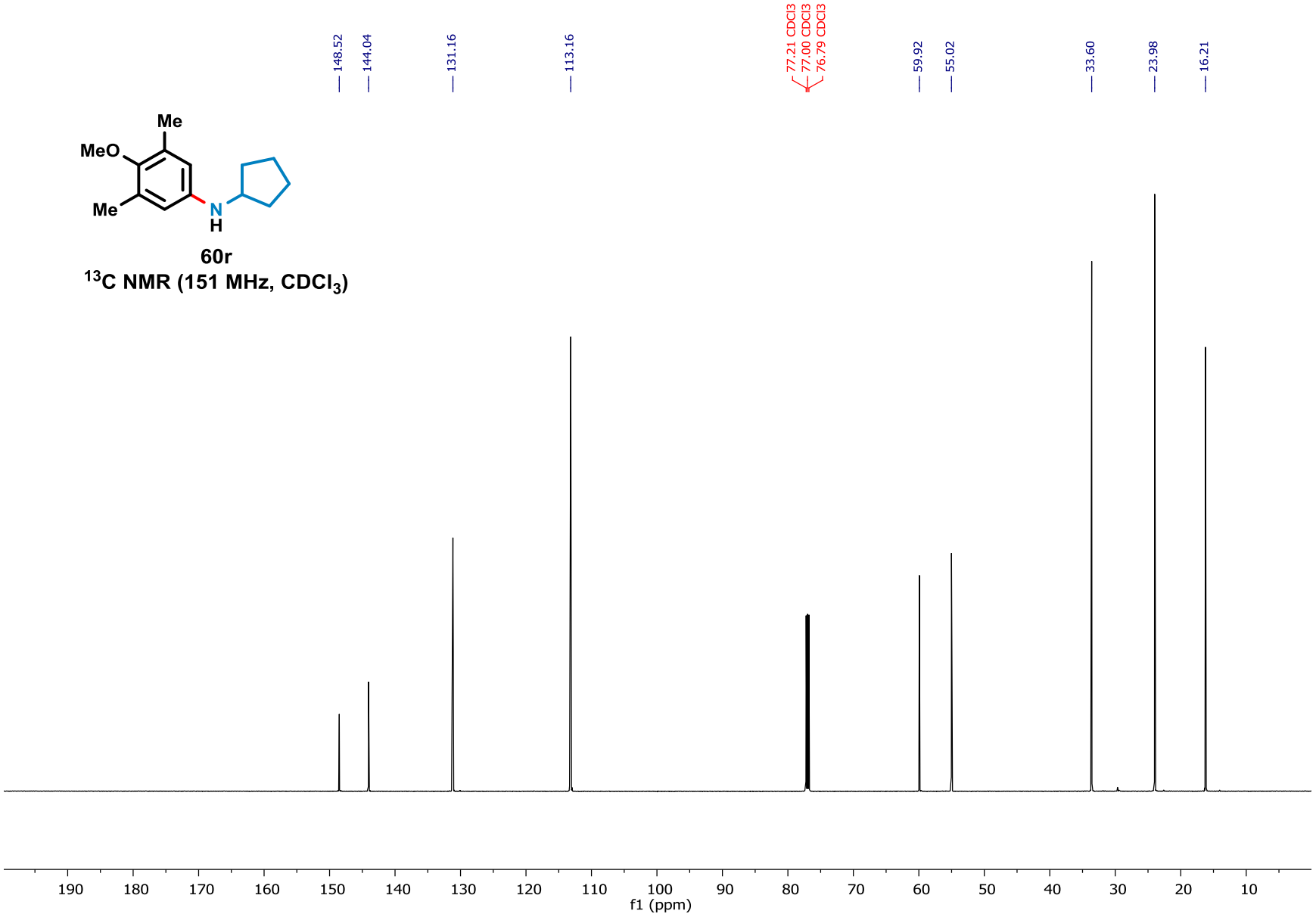
^{1}H NMR (600 MHz, $CDCl_3$)

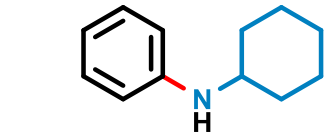


60q

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

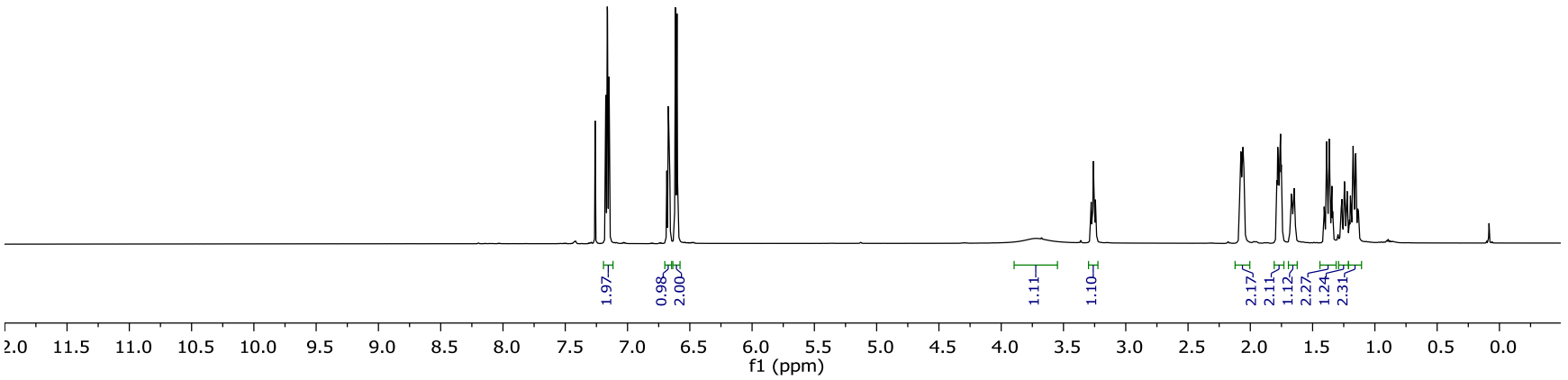

Me
MeO
Me
N
H
60r
1H NMR (600 MHz, CDCl3)
7.26
6.29
3.76
3.75
3.74
3.73
3.72
3.68
3.34
2.25
2.04
2.03
2.02
2.01
2.00
1.99
1.75
1.74
1.73
1.72
1.66
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.60
1.49
1.48
1.47
1.46
1.45
1.44
2.00
1.05
3.07
0.92
6.10
2.03
2.00
2.03
2.04
f1 (ppm)

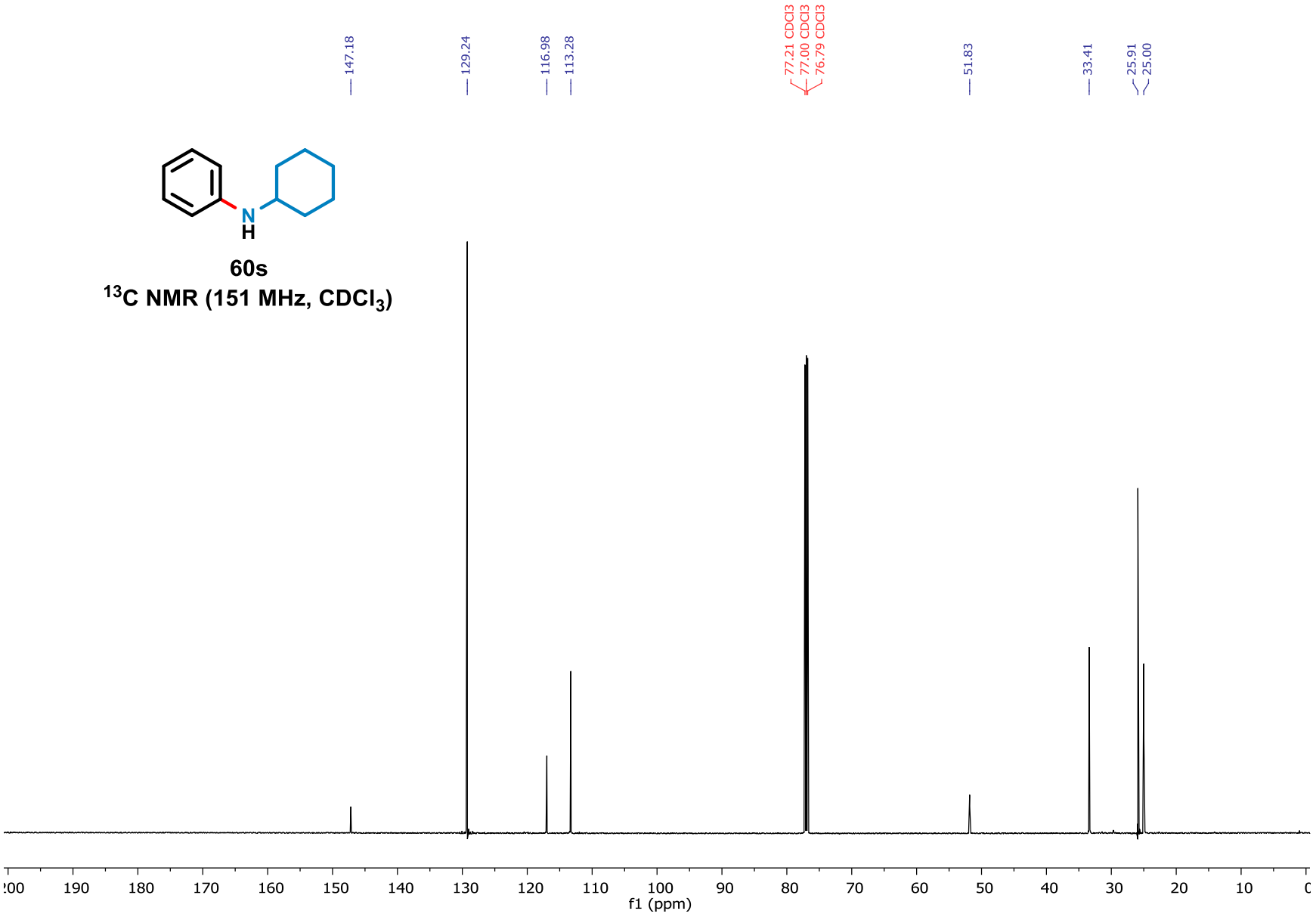

148.52
144.04
131.16
113.16
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
59.92
55.02
33.60
23.98
16.21
Me
MeO
Me
N
H
60r
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

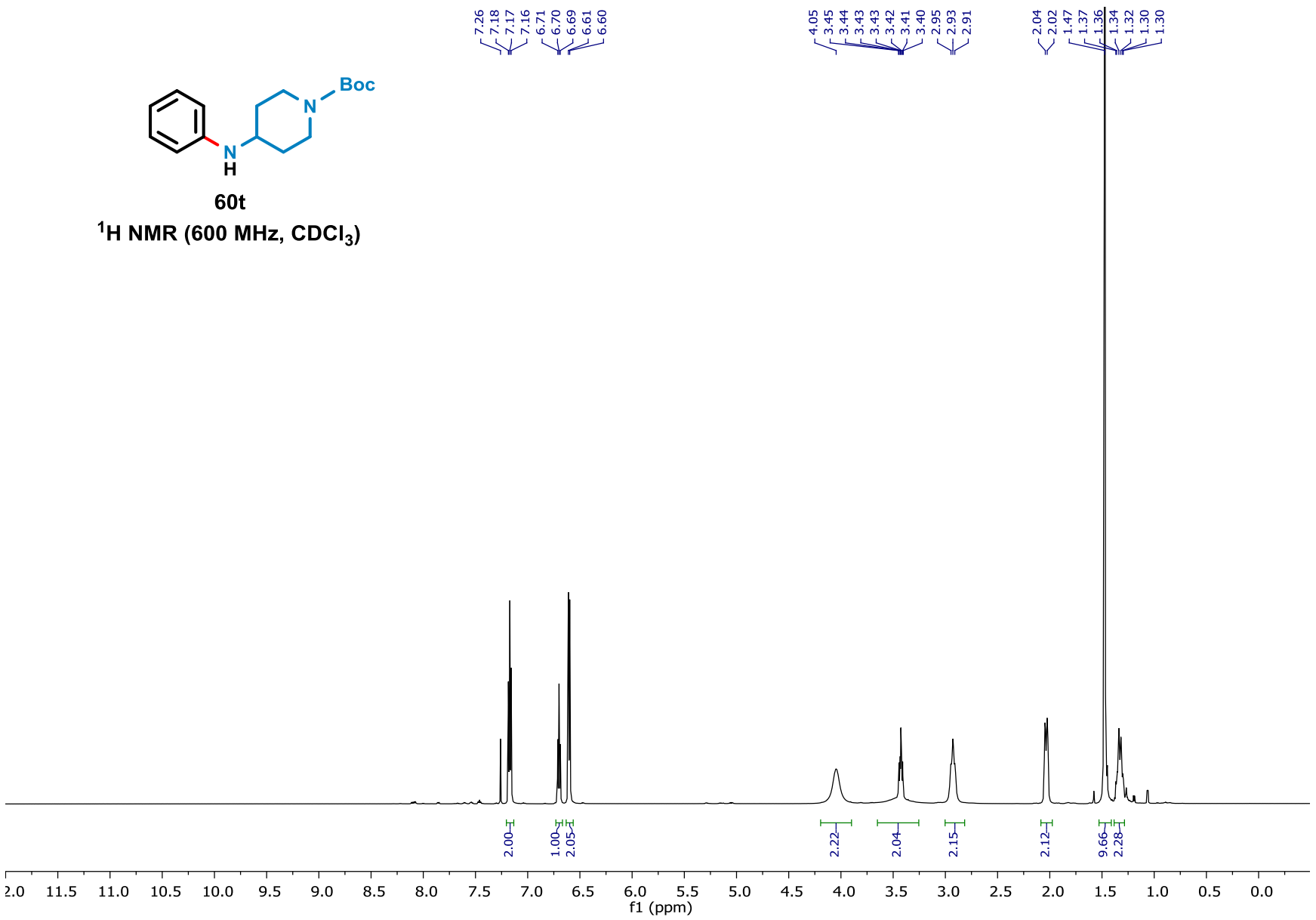


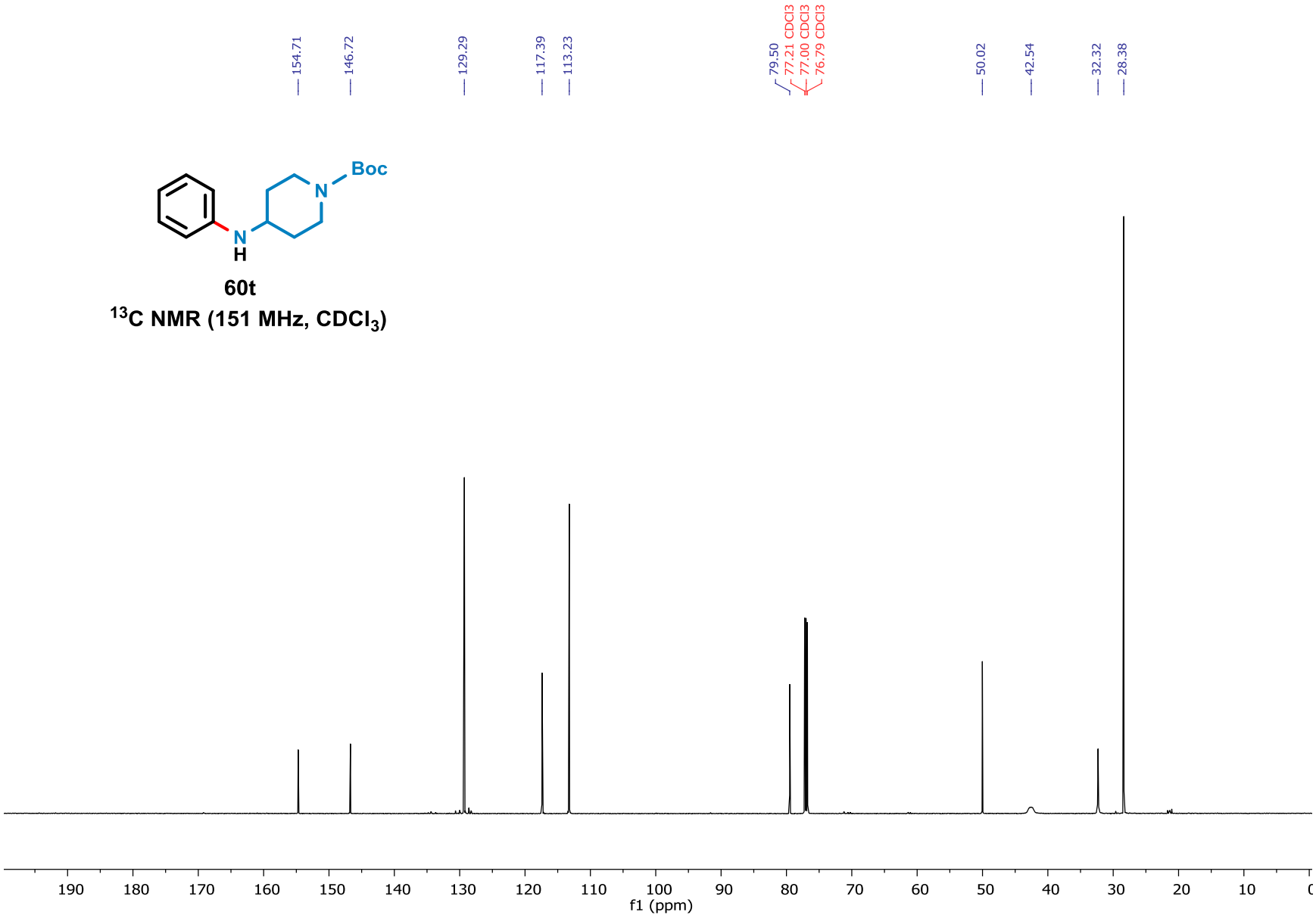
60s

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



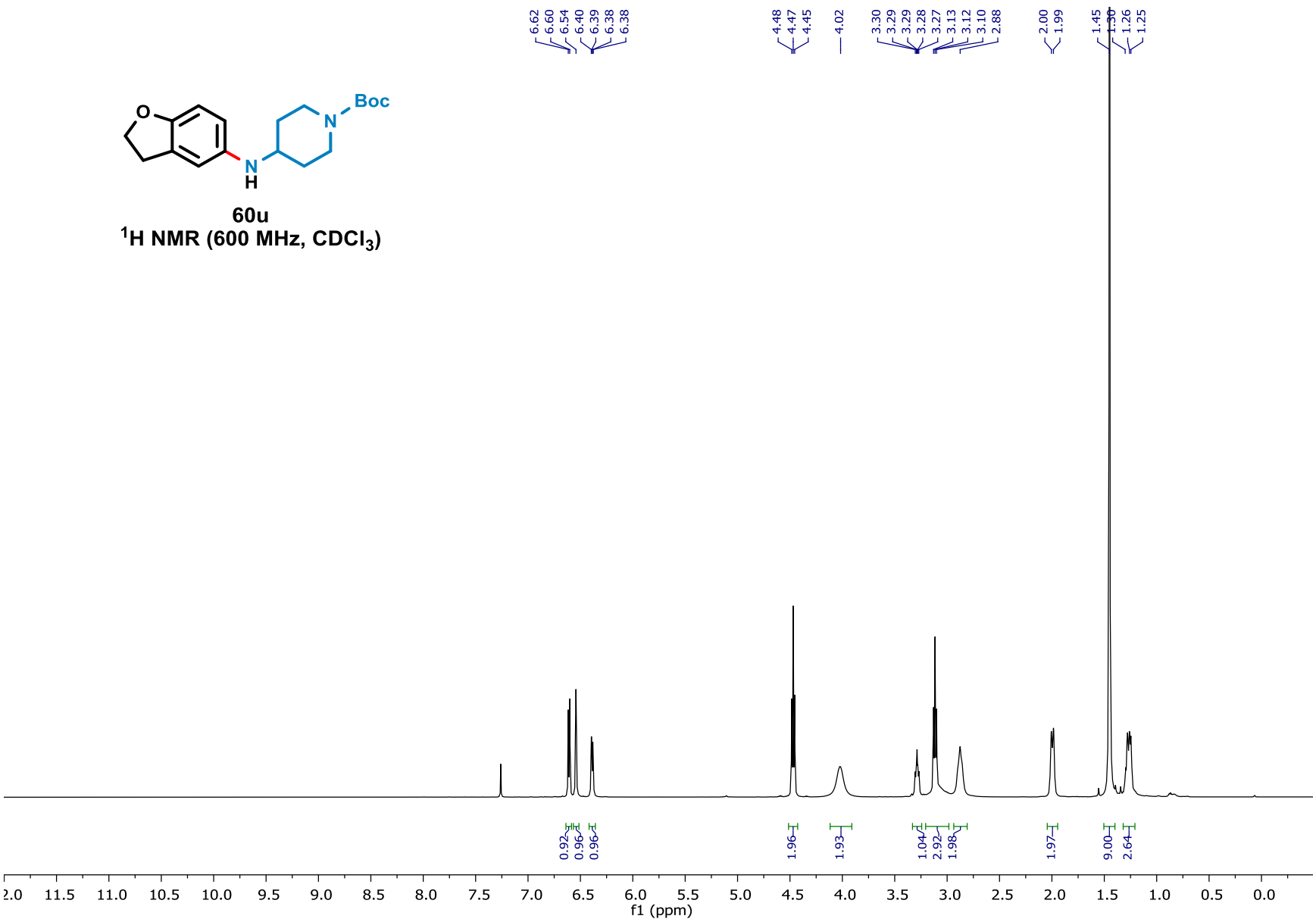

147.18
129.24
116.98
113.28
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
51.83
33.41
25.91
25.00
N
H
60s
13C NMR (151 MHz, CDCl3)
f1 (ppm)


Boc
N
N
H
60t
1H NMR (600 MHz, CDCl3)
7.26
7.18
7.17
7.16
6.71
6.70
6.69
6.61
6.60
4.05
3.45
3.44
3.43
3.43
3.42
3.41
3.40
2.95
2.93
2.91
2.04
2.02
1.47
1.37
1.36
1.34
1.32
1.30
1.30
2.00
1.00
2.05
2.22
2.04
2.15
2.12
9.66
2.28
f1 (ppm)



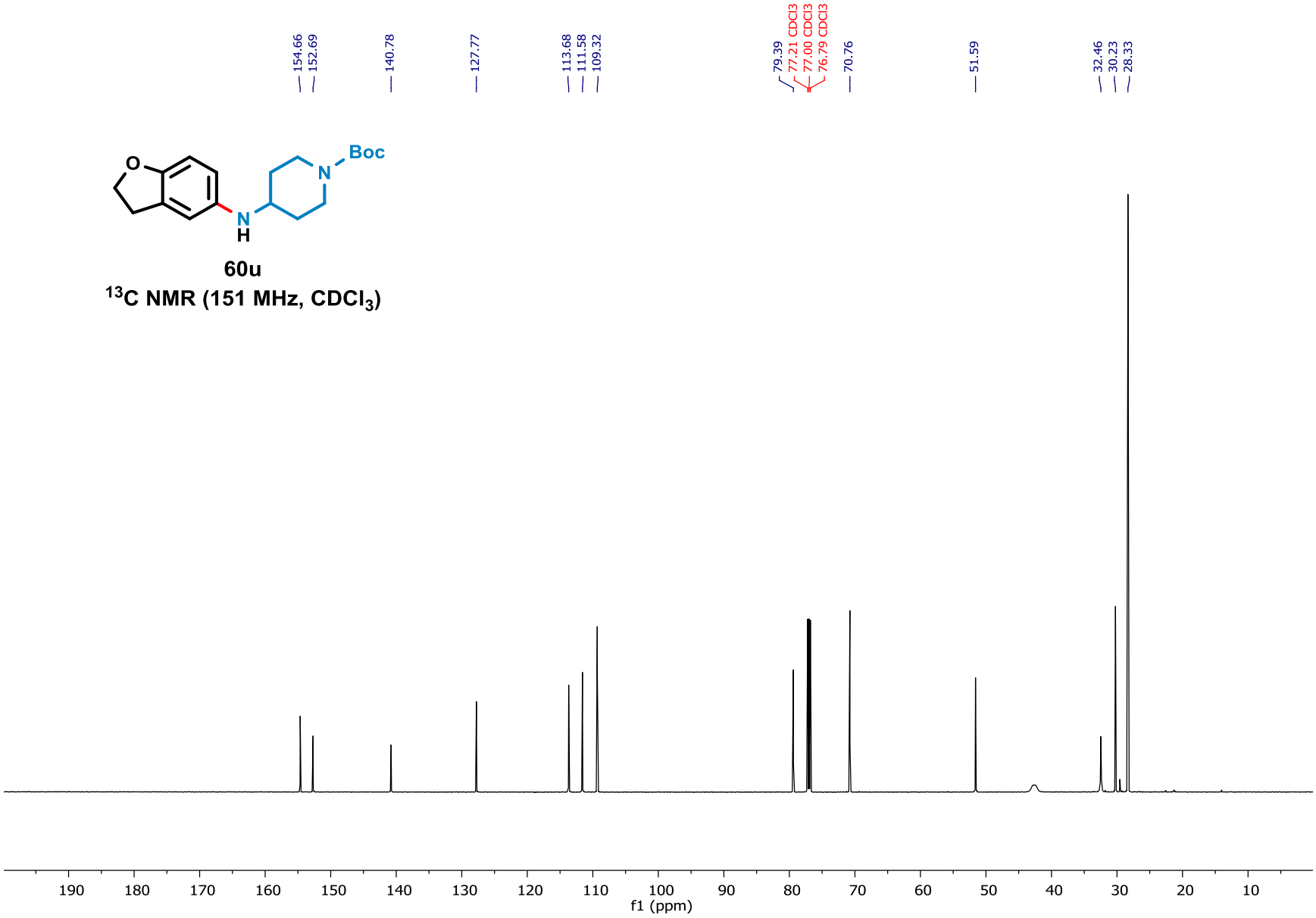
60t

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



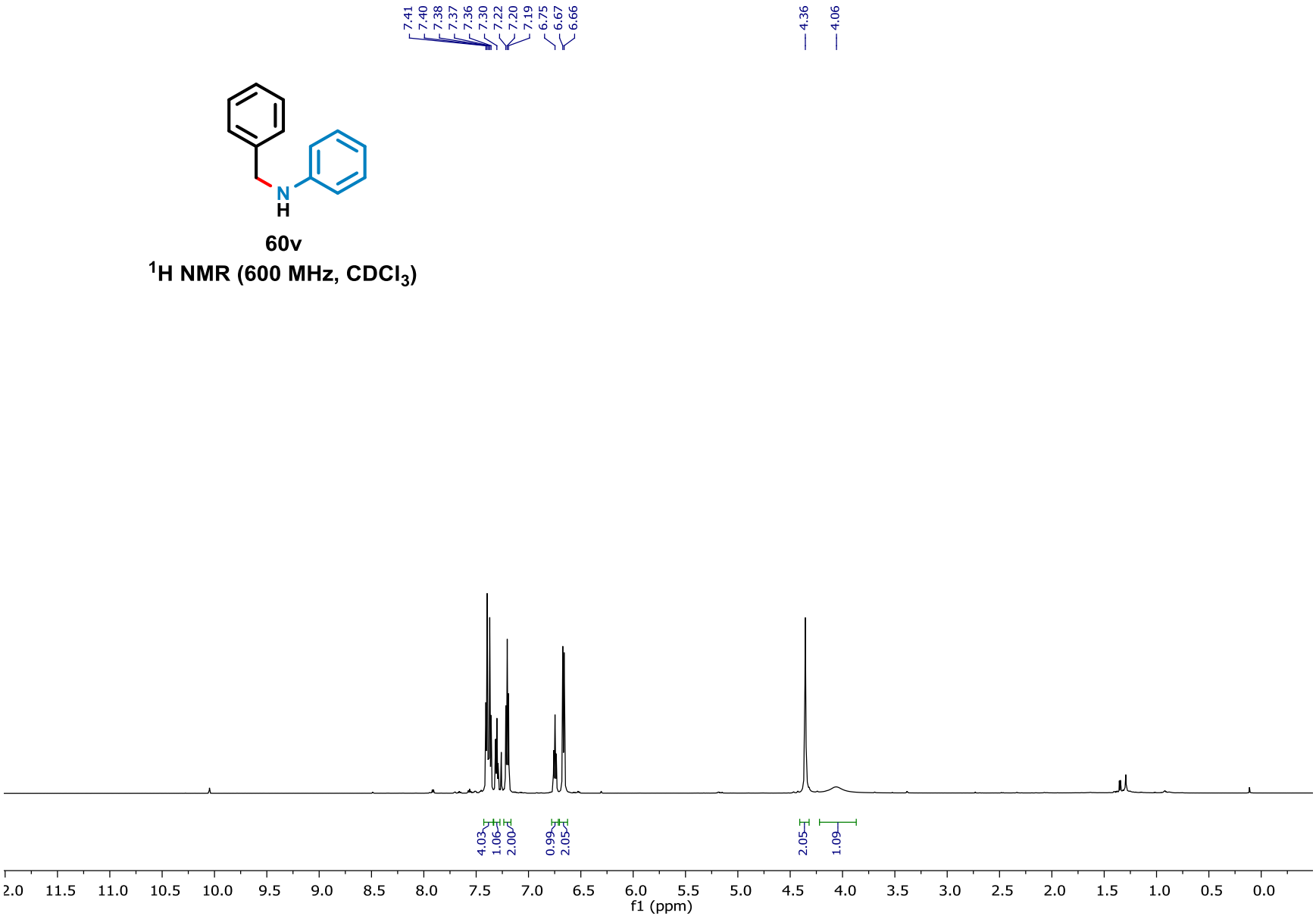
60u

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



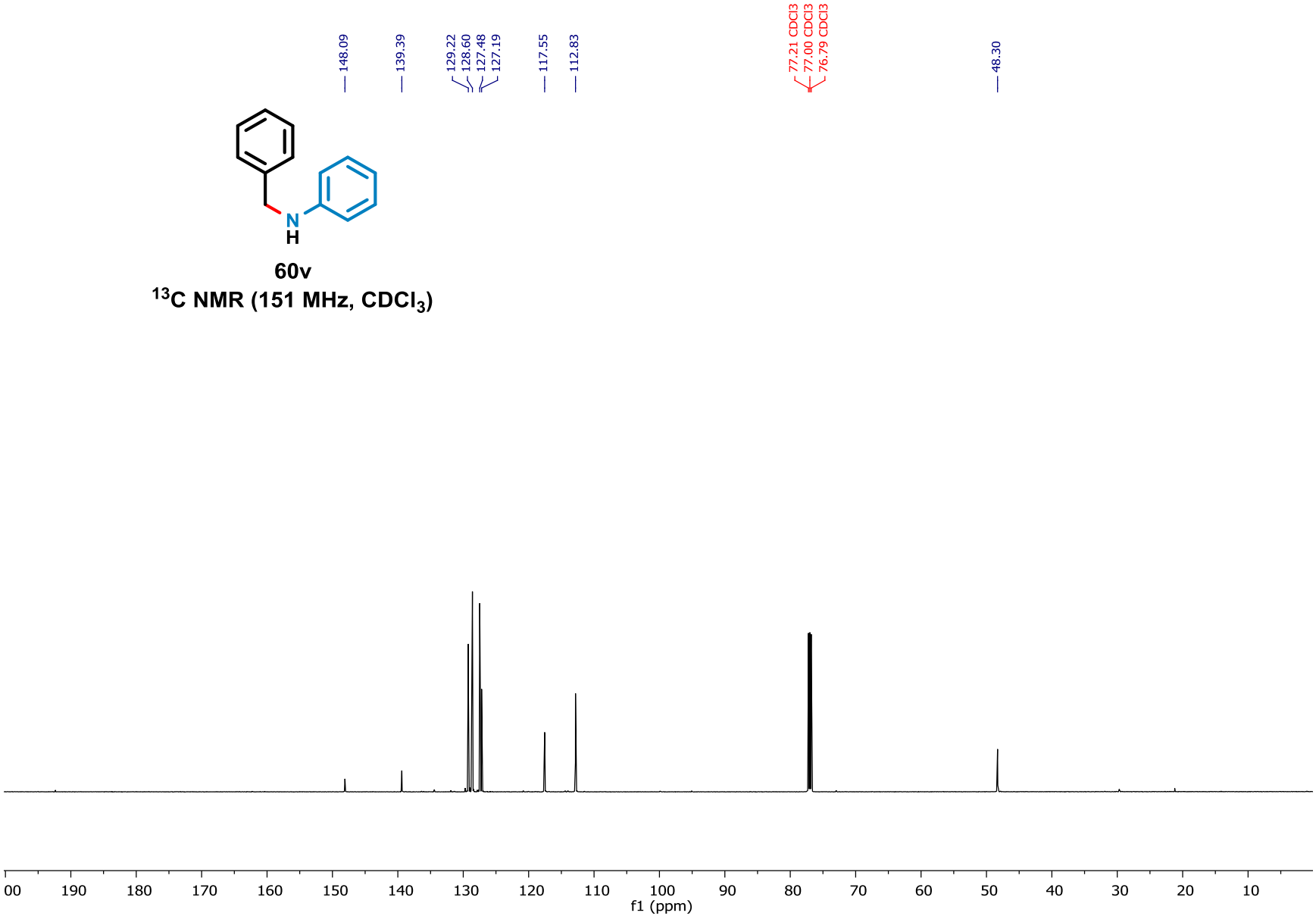
60u

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



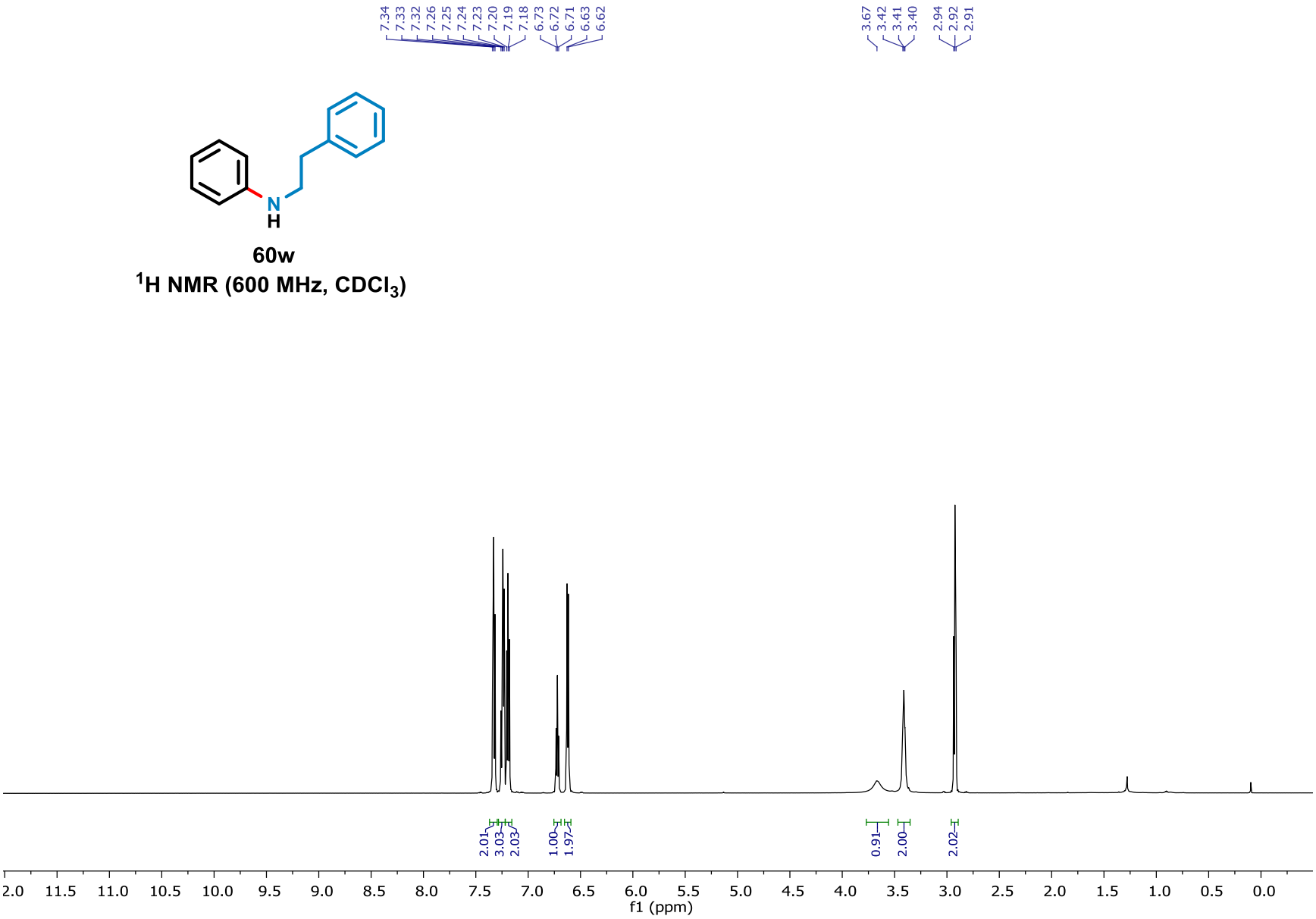
60v

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



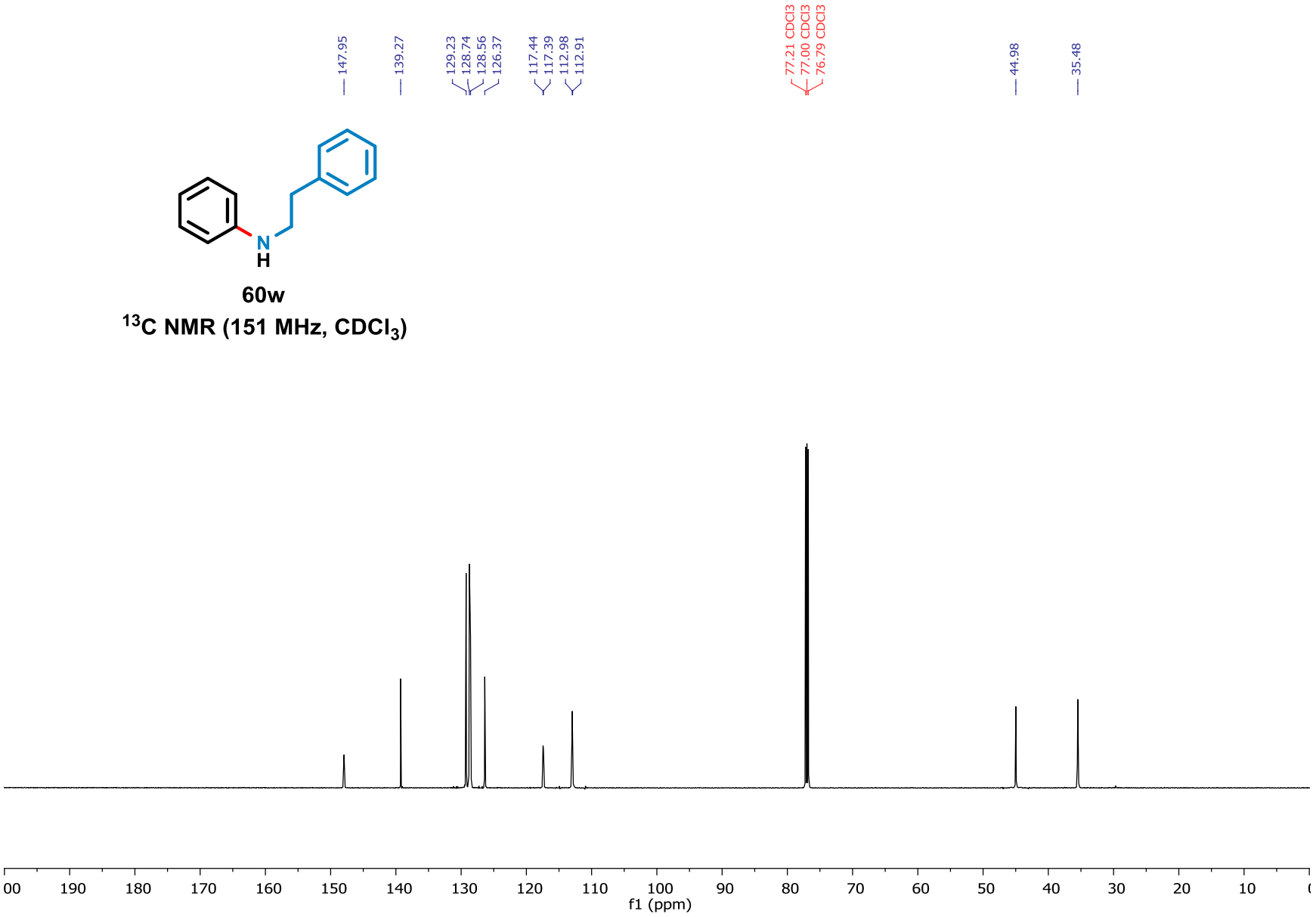
60v

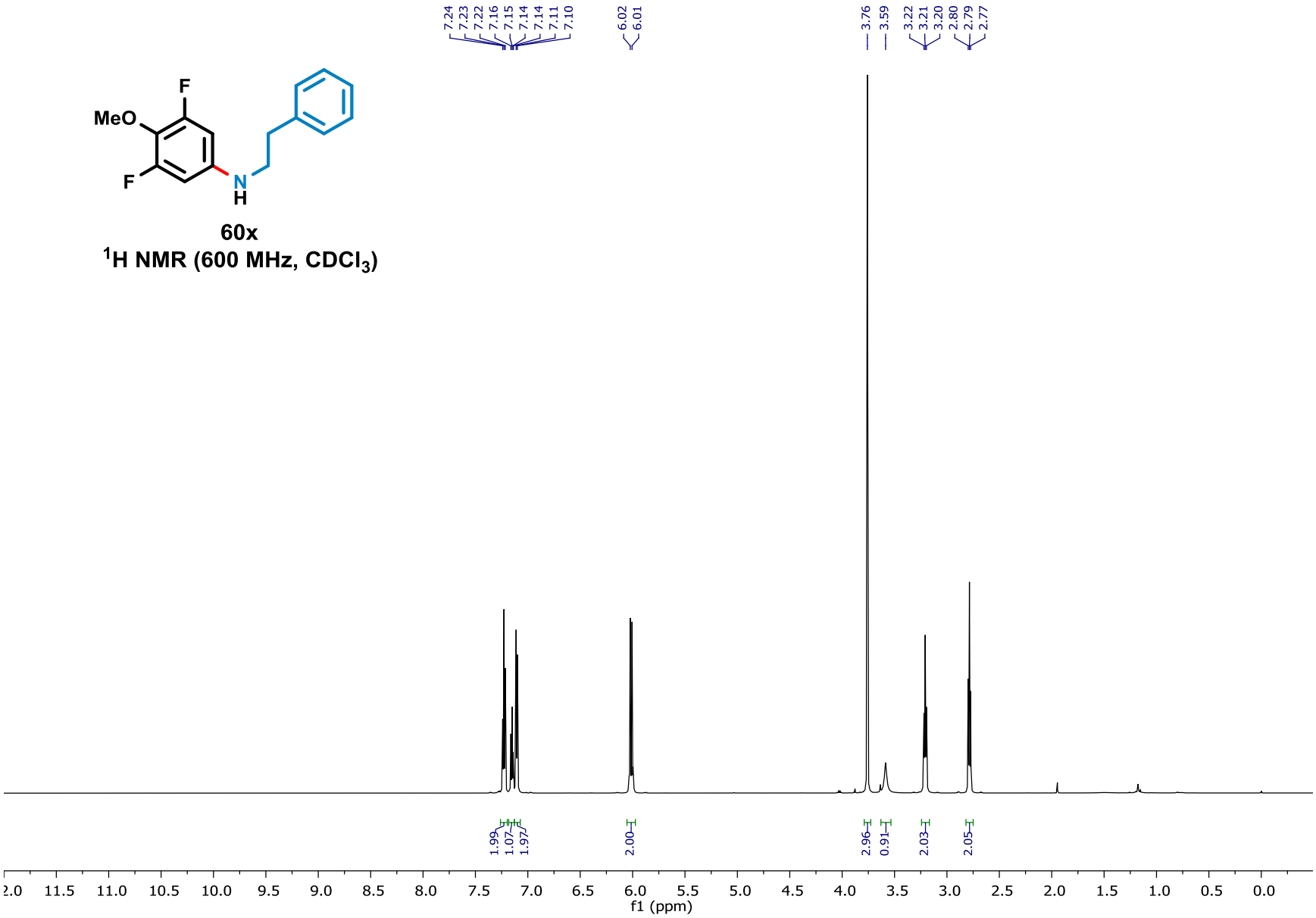
^{13}C NMR (151 MHz, $CDCl_3$)

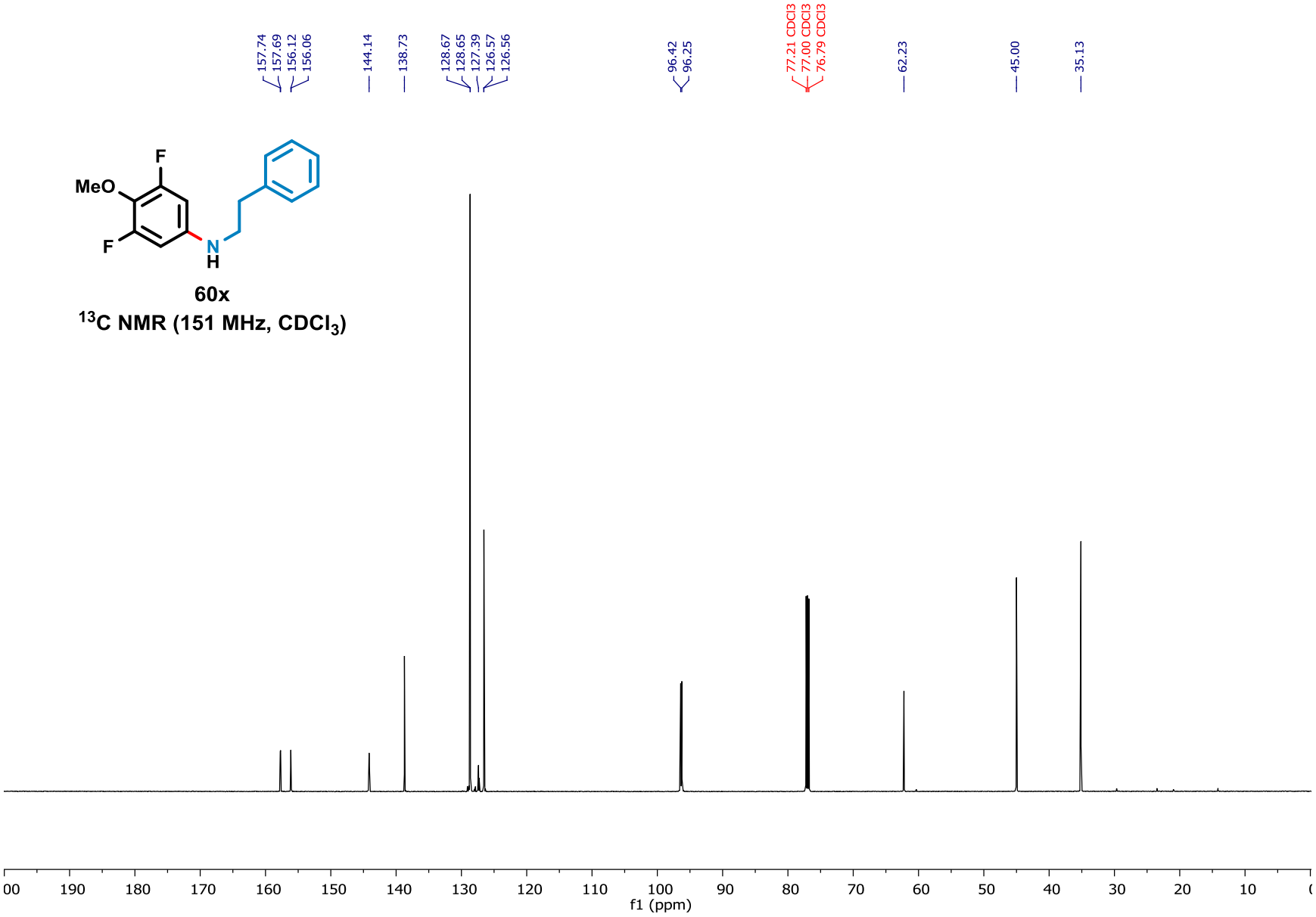


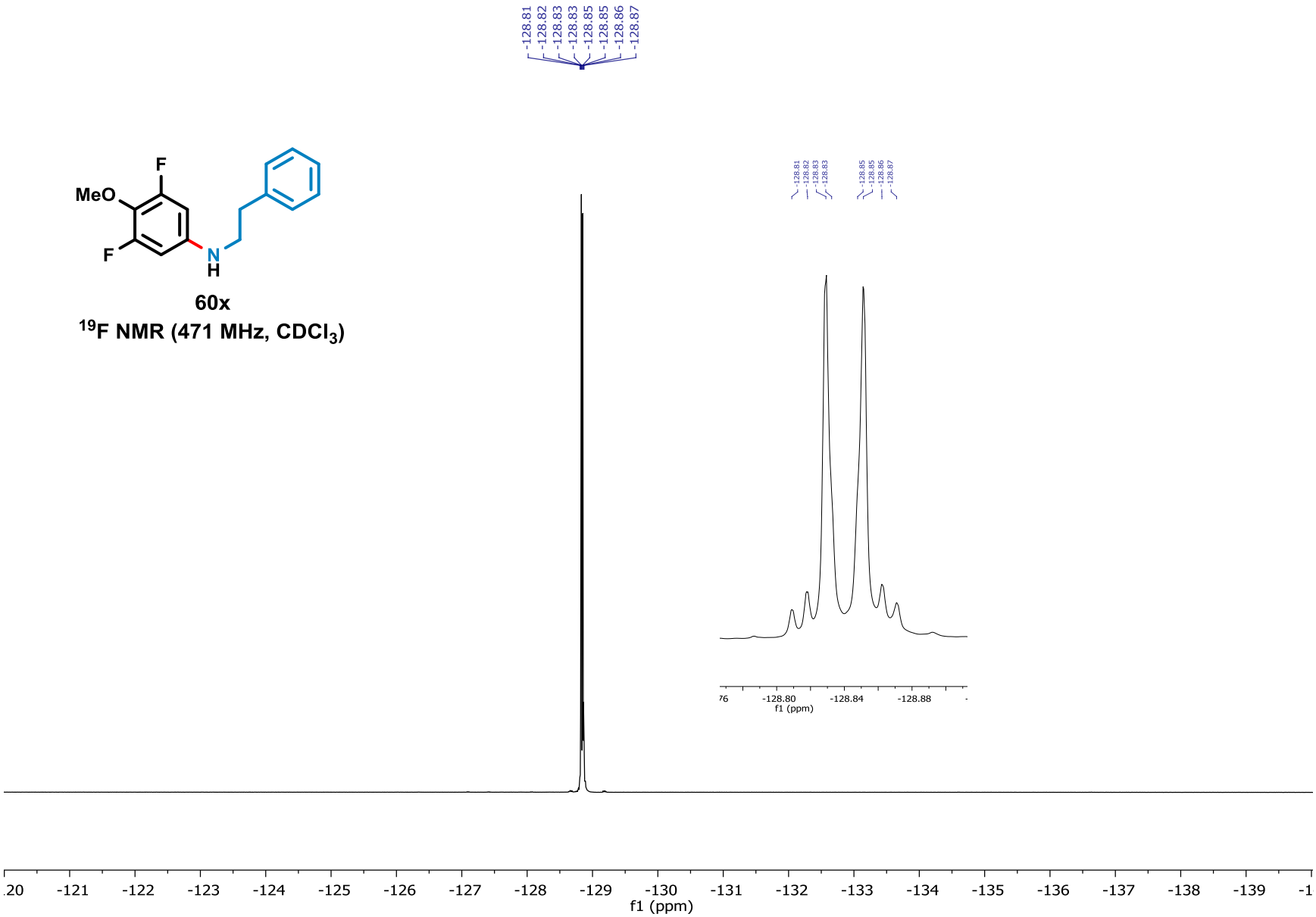
60w

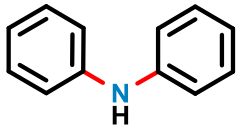
^{1}H NMR (600 MHz, $CDCl_3$)


147.95
139.27
129.23
128.74
128.56
126.37
117.44
117.39
112.98
112.91
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
44.98
35.48
N
H
60w
13C NMR (151 MHz, CDCl3)
f1 (ppm)


F
MeO
F
N
H
60x
1H NMR (600 MHz, CDCl3)
7.24
7.23
7.22
7.16
7.15
7.14
7.14
7.11
7.10
6.02
6.01
3.76
3.59
3.22
3.21
3.20
2.80
2.79
2.77
1.99
1.07
1.97
2.00
2.96
0.91
2.03
2.05
f1 (ppm)

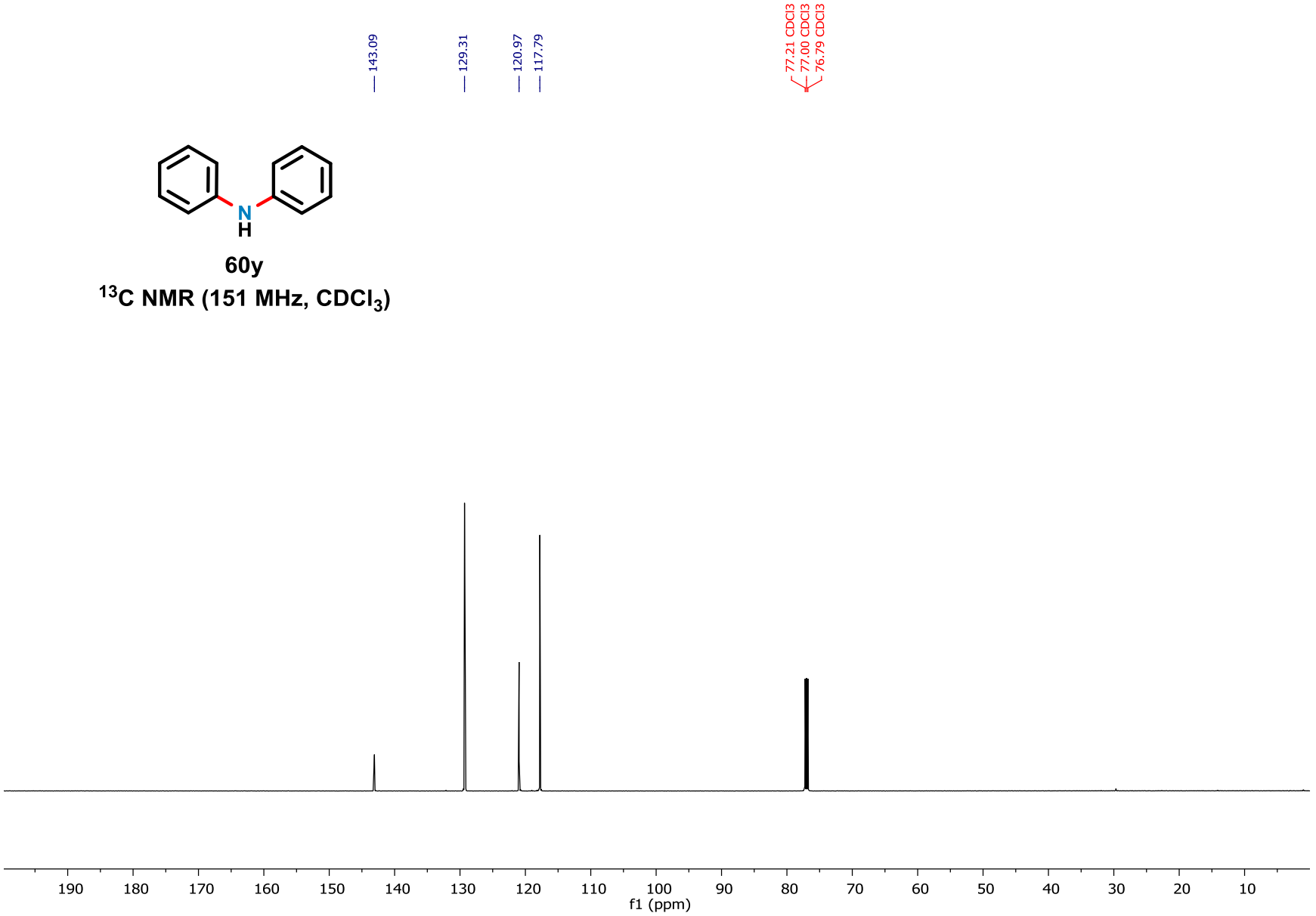

157.74
157.69
156.12
156.06
144.14
138.73
128.67
128.65
127.39
126.57
126.56
96.42
96.25
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
62.23
45.00
35.13
F
MeO
F
N
H
60x
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-128.81
-128.82
-128.83
-128.83
-128.85
-128.85
-128.86
-128.87
F
MeO
F
N
H
60x
19F NMR (471 MHz, CDCl3)
-128.80
-128.84
-128.88
f1 (ppm)
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
f1 (ppm)



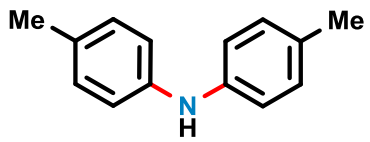
60y

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



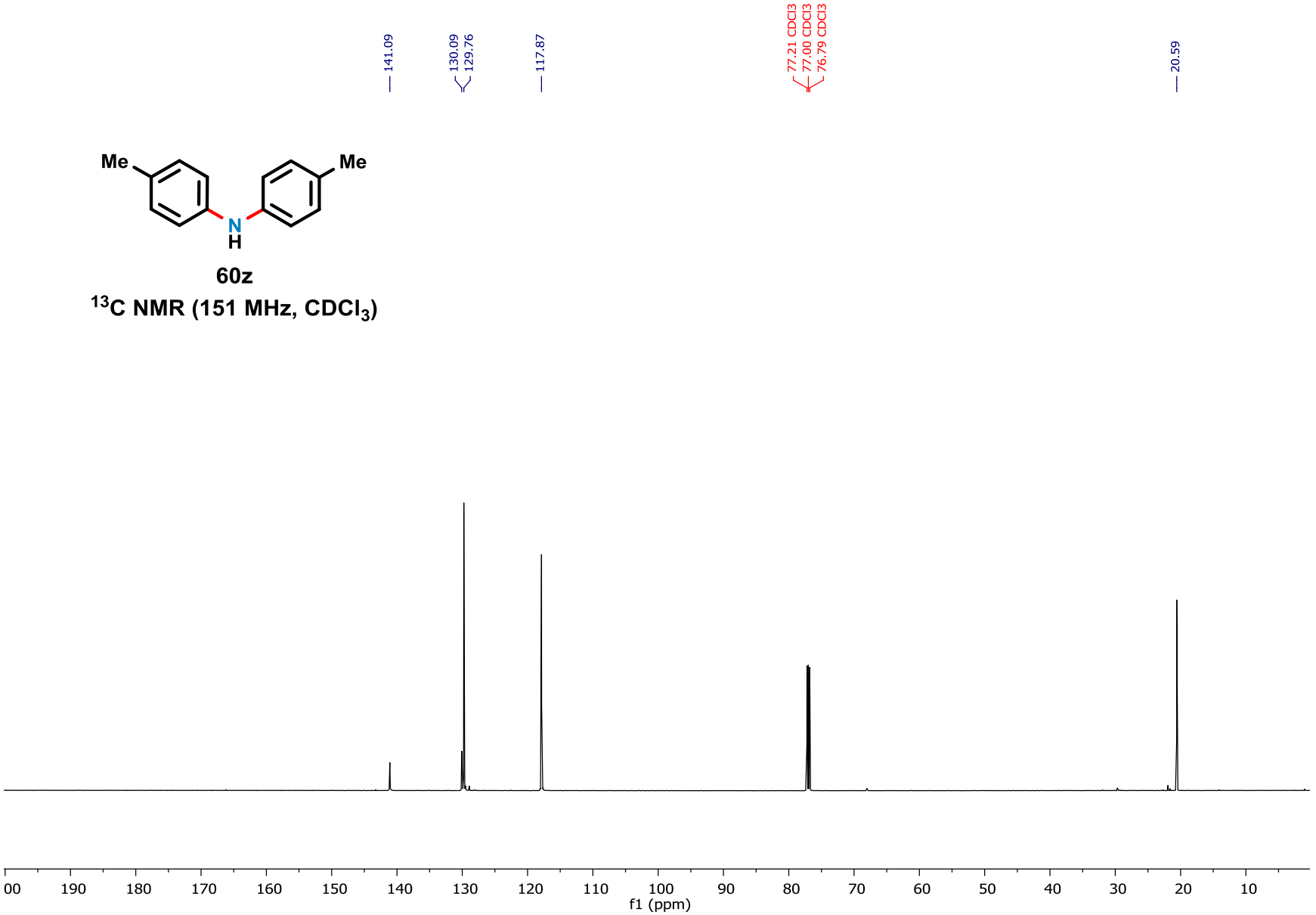
60y

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



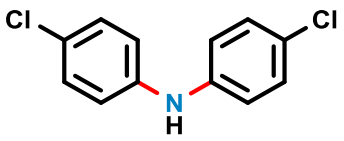
60z

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



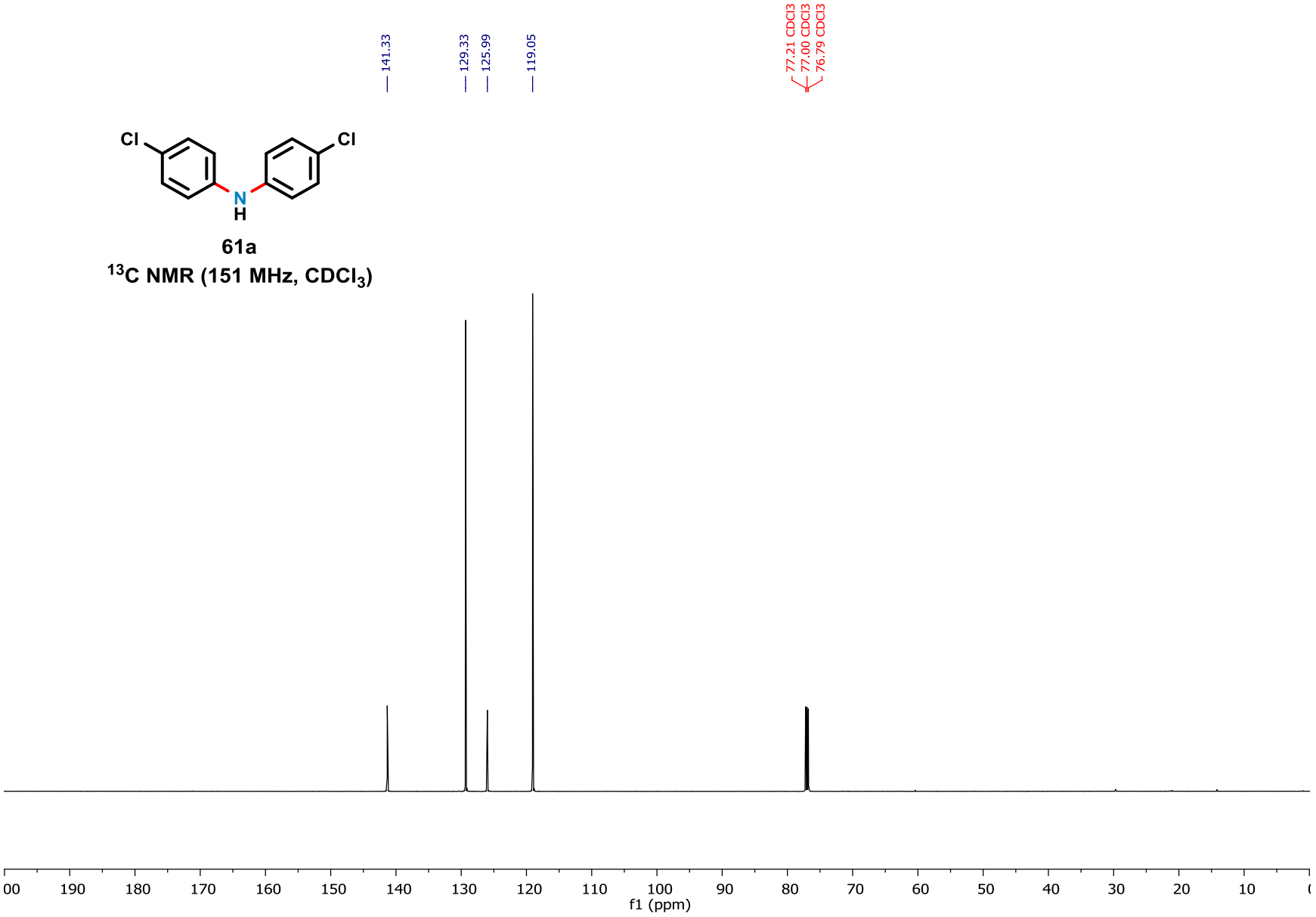
60z

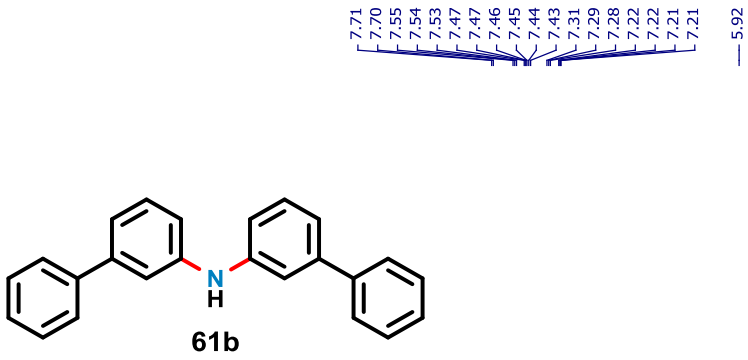
^{13}C NMR (151 MHz, $CDCl_3$)



61a

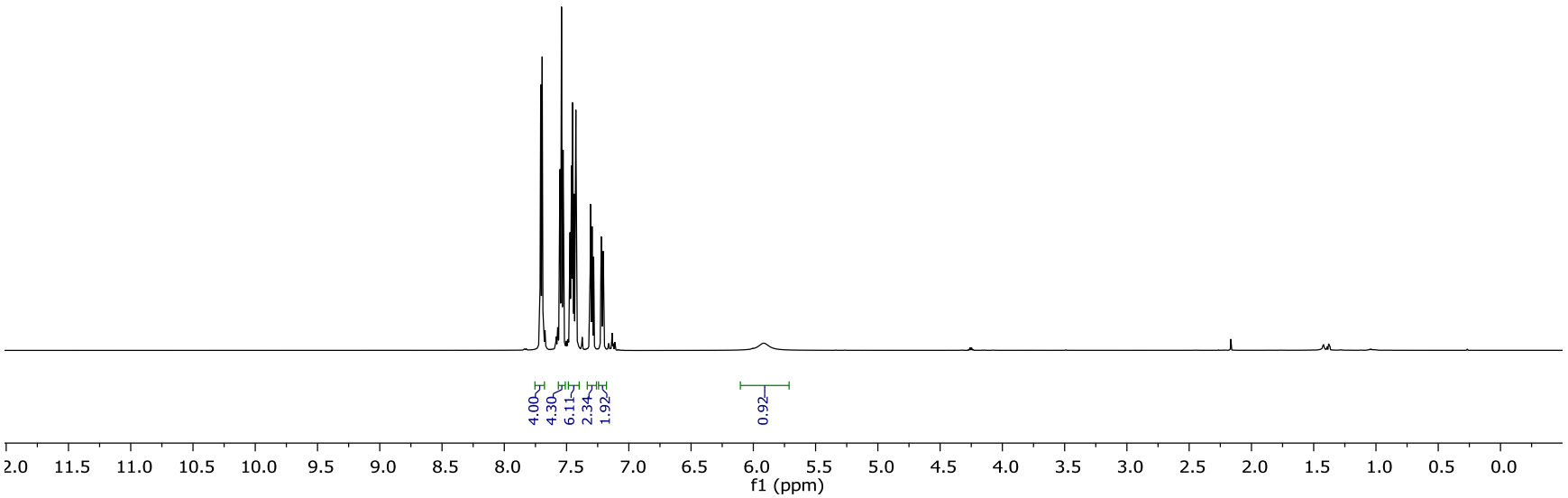
^{1}H NMR (600 MHz, $CDCl_3$)

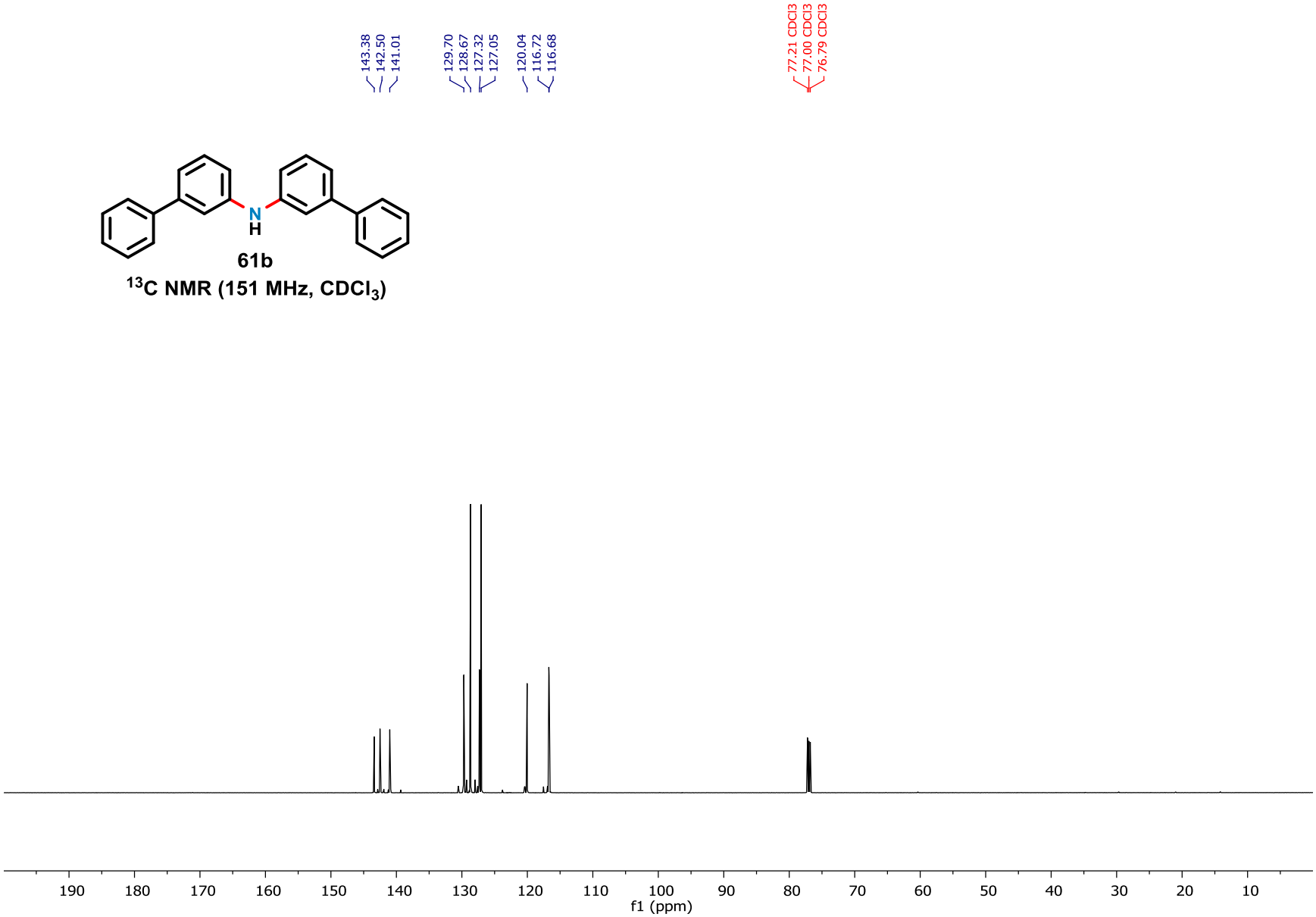

141.33
129.33
125.99
119.05
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
Cl
Cl
N
H
61a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

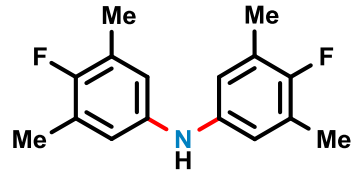


61b

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

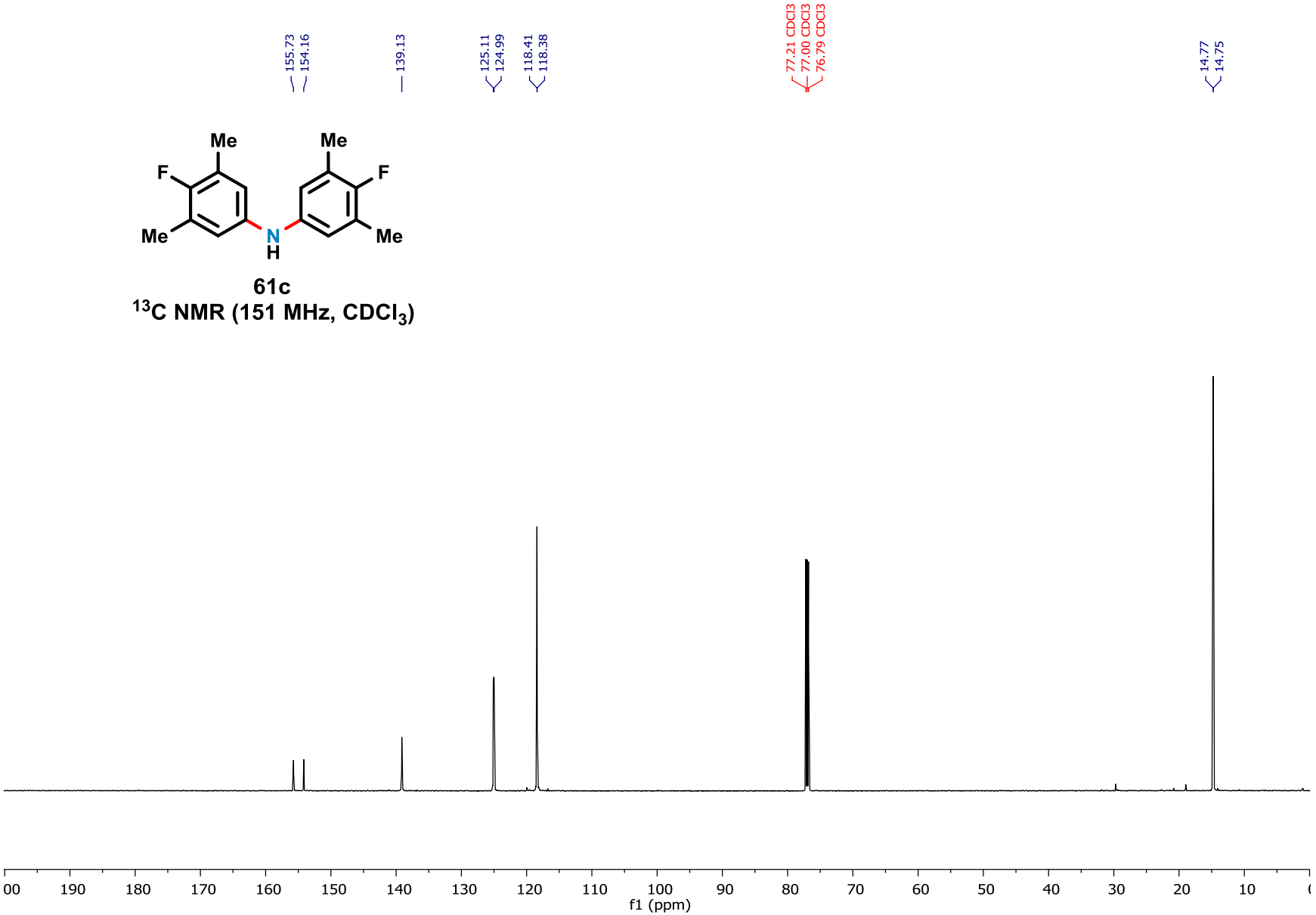


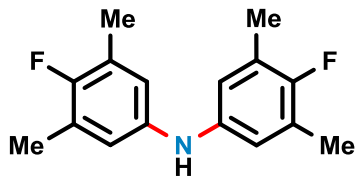

143.38
142.50
141.01
129.70
128.67
127.32
127.05
120.04
116.72
116.68
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
N
H
61b
13C NMR (151 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



61c

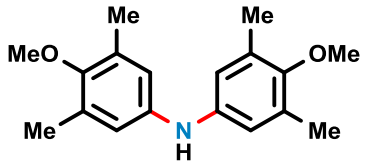
^{1}H NMR (600 MHz, $CDCl_3$)


155.73
154.16
139.13
125.11
124.99
118.41
118.38
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
14.77
14.75
Me
F
Me
N
H
Me
F
Me
61c
13C NMR (151 MHz, CDCl3)
f1 (ppm)



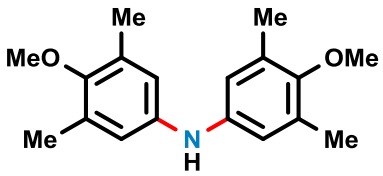
61c

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



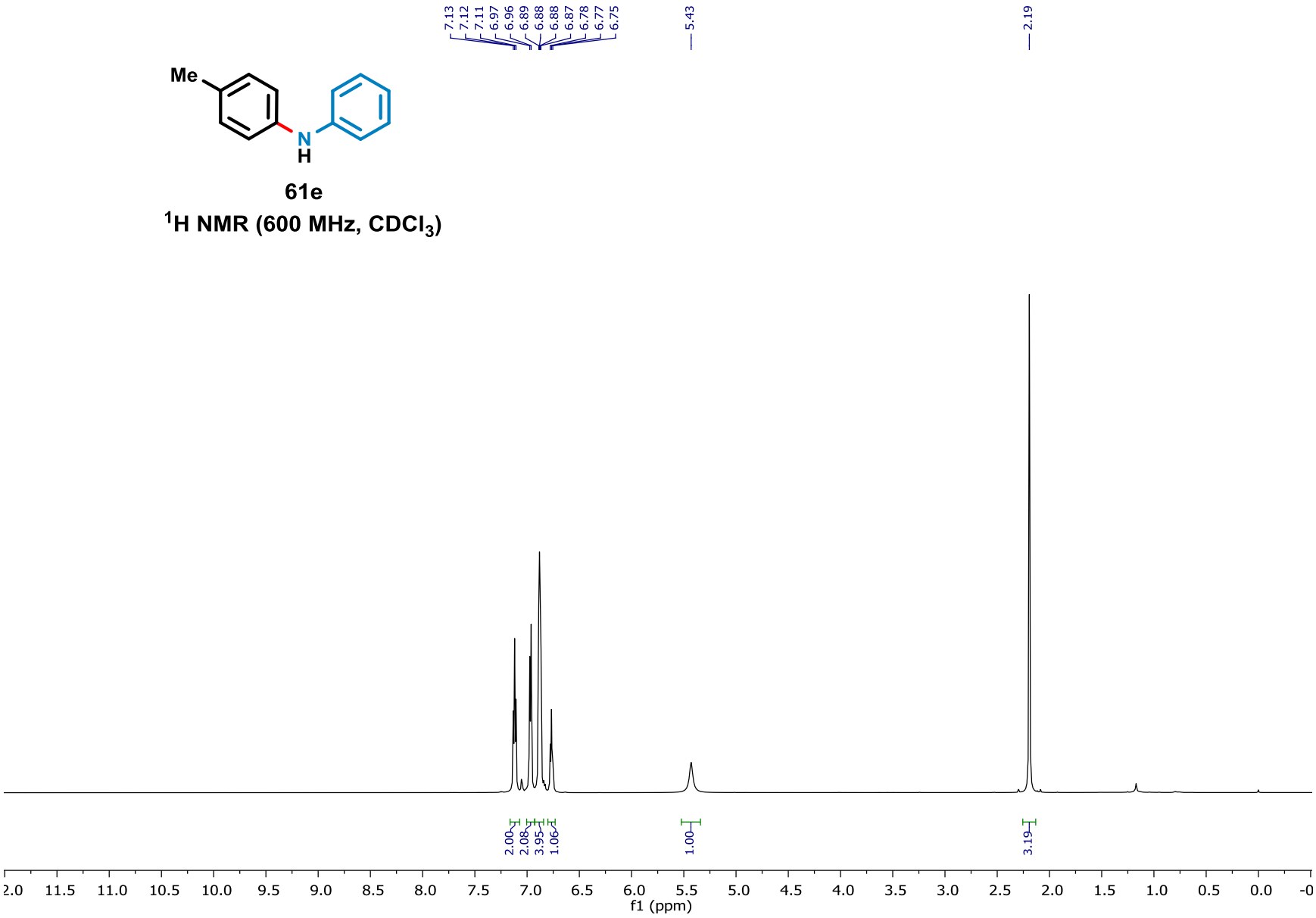
61d

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



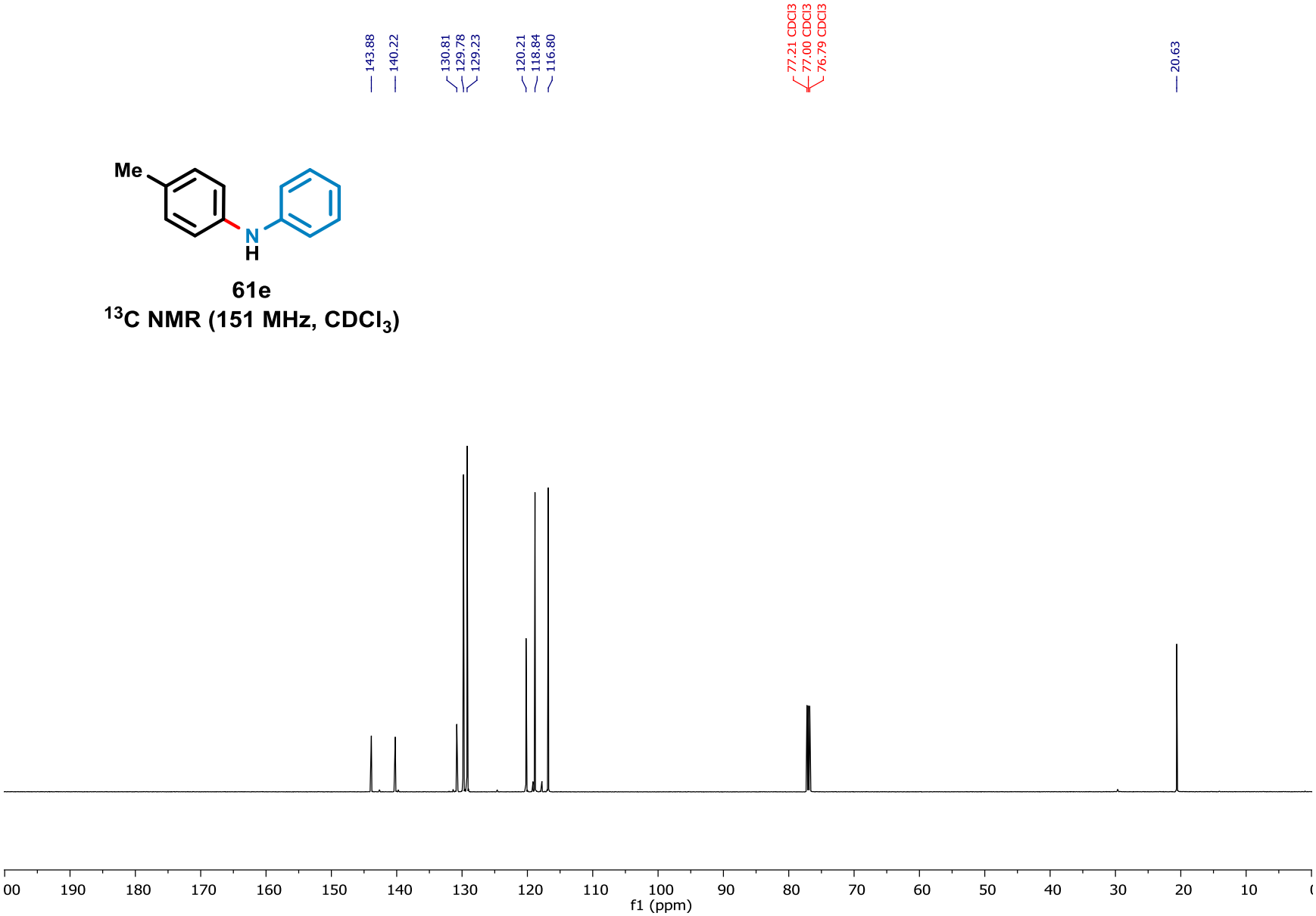
61d

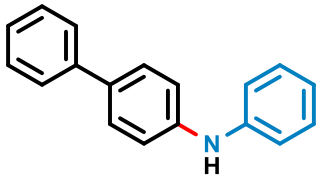
^{13}C NMR (151 MHz, $CDCl_3$)



61e

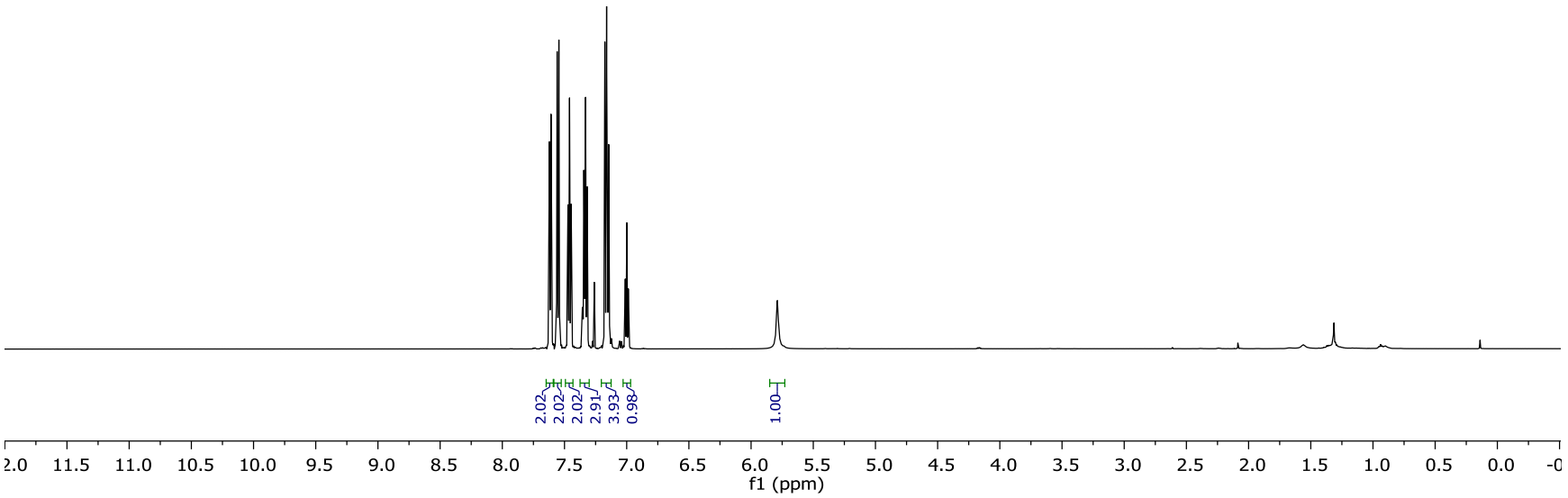
^{1}H NMR (600 MHz, $CDCl_3$)

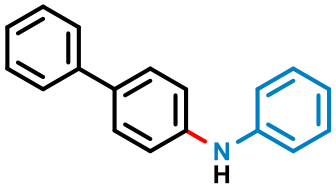

143.88
140.22
130.81
129.78
129.23
120.21
118.84
116.80
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
20.63
Me
N
H
61e
13C NMR (151 MHz, CDCl3)
f1 (ppm)



61f

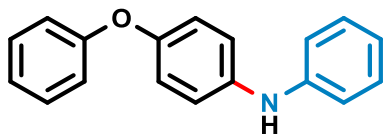
^{1}H NMR (600 MHz, $CDCl_3$)





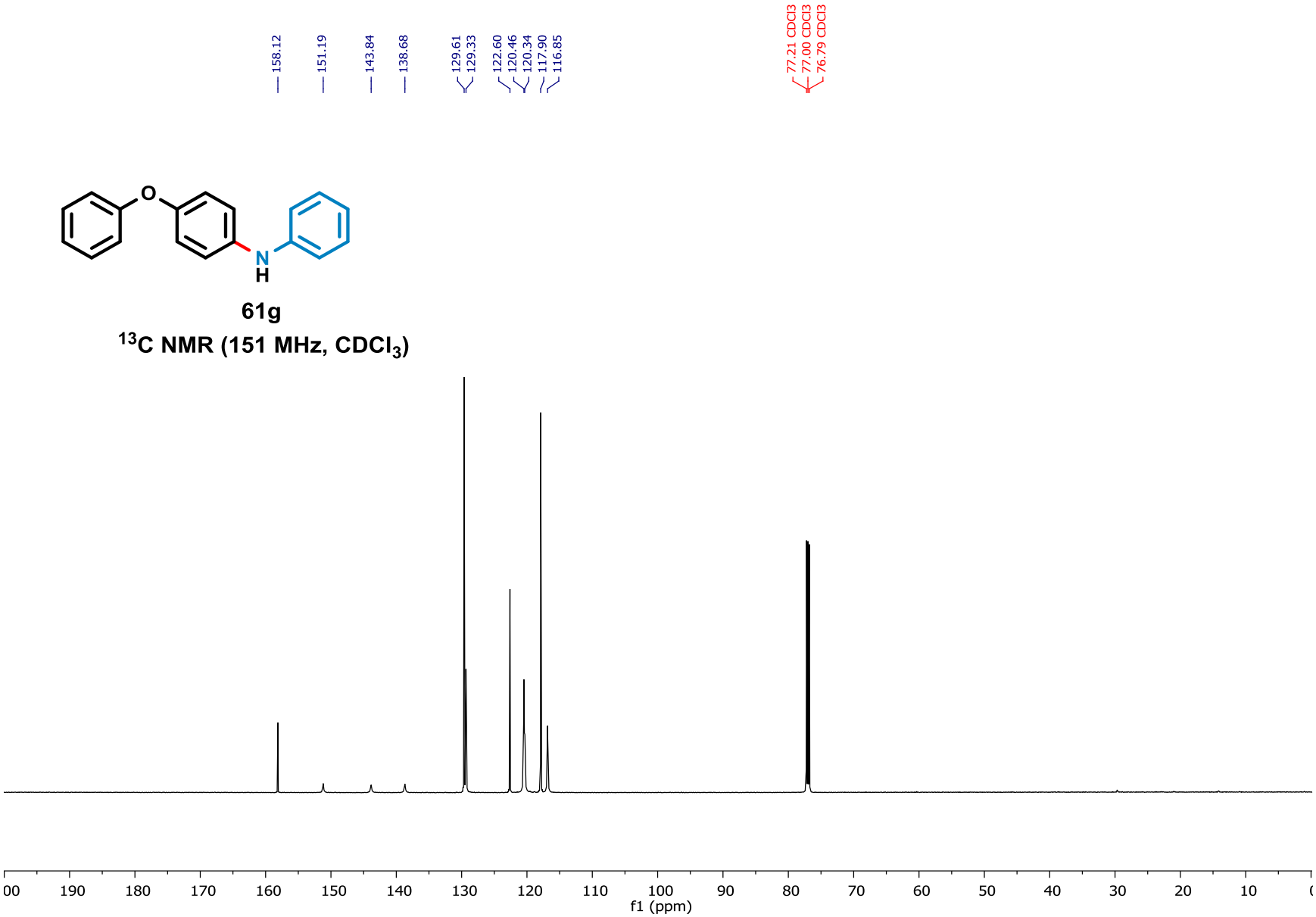
61f

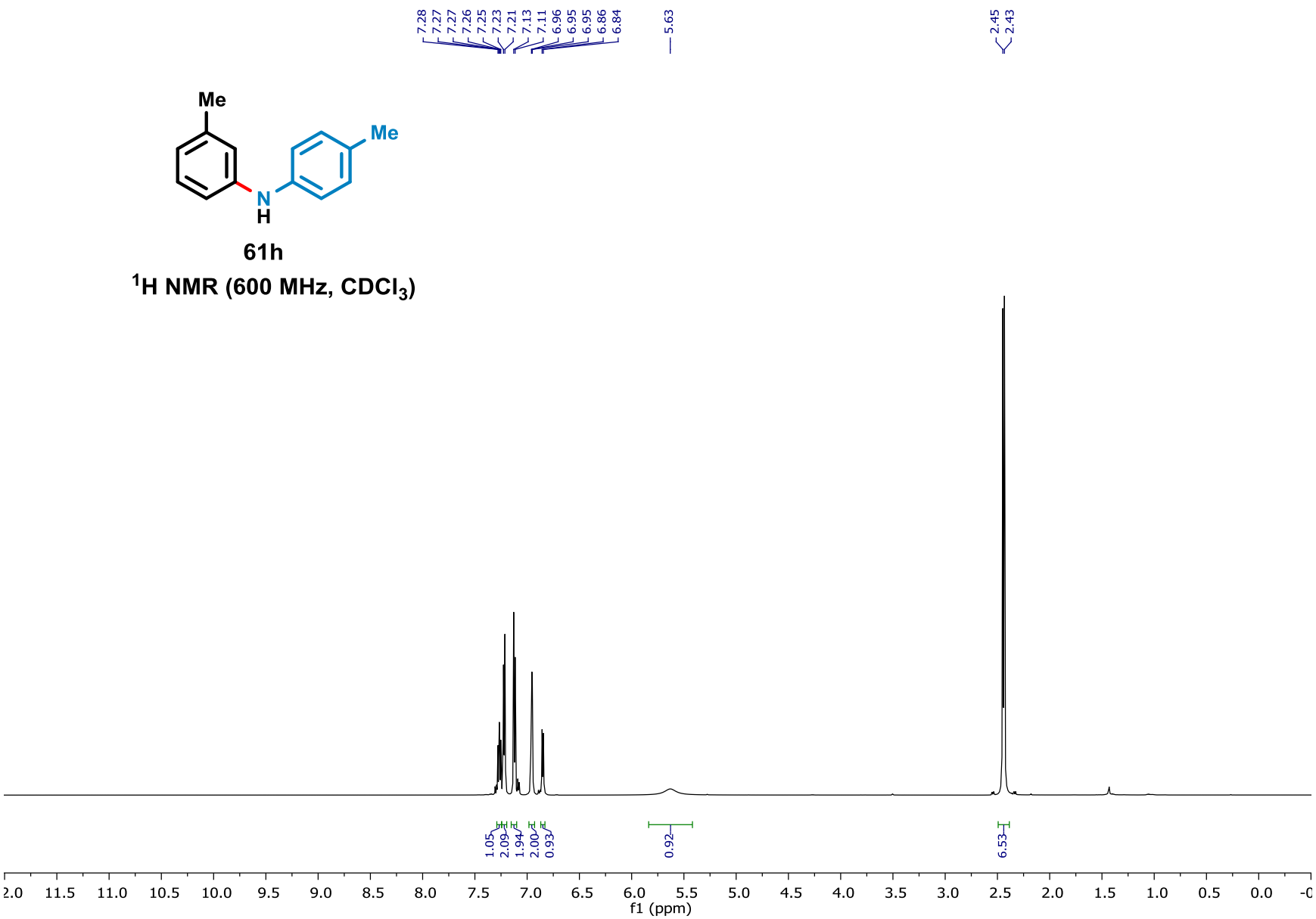
^{13}C NMR (151 MHz, $CDCl_3$)

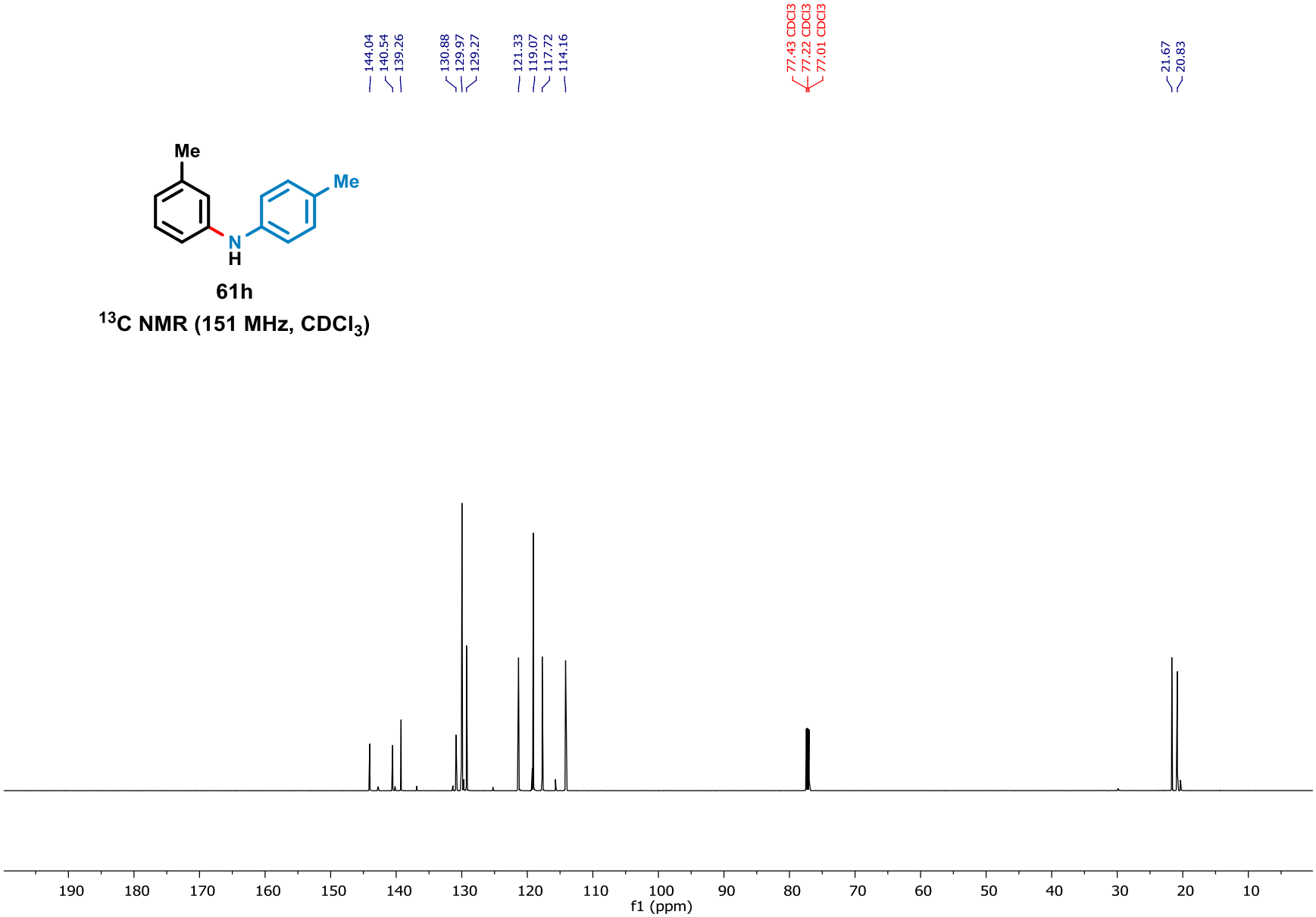


61g

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

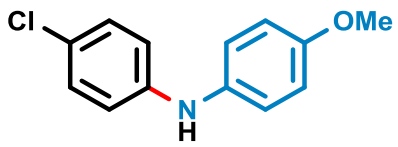

158.12
151.19
143.84
138.68
129.61
129.33
122.60
120.46
120.34
117.90
116.85
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
O
N
H
61g
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.28
7.27
7.27
7.26
7.25
7.23
7.21
7.13
7.11
6.96
6.95
6.95
6.86
6.84
5.63
2.45
2.43
Me
Me
N
H
61h
1H NMR (600 MHz, CDCl3)
1.05
2.09
1.94
2.00
0.93
0.92
6.53
f1 (ppm)



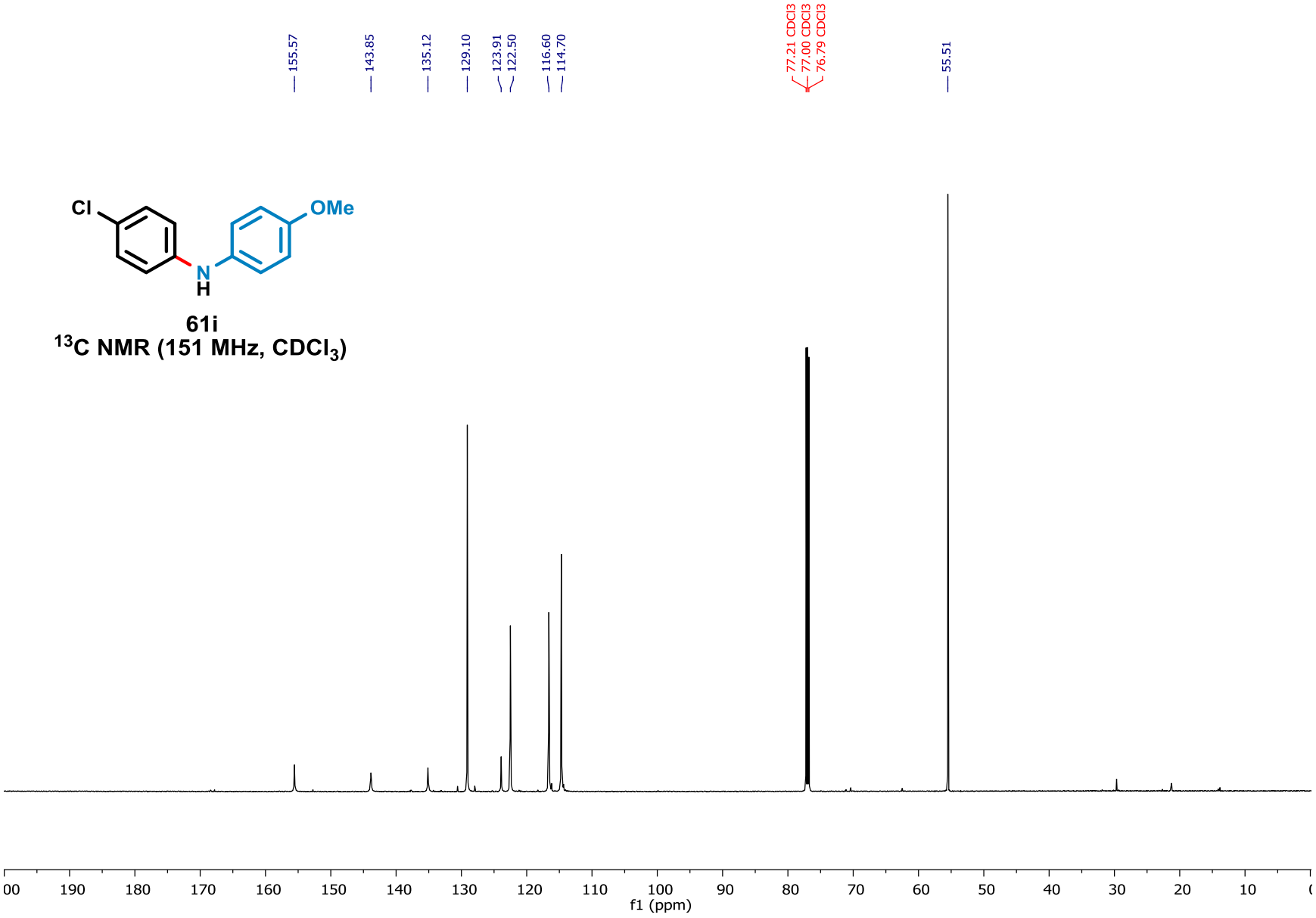
61h

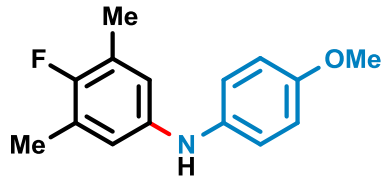
^{13}C NMR (151 MHz, $CDCl_3$)



61i

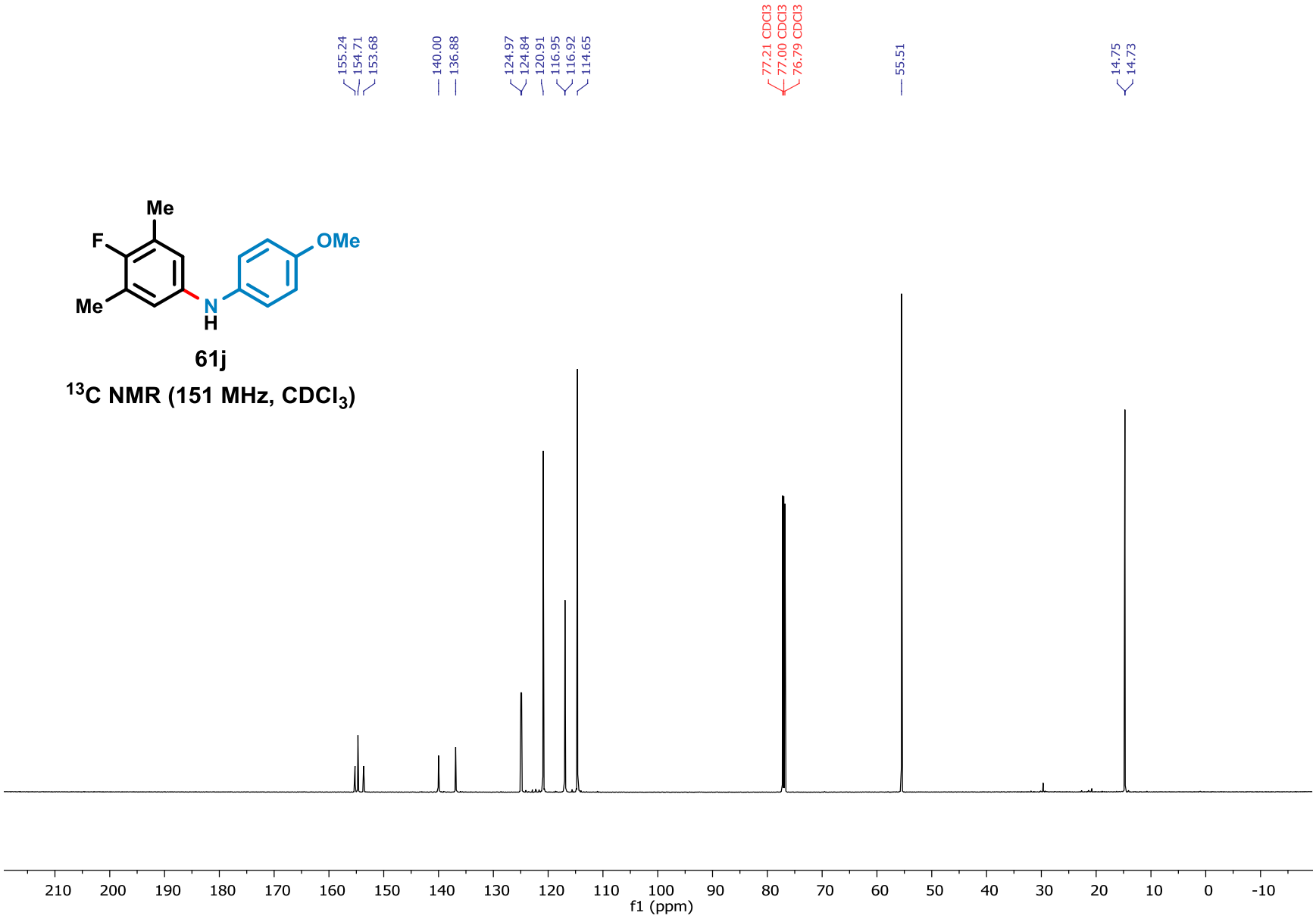
^{1}H NMR (600 MHz, $CDCl_3$)

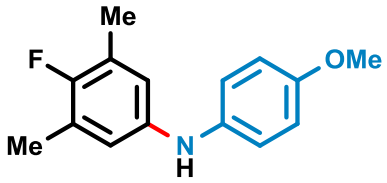

155.57
143.85
135.12
129.10
123.91
122.50
116.60
114.70
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
55.51
Cl
OMe
N
H
61i
13C NMR (151 MHz, CDCl3)
f1 (ppm)



61j

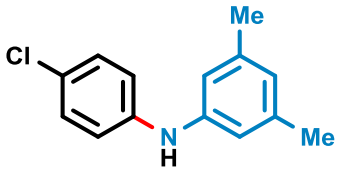
^{1}H NMR (600 MHz, $CDCl_3$)


155.24
154.71
153.68
140.00
136.88
124.97
124.84
120.91
116.95
116.92
114.65
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
55.51
14.75
14.73
Me
F
Me
N
H
OMe
61j
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



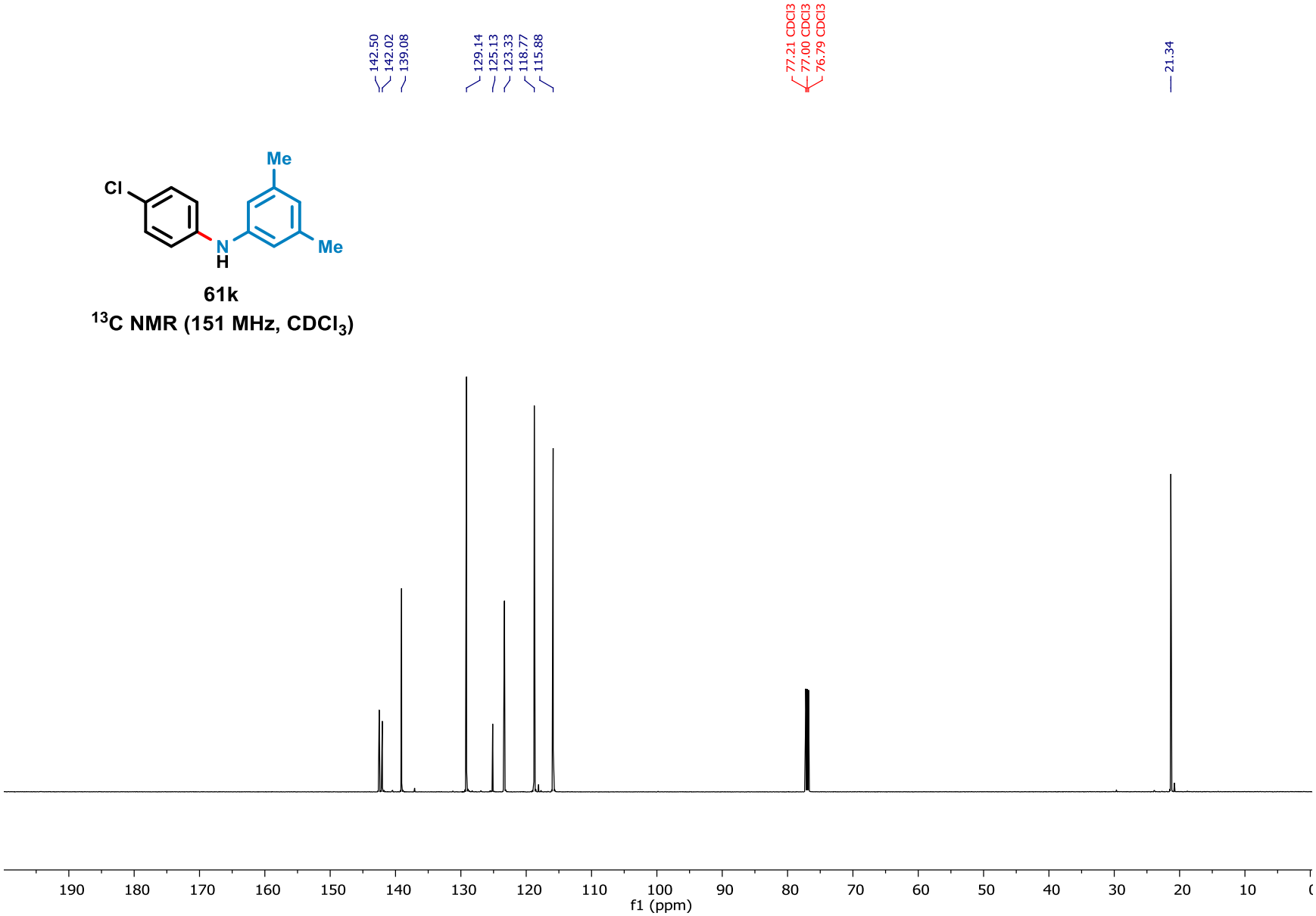
61j

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



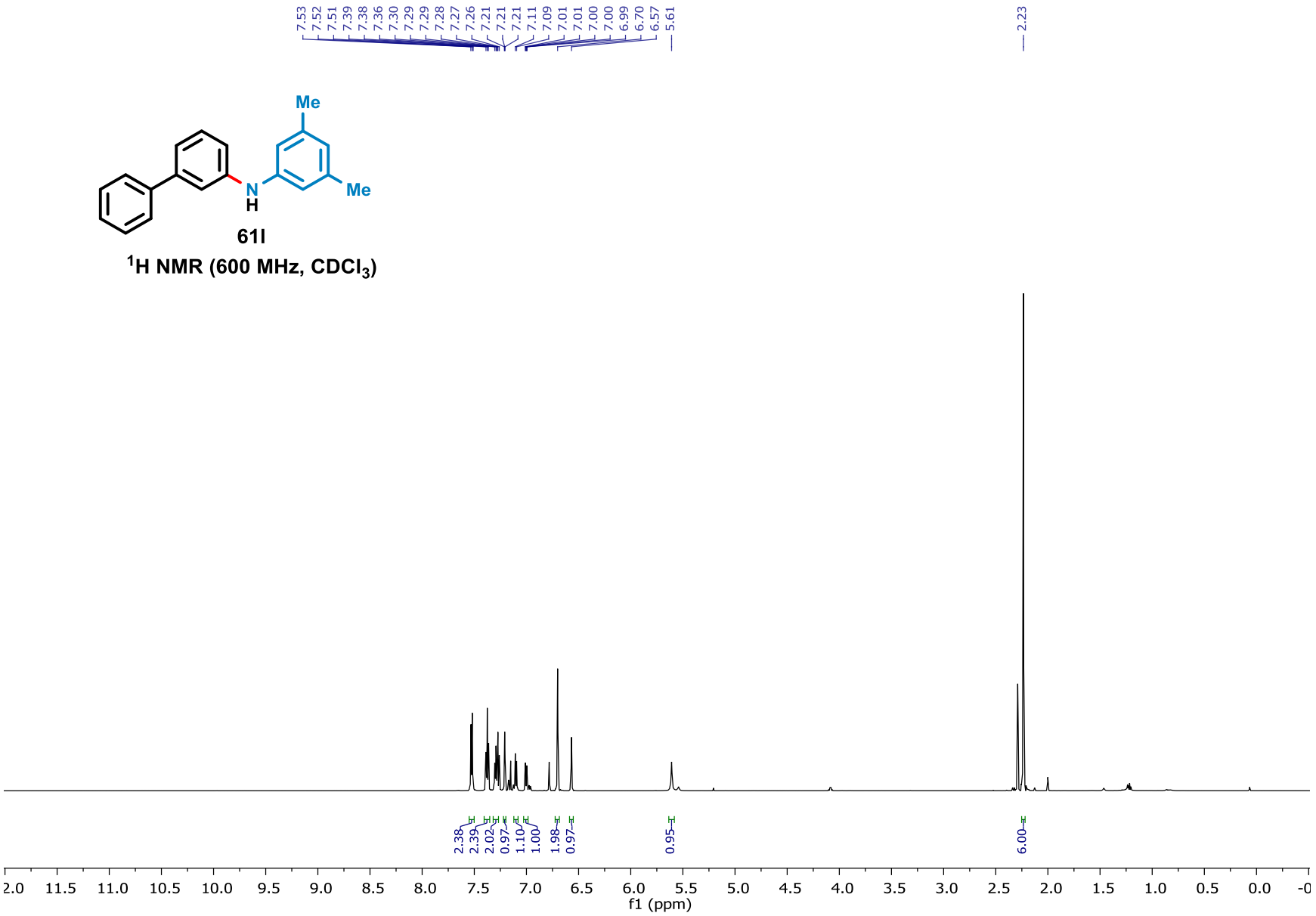
61k

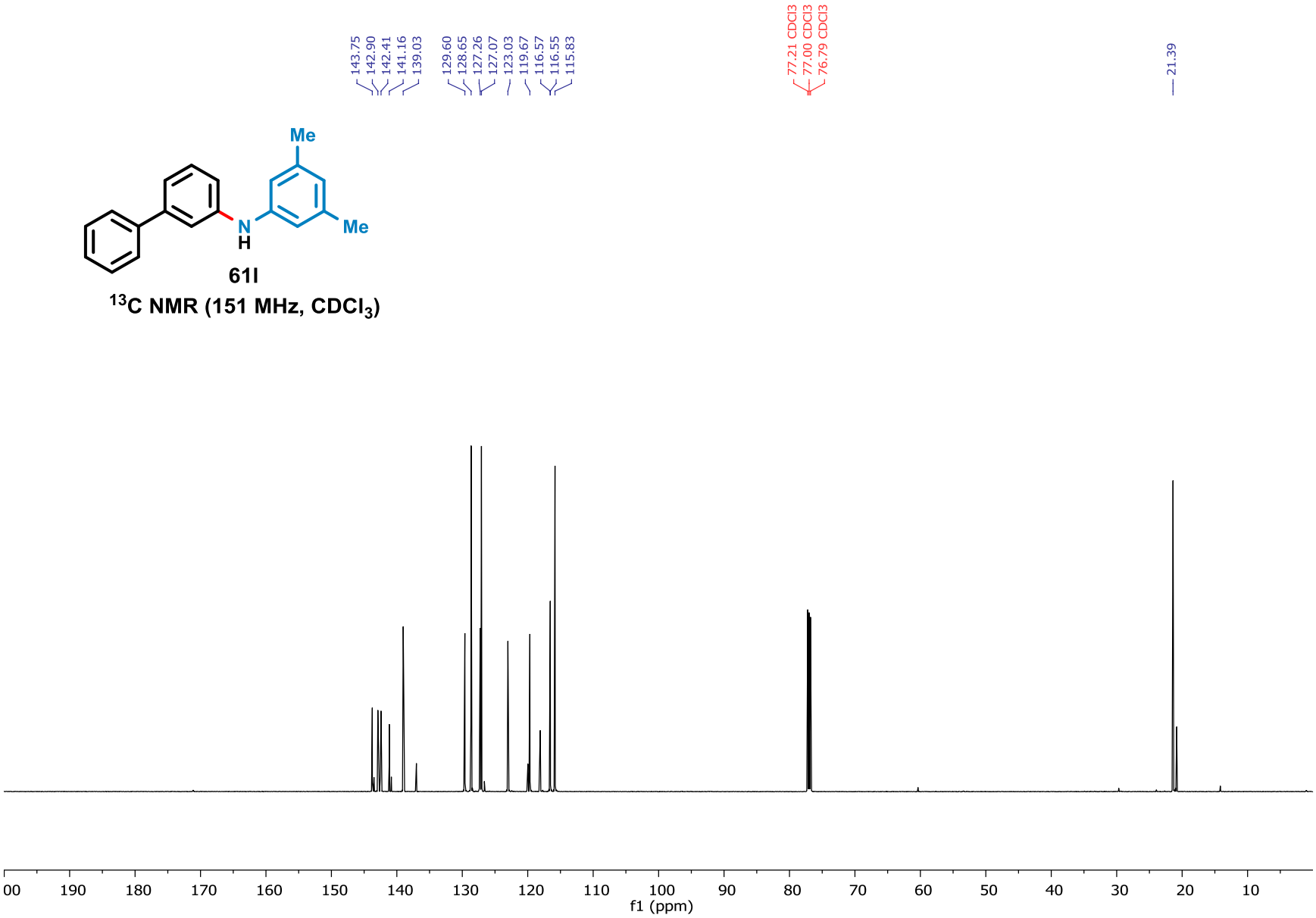
^{1}H NMR (600 MHz, $CDCl_3$)



61k

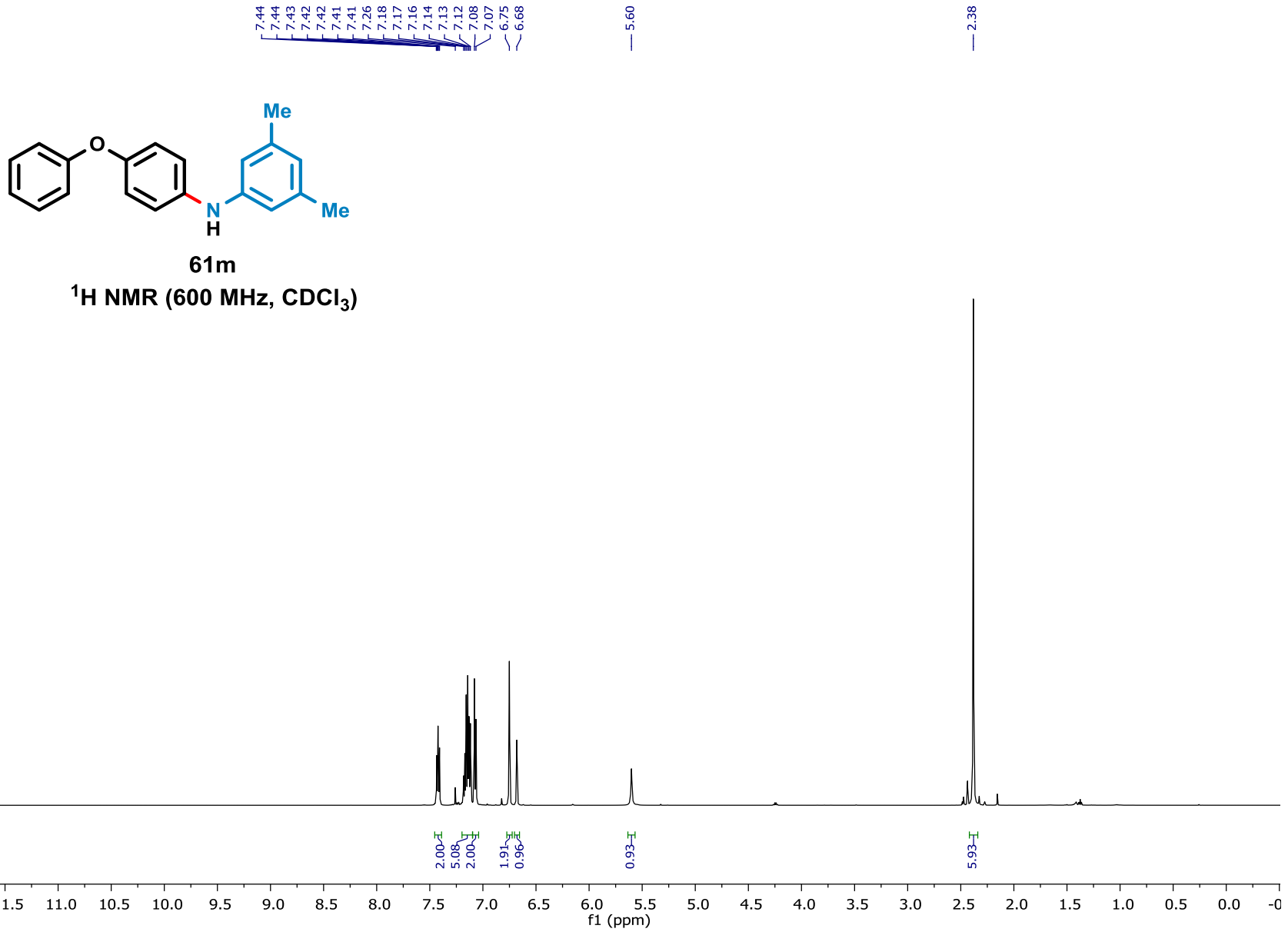
^{13}C NMR (151 MHz, $CDCl_3$)


7.53
7.52
7.51
7.39
7.38
7.36
7.30
7.29
7.29
7.28
7.27
7.26
7.21
7.21
7.21
7.11
7.09
7.01
7.01
7.00
7.00
6.99
6.70
6.57
5.61
2.23
Me
Me
N
H
61l
1H NMR (600 MHz, CDCl3)
2.38
2.39
2.02
0.97
1.10
1.00
1.98
0.97
0.95
6.00
f1 (ppm)



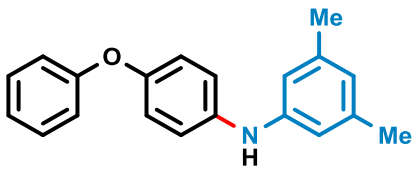
61l

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



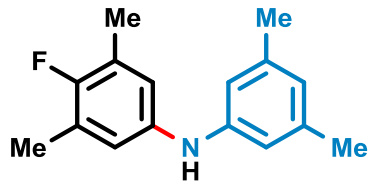
61m

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



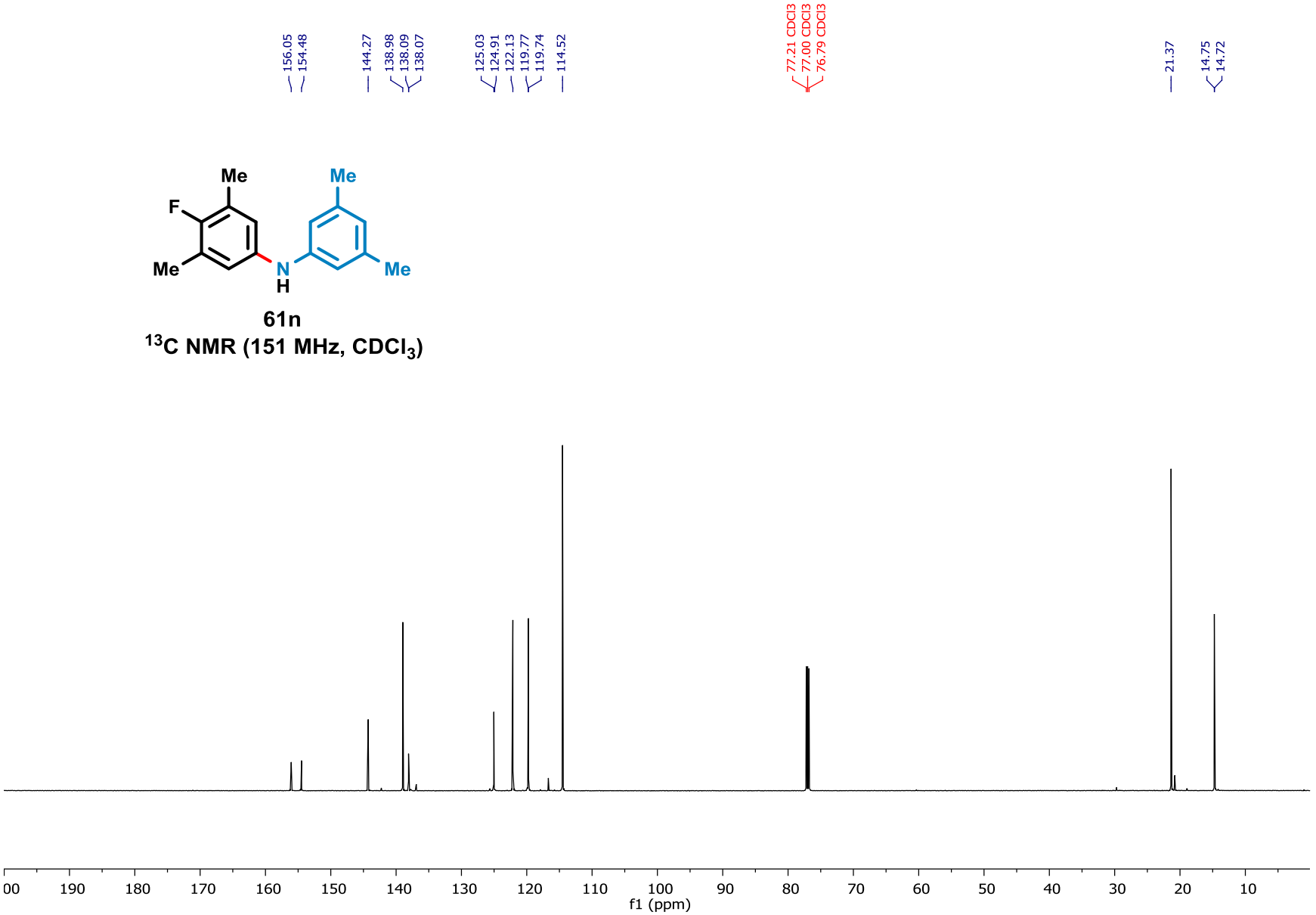
61m

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



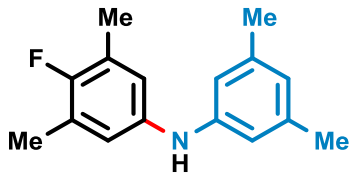
61n

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



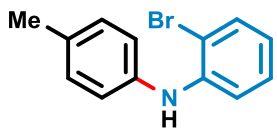
61n

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



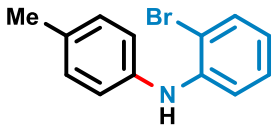
61n

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



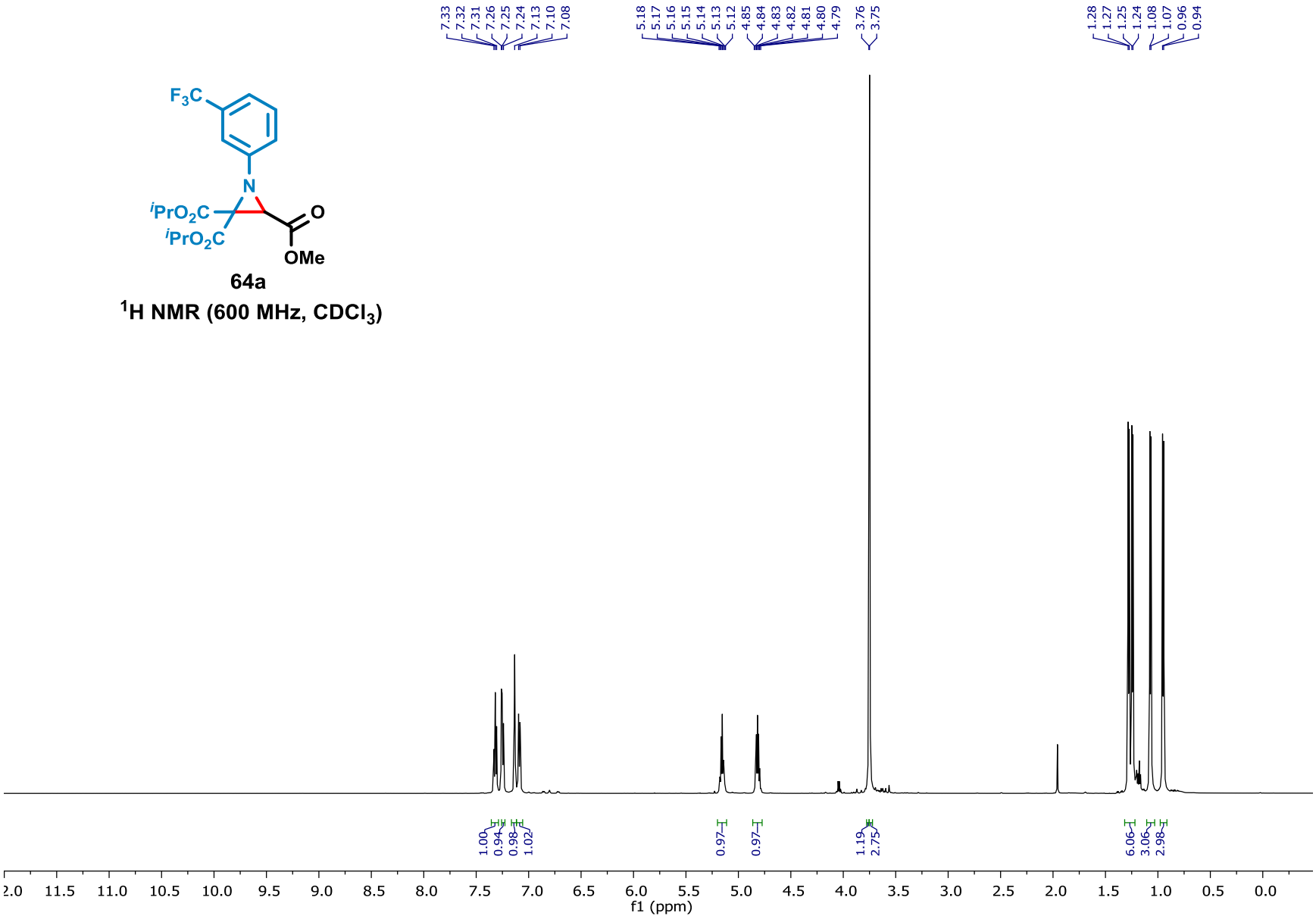
61o

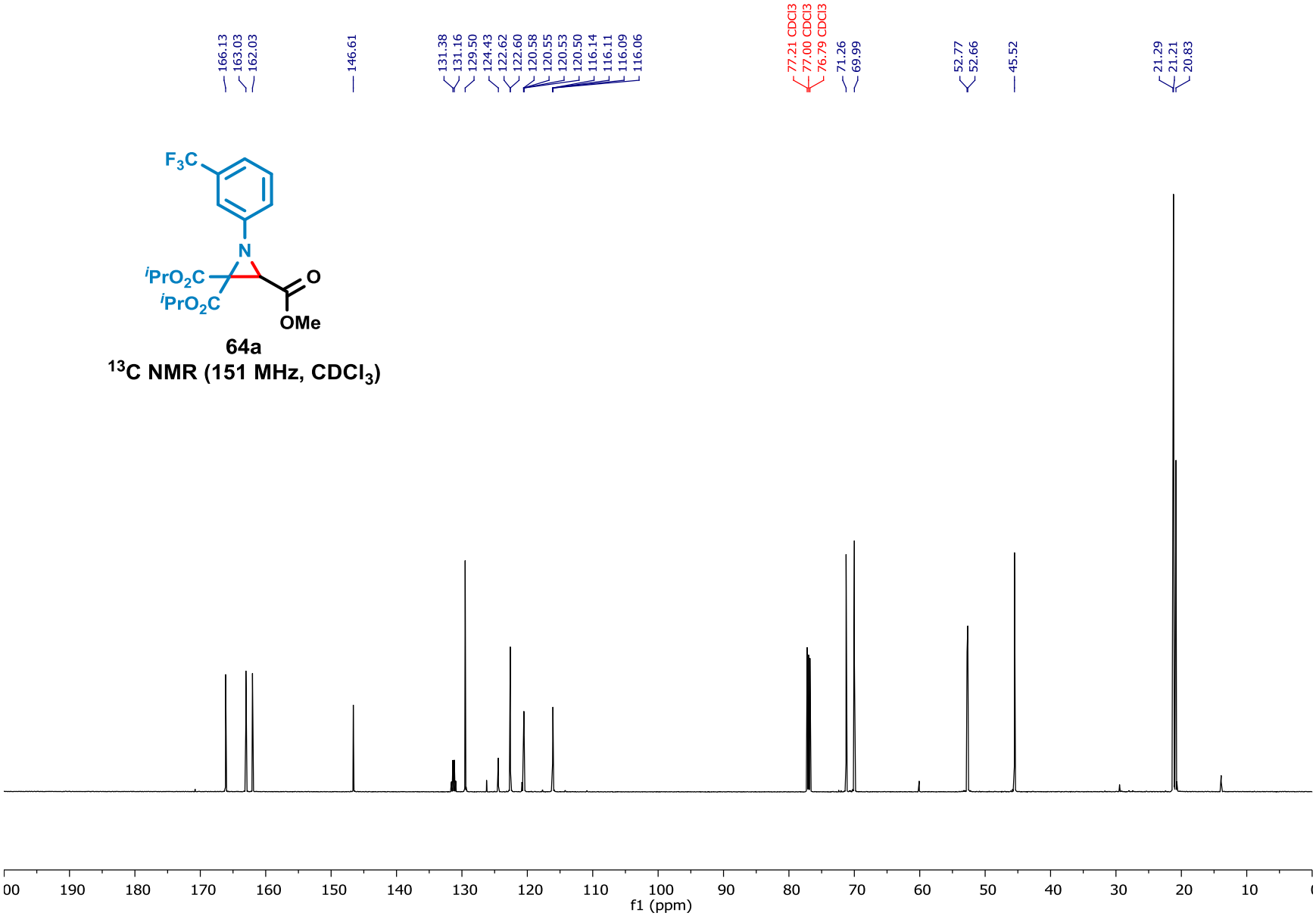
^{1}H NMR (600 MHz, $CDCl_3$)

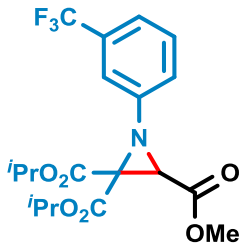


61o

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

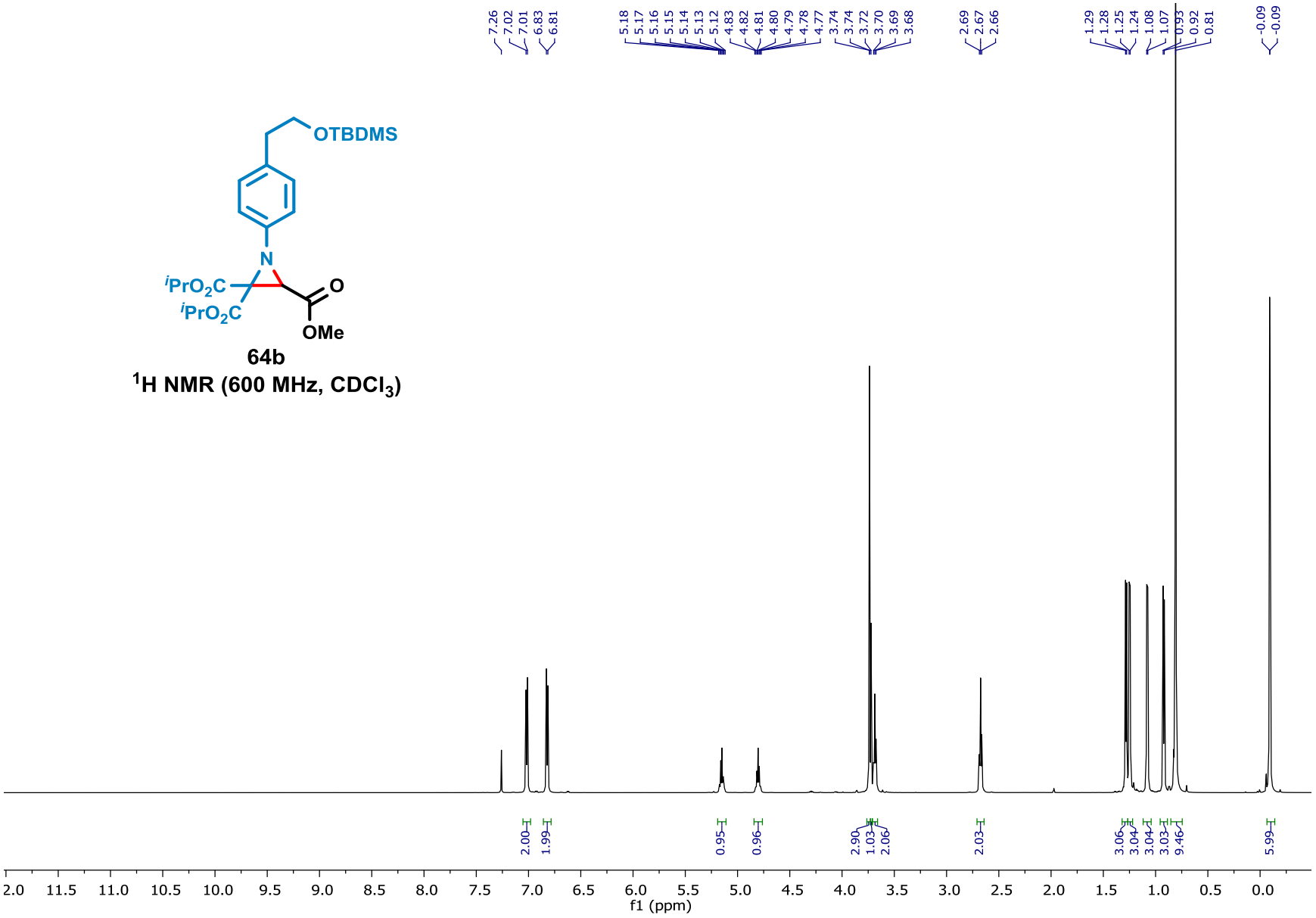

F3C
N
iPrO2C
iPrO2C
O
OMe
64a
1H NMR (600 MHz, CDCl3)
7.33
7.32
7.31
7.26
7.25
7.24
7.13
7.10
7.08
5.18
5.17
5.16
5.15
5.14
5.13
5.12
4.85
4.84
4.83
4.82
4.81
4.80
4.79
3.76
3.75
1.28
1.27
1.25
1.24
1.08
1.07
0.96
0.94
1.00
0.94
0.98
1.02
0.97
0.97
1.19
2.75
6.06
3.06
2.98
f1 (ppm)

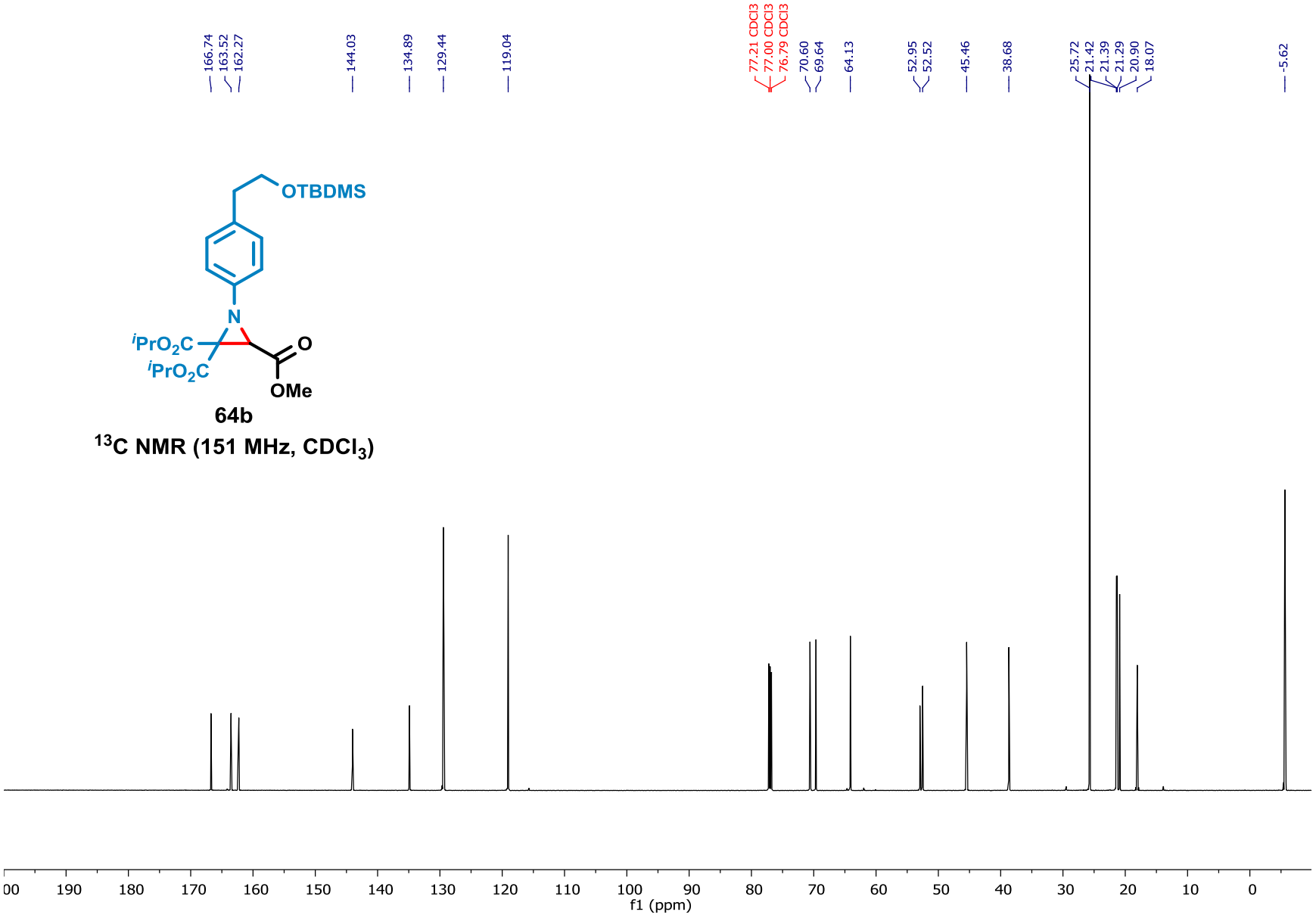

166.13
163.03
162.03
146.61
131.38
131.16
129.50
124.43
122.62
122.60
120.58
120.55
120.53
120.50
116.14
116.11
116.09
116.06
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
71.26
69.99
52.77
52.66
45.52
21.29
21.21
20.83
F3C
N
iPrO2C
iPrO2C
O
OMe
64a
13C NMR (151 MHz, CDCl3)
f1 (ppm)



64a

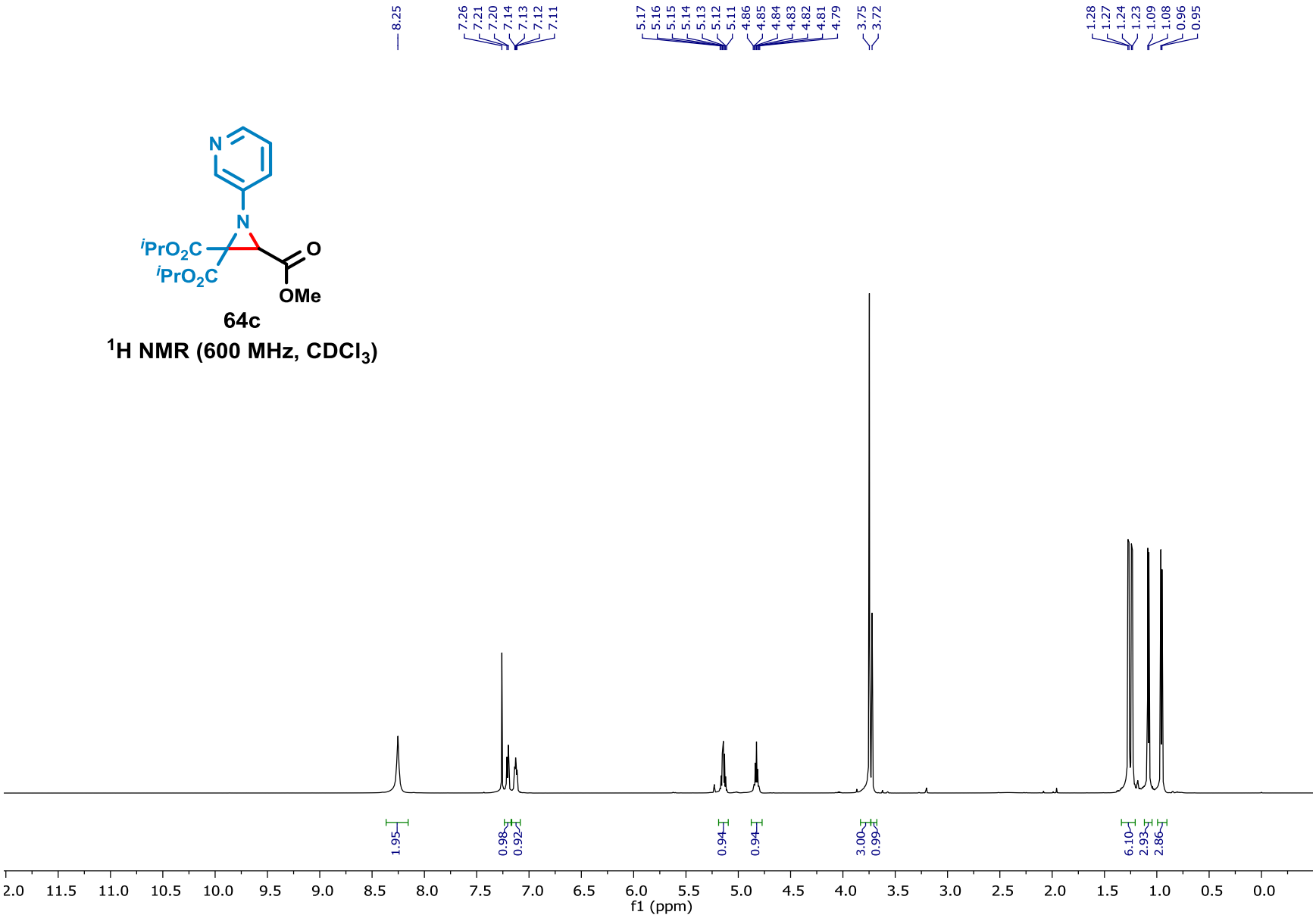
^{19}F NMR (471 MHz, $CDCl_3$)

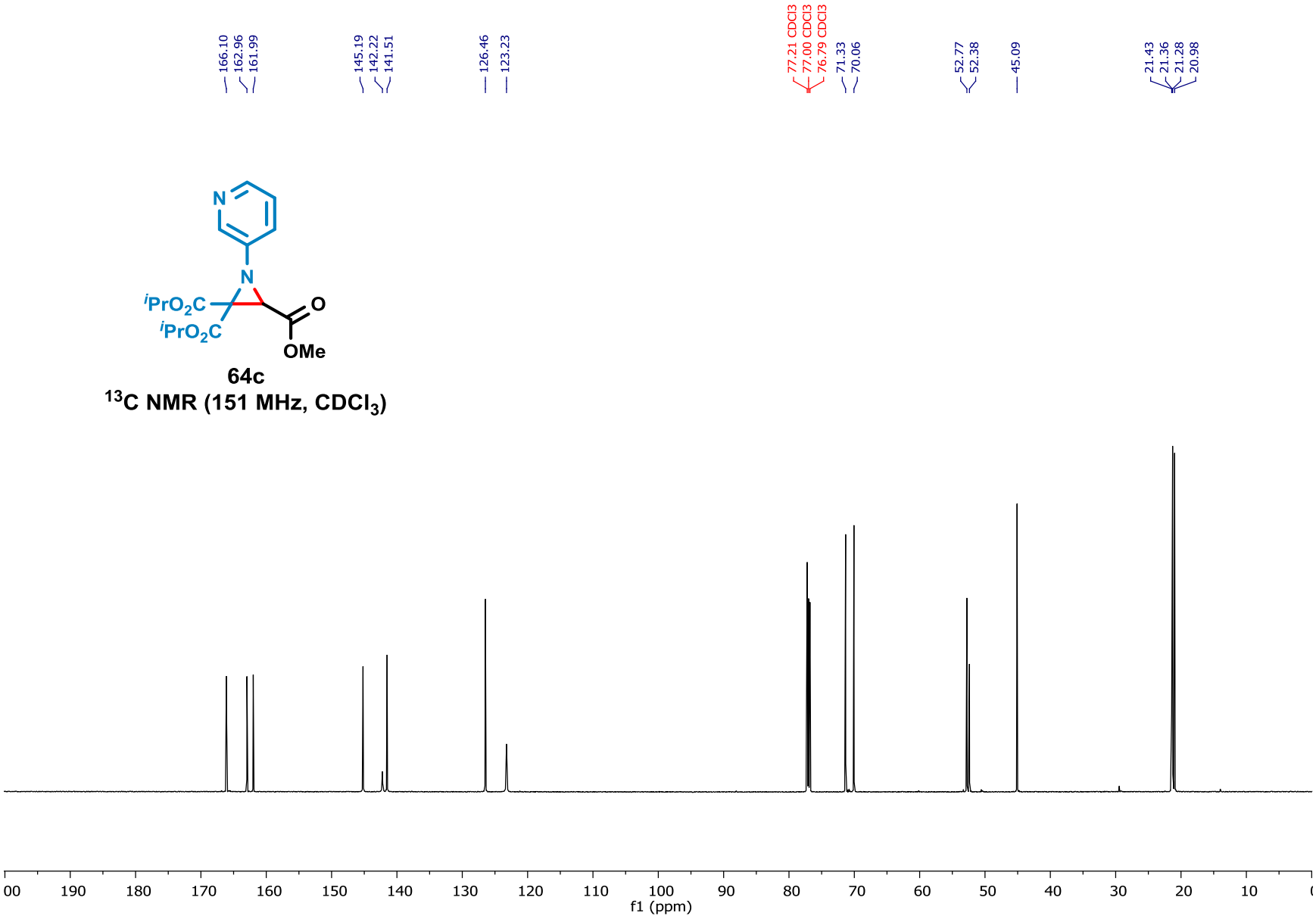

OTBDMS
N
$^{i}PrO_2C$
$^{i}PrO_2C$
O
OMe
64b
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)



64b

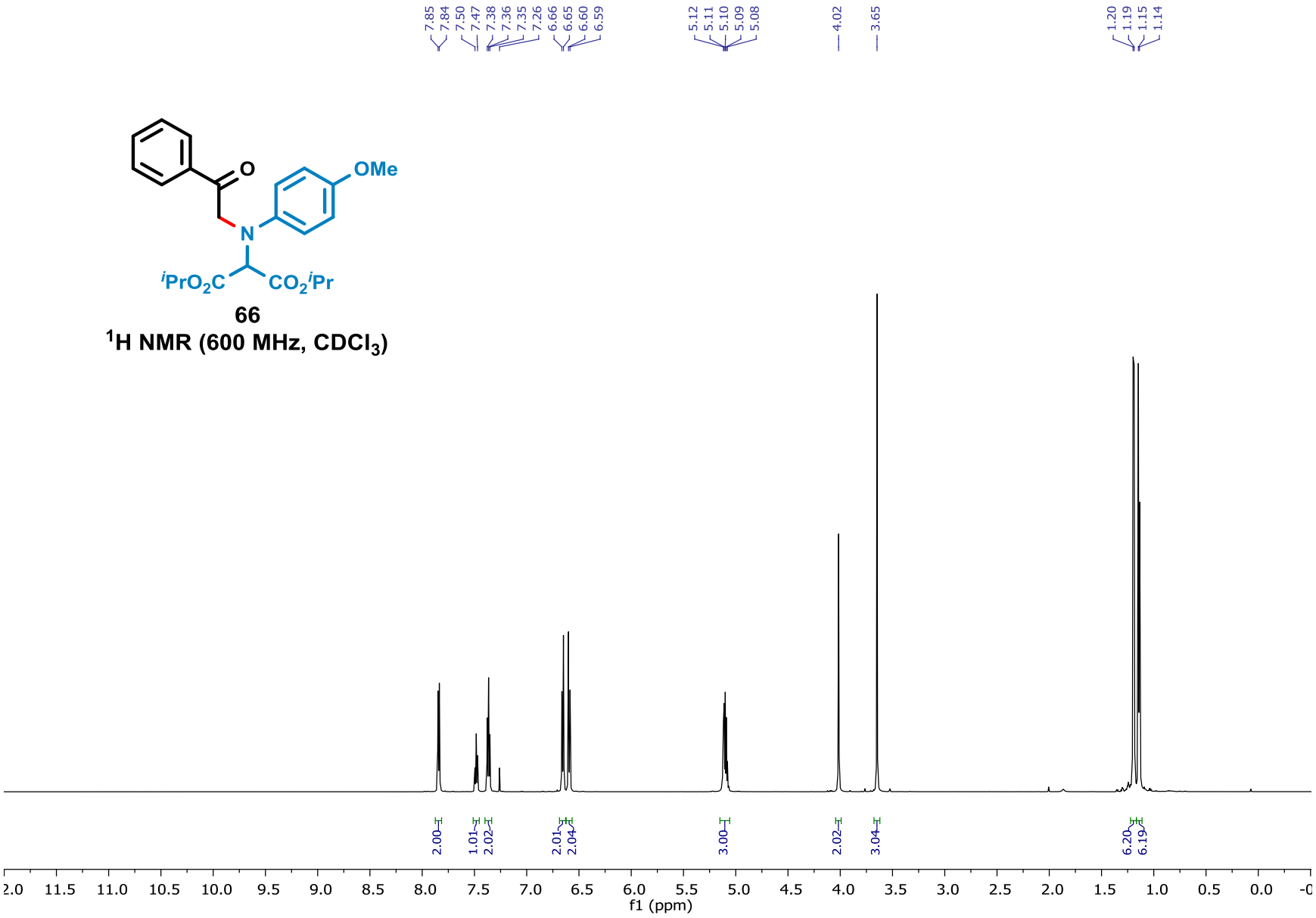
^{13}C NMR (151 MHz, $CDCl_3$)

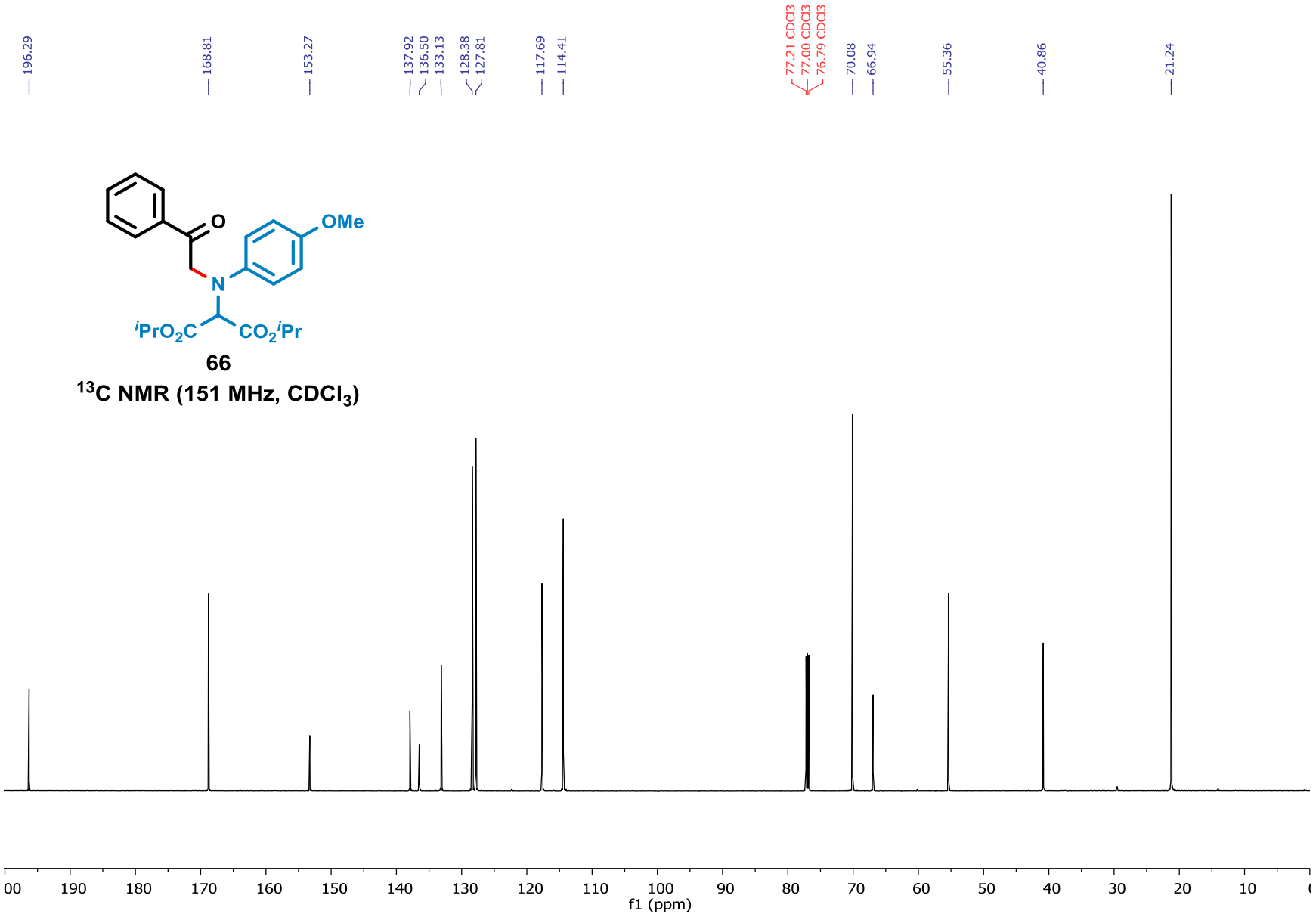

8.25
7.26
7.21
7.20
7.14
7.13
7.12
7.11
5.17
5.16
5.15
5.14
5.13
5.12
5.11
4.86
4.85
4.84
4.83
4.82
4.81
4.79
3.75
3.72
1.28
1.27
1.24
1.23
1.09
1.08
0.96
0.95
N
N
iPrO2C
iPrO2C
O
OMe
64c
1H NMR (600 MHz, CDCl3)
1.95
0.98
0.92
0.94
0.94
3.00
0.99
6.10
2.93
2.86
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

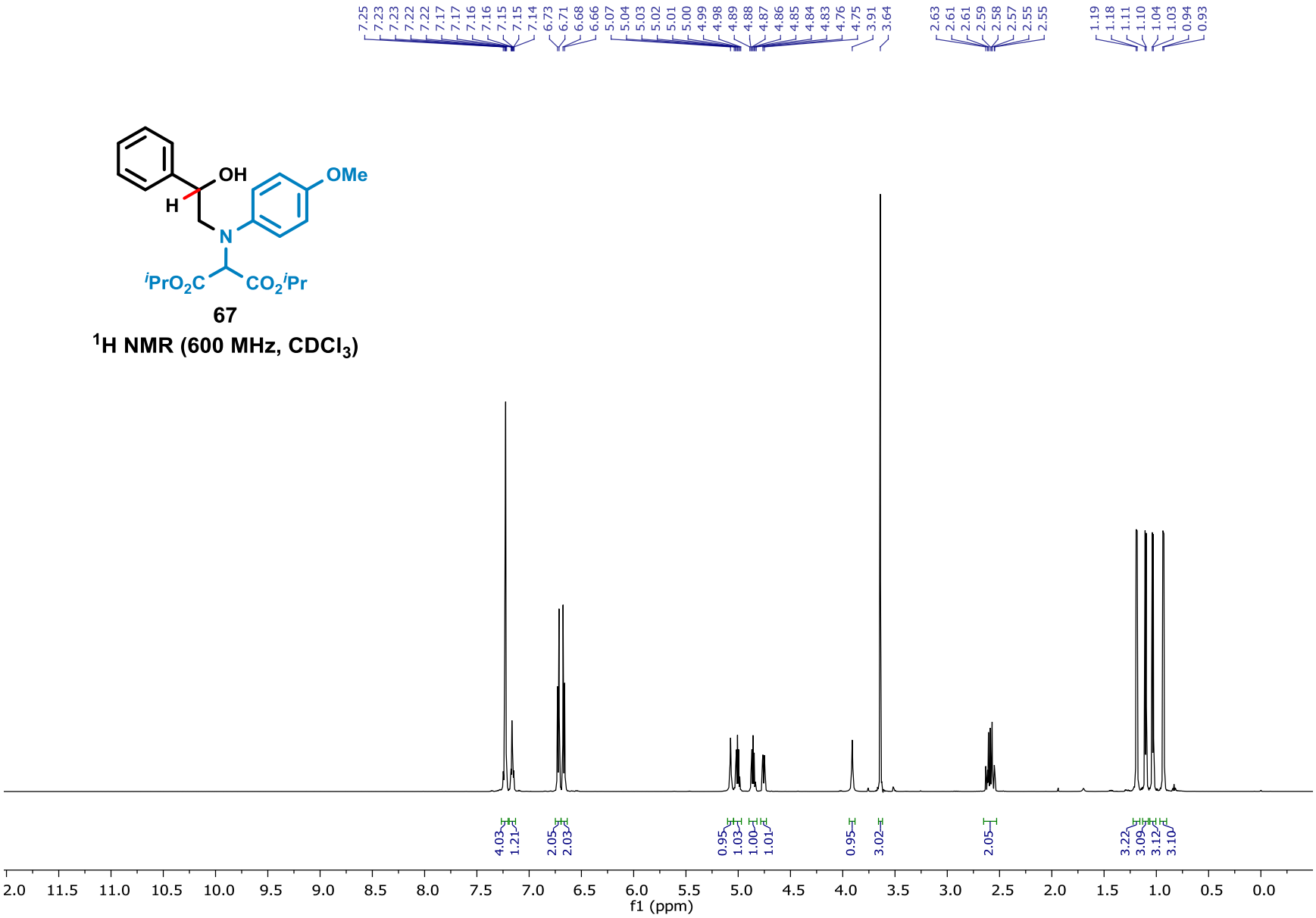


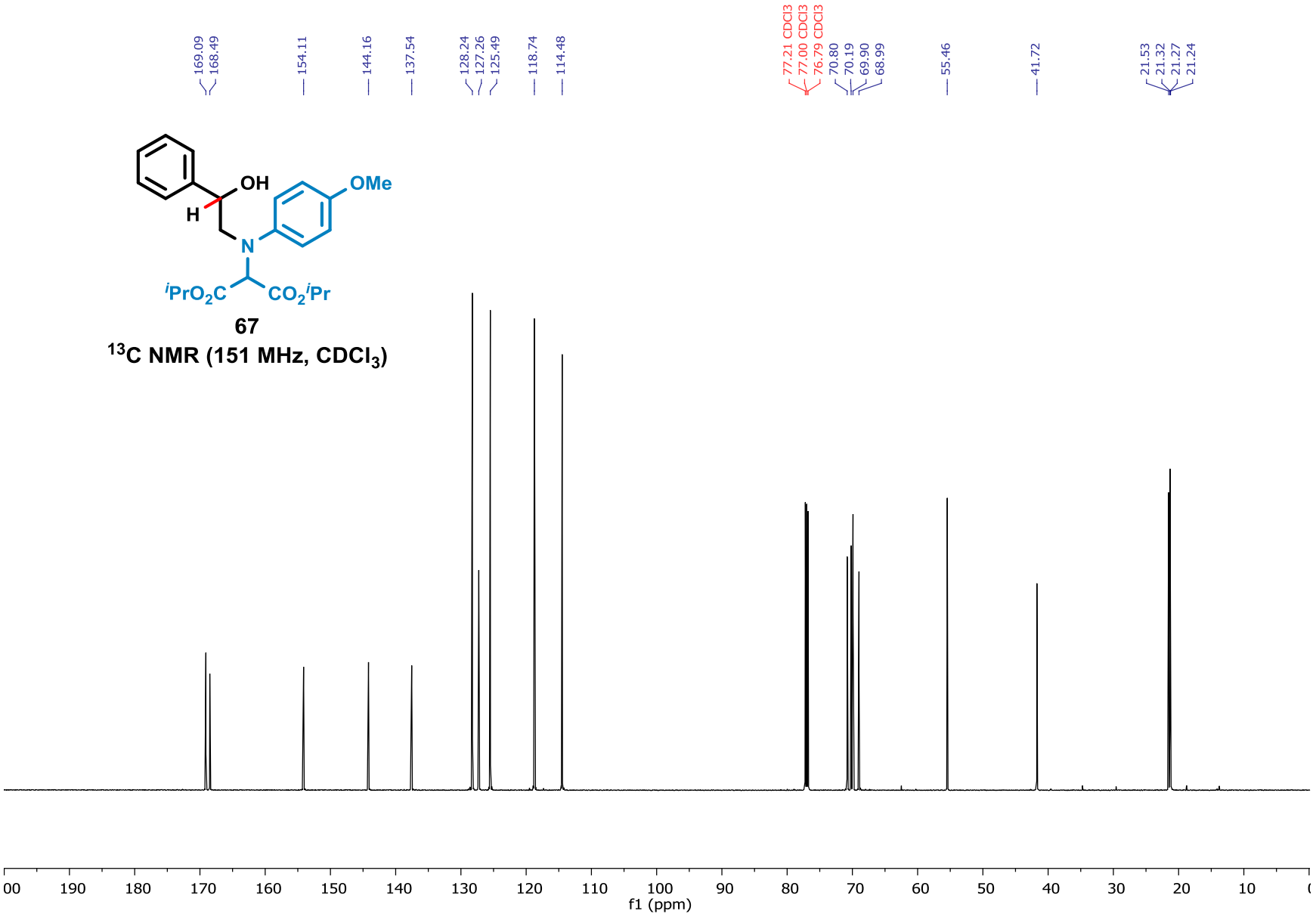
64c

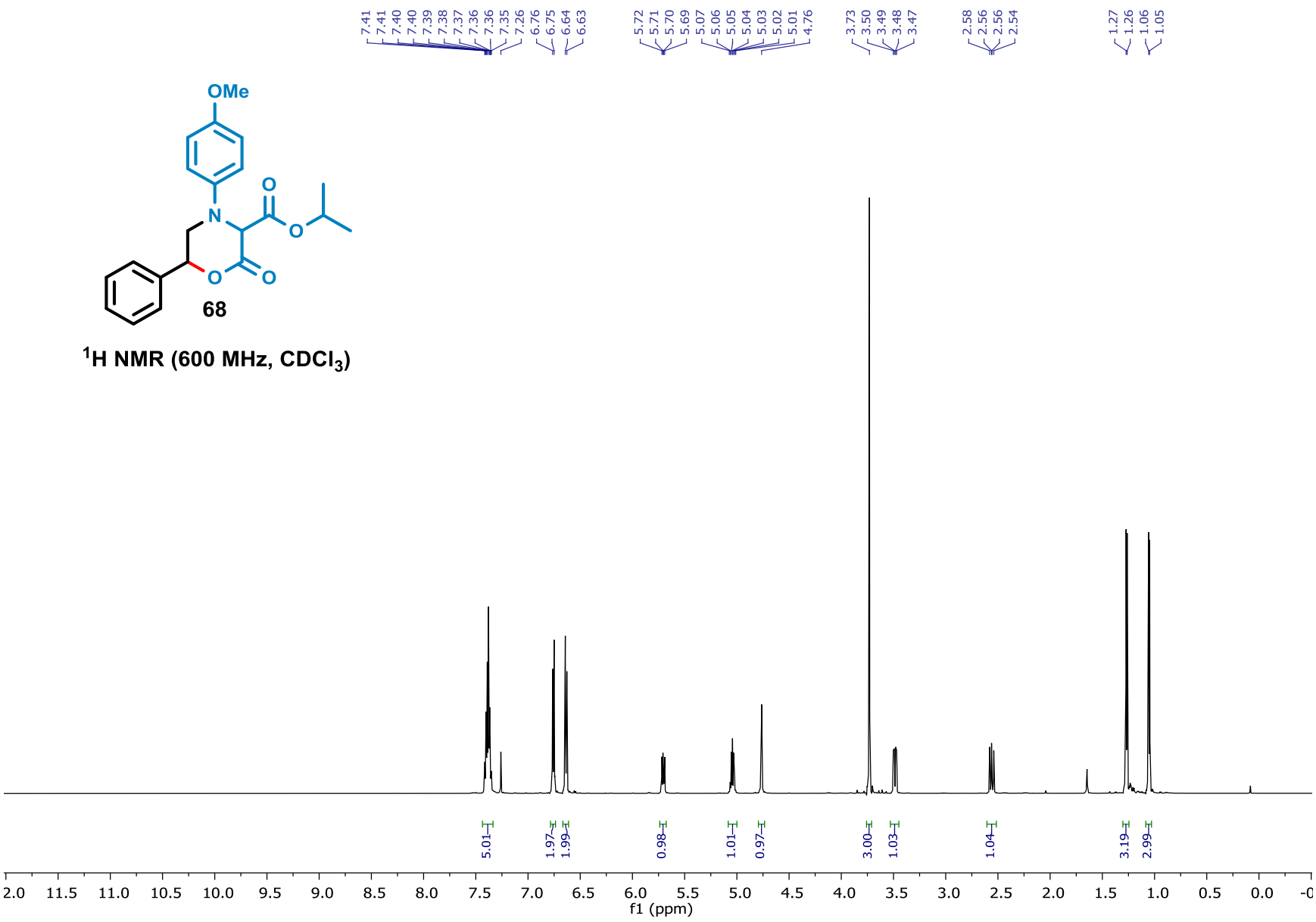
^{13}C NMR (151 MHz, $CDCl_3$)


7.85
7.84
7.50
7.47
7.38
7.36
7.35
7.26
6.66
6.65
6.60
6.59
5.12
5.11
5.10
5.09
5.08
4.02
3.65
1.20
1.19
1.15
1.14
OMe
O
N
iPrO2C
CO2iPr
66
1H NMR (600 MHz, CDCl3)
2.00
1.01
2.02
2.01
2.04
3.00
2.02
3.04
6.20
6.19
f1 (ppm)

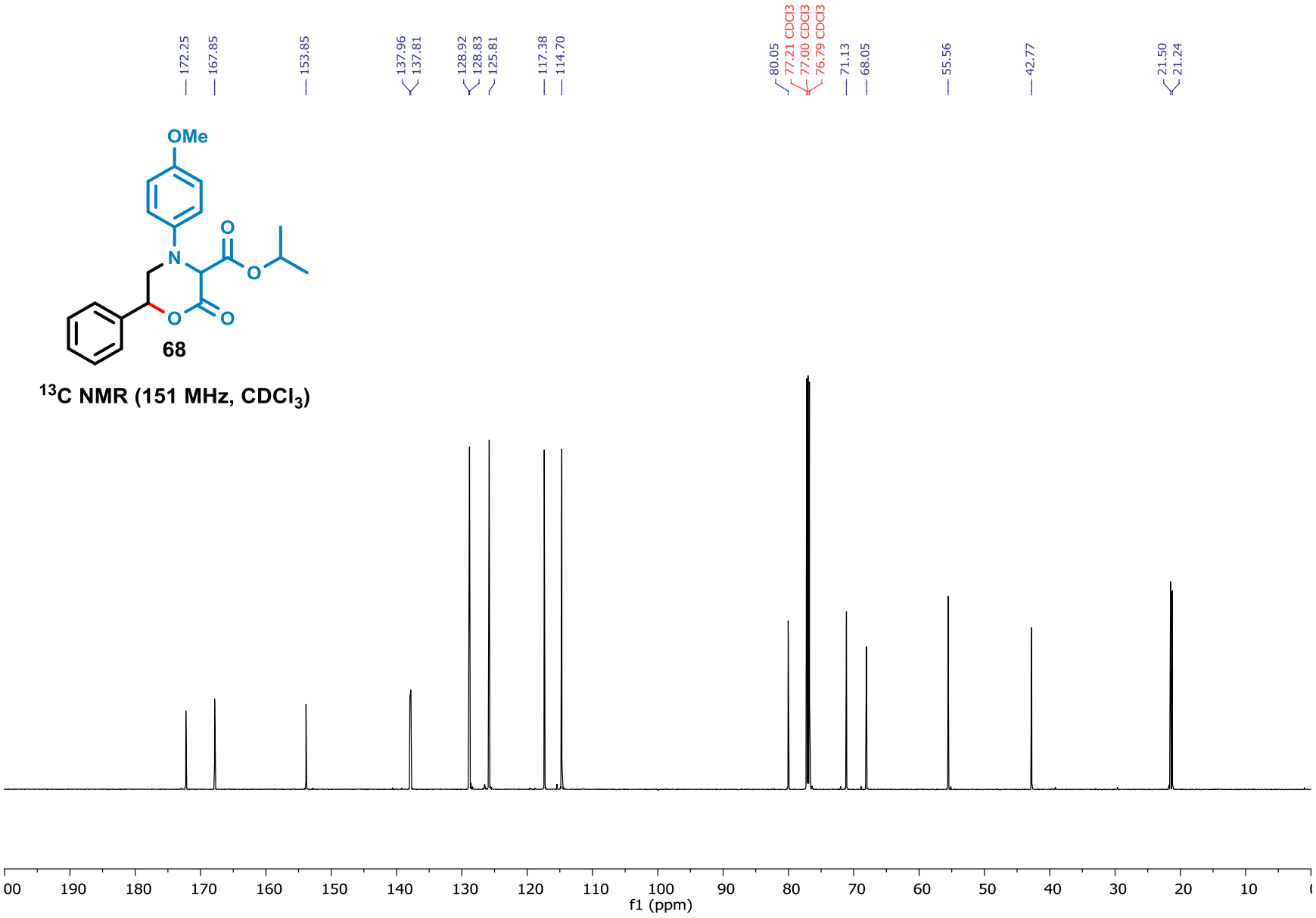

196.29
168.81
153.27
137.92
136.50
133.13
128.38
127.81
117.69
114.41
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.08
66.94
55.36
40.86
21.24
O
OMe
N
iPrO2C
CO2iPr
66
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.25
7.23
7.23
7.22
7.22
7.17
7.17
7.16
7.16
7.15
7.15
7.14
6.73
6.71
6.68
6.66
5.07
5.04
5.03
5.02
5.01
5.00
4.99
4.98
4.89
4.88
4.87
4.86
4.85
4.84
4.83
4.76
4.75
3.91
3.64
2.63
2.61
2.61
2.59
2.58
2.57
2.55
2.55
1.19
1.18
1.11
1.10
1.04
1.03
0.94
0.93
OH
H
N
OMe
iPrO2C
CO2iPr
67
1H NMR (600 MHz, CDCl3)
4.03
1.21
2.05
2.03
0.95
1.03
1.00
1.01
0.95
3.02
2.05
3.22
3.09
3.12
3.10
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

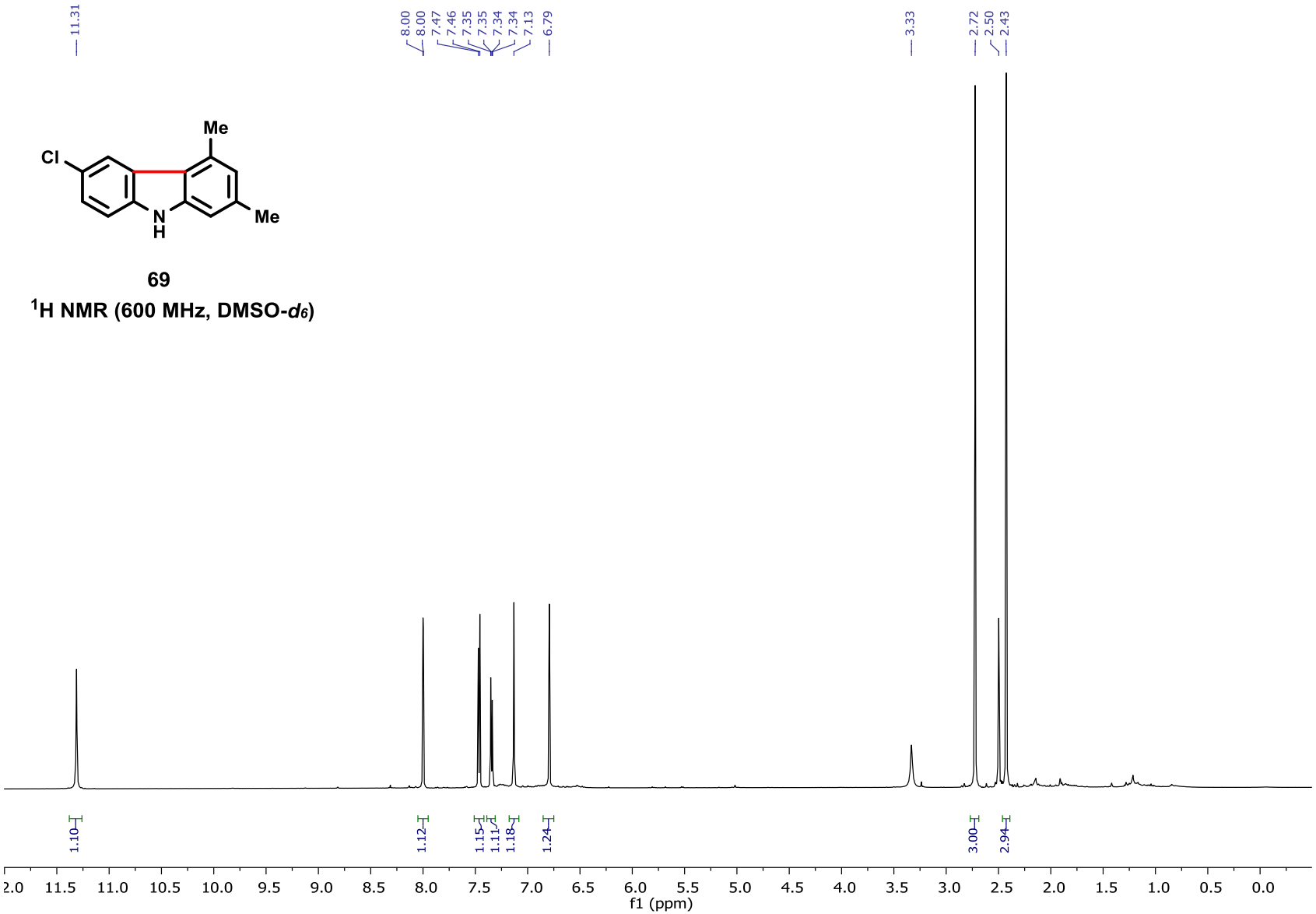

169.09
168.49
154.11
144.16
137.54
128.24
127.26
125.49
118.74
114.48
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.80
70.19
69.90
68.99
55.46
41.72
21.53
21.32
21.27
21.24
OH
H
N
OMe
iPrO2C
CO2iPr
67
13C NMR (151 MHz, CDCl3)
f1 (ppm)



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

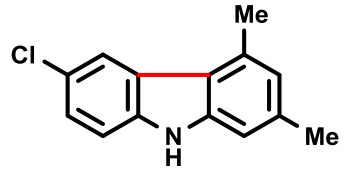


^{13}C NMR (151 MHz, $CDCl_3$)



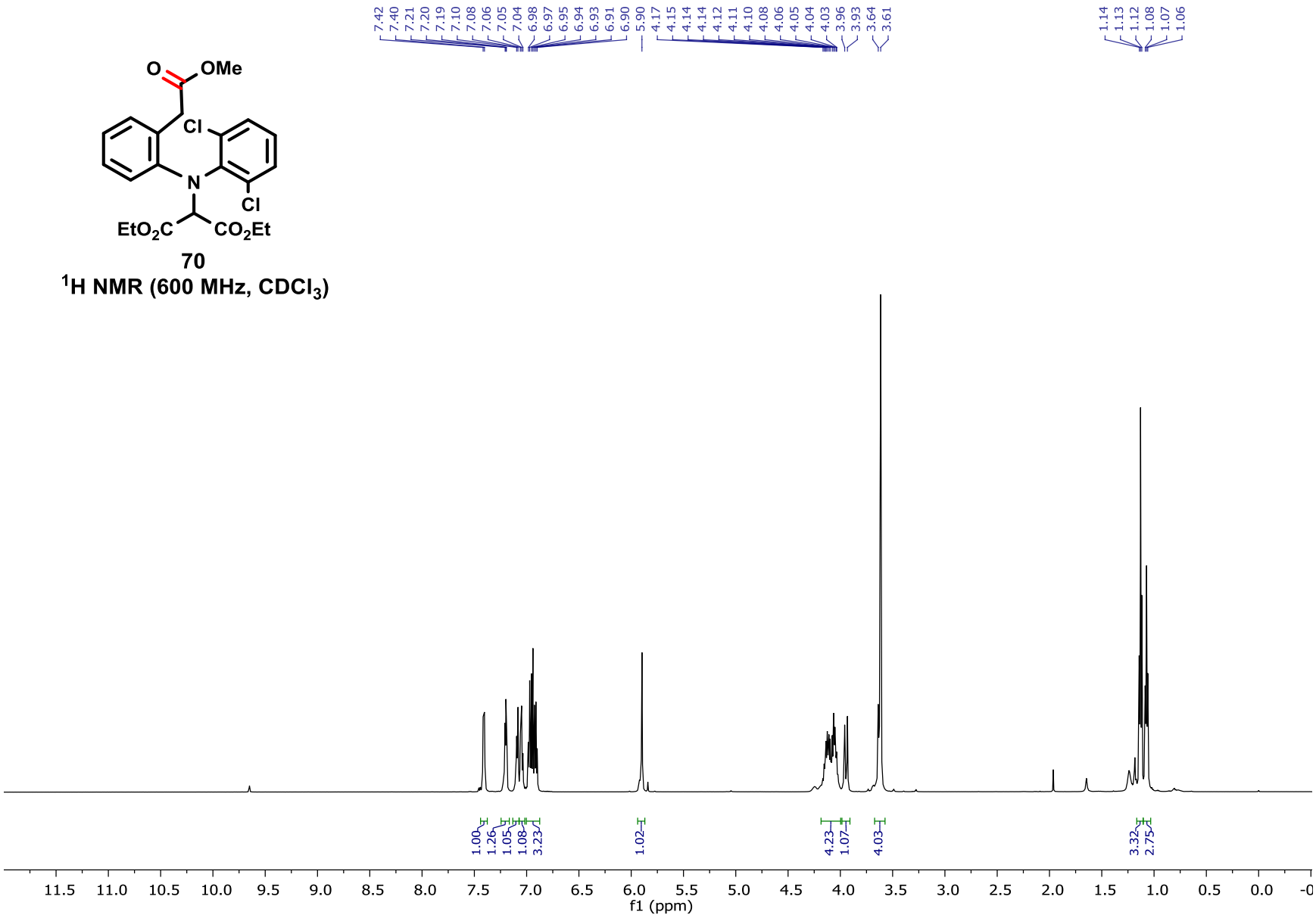
69

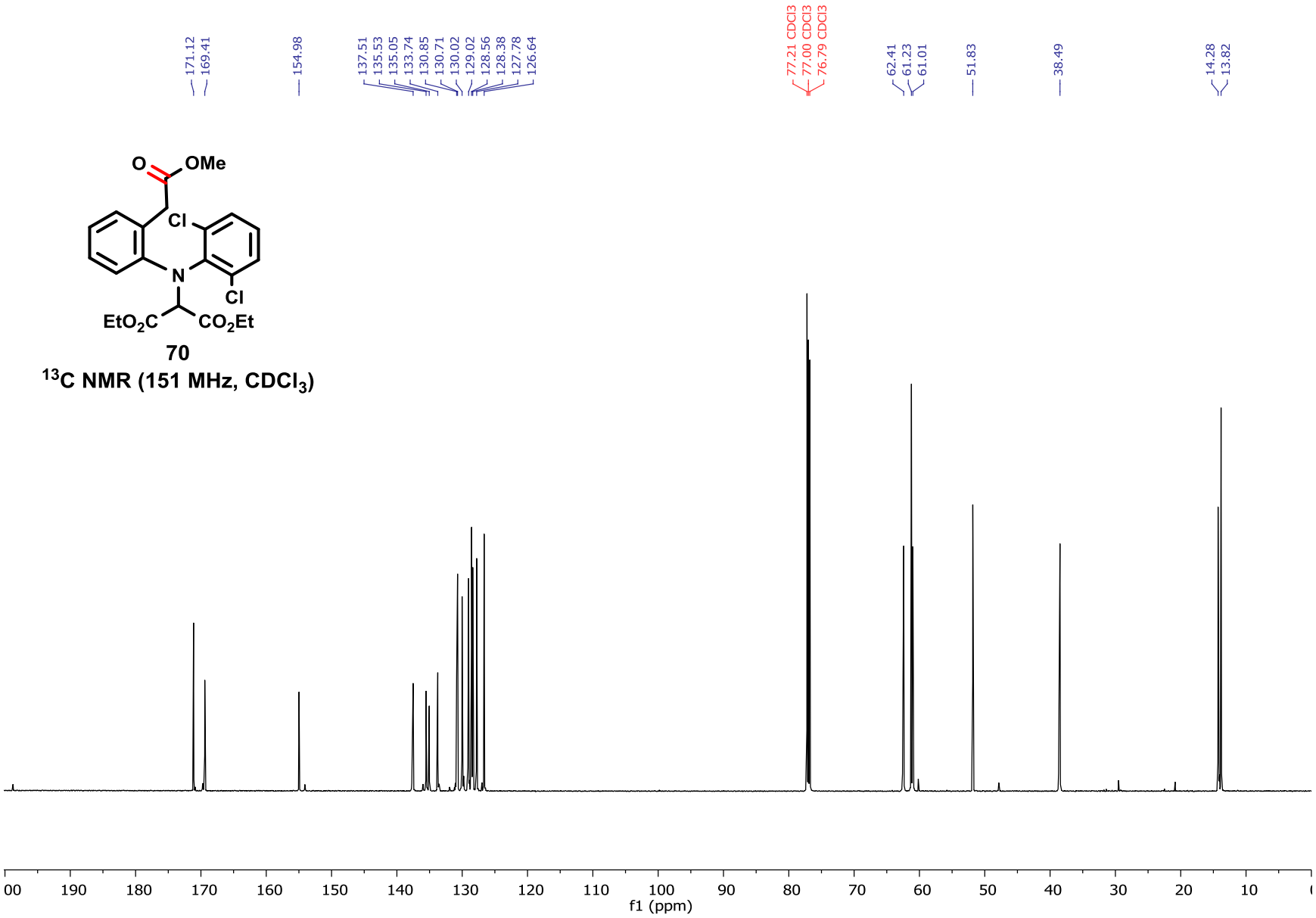
^{1}H NMR (600 MHz, DMSO-*d*$_6$)

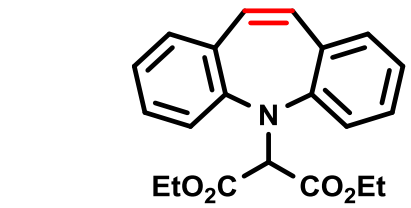


69

^{13}C NMR (151 MHz, DMSO-*d*$_6$)

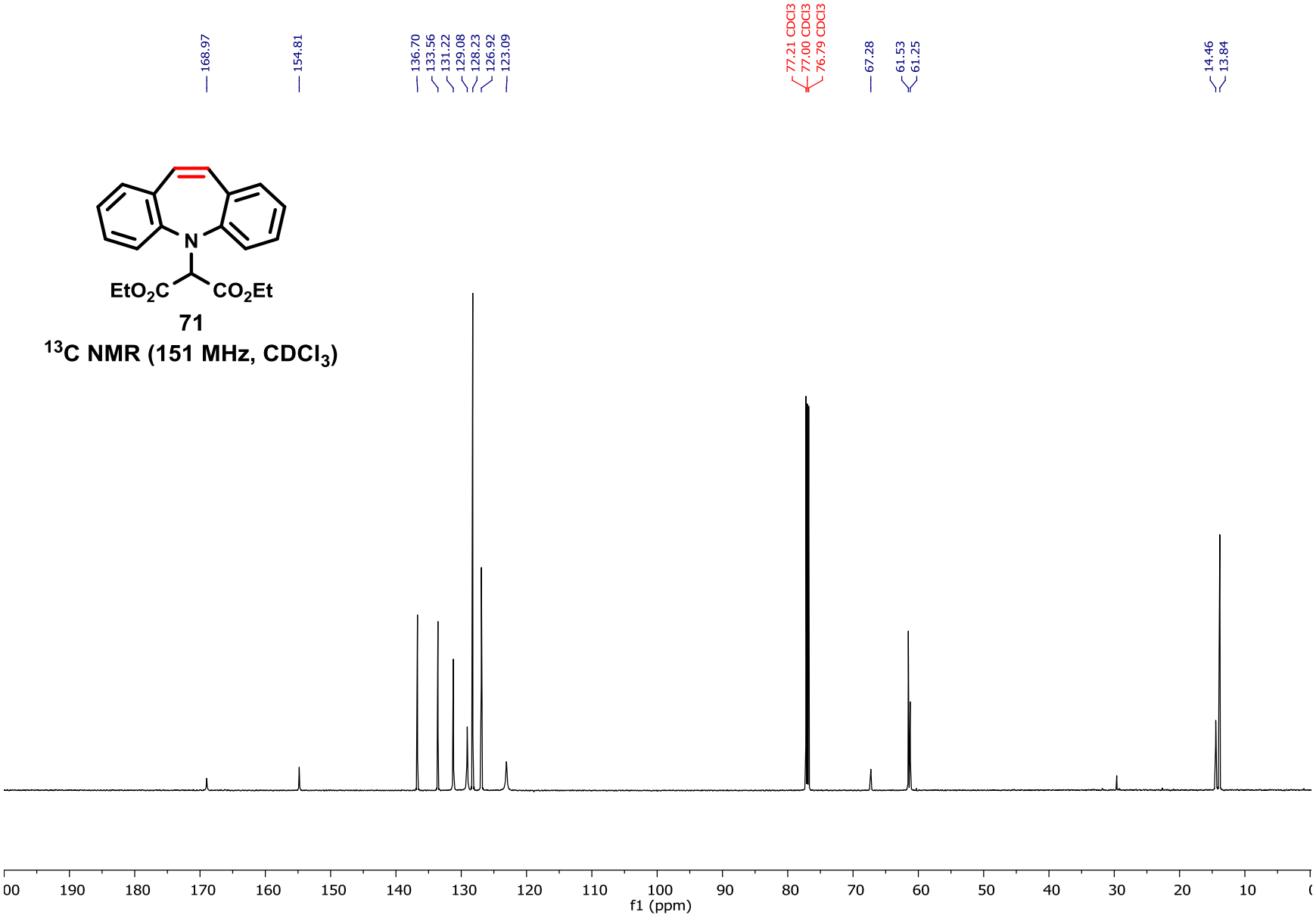

O
OMe
Cl
N
Cl
EtO2C
CO2Et
70
1H NMR (600 MHz, CDCl3)
7.42
7.40
7.21
7.20
7.19
7.10
7.08
7.06
7.05
7.04
6.98
6.97
6.95
6.94
6.93
6.91
6.90
5.90
4.17
4.15
4.14
4.14
4.12
4.11
4.10
4.08
4.06
4.05
4.04
4.03
3.96
3.93
3.64
3.61
1.14
1.13
1.12
1.08
1.07
1.06
1.00
1.26
1.05
1.08
3.23
1.02
4.23
1.07
4.03
3.32
2.75
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

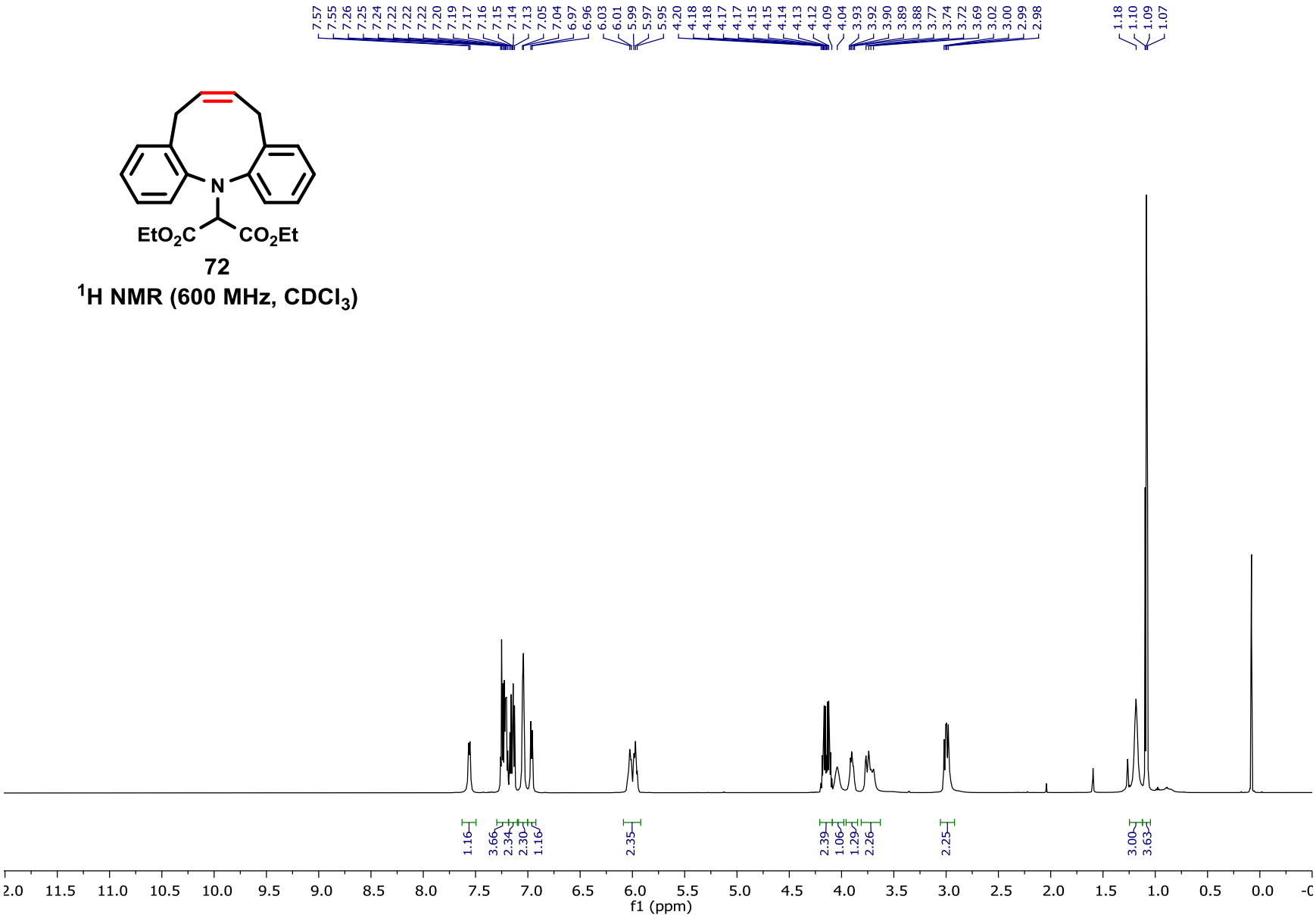

171.12
169.41
154.98
137.51
135.53
135.05
133.74
130.85
130.71
130.02
129.02
128.56
128.38
127.78
126.64
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
62.41
61.23
61.01
51.83
38.49
14.28
13.82
O
OMe
Cl
N
Cl
EtO2C
CO2Et
70
13C NMR (151 MHz, CDCl3)
f1 (ppm)



71

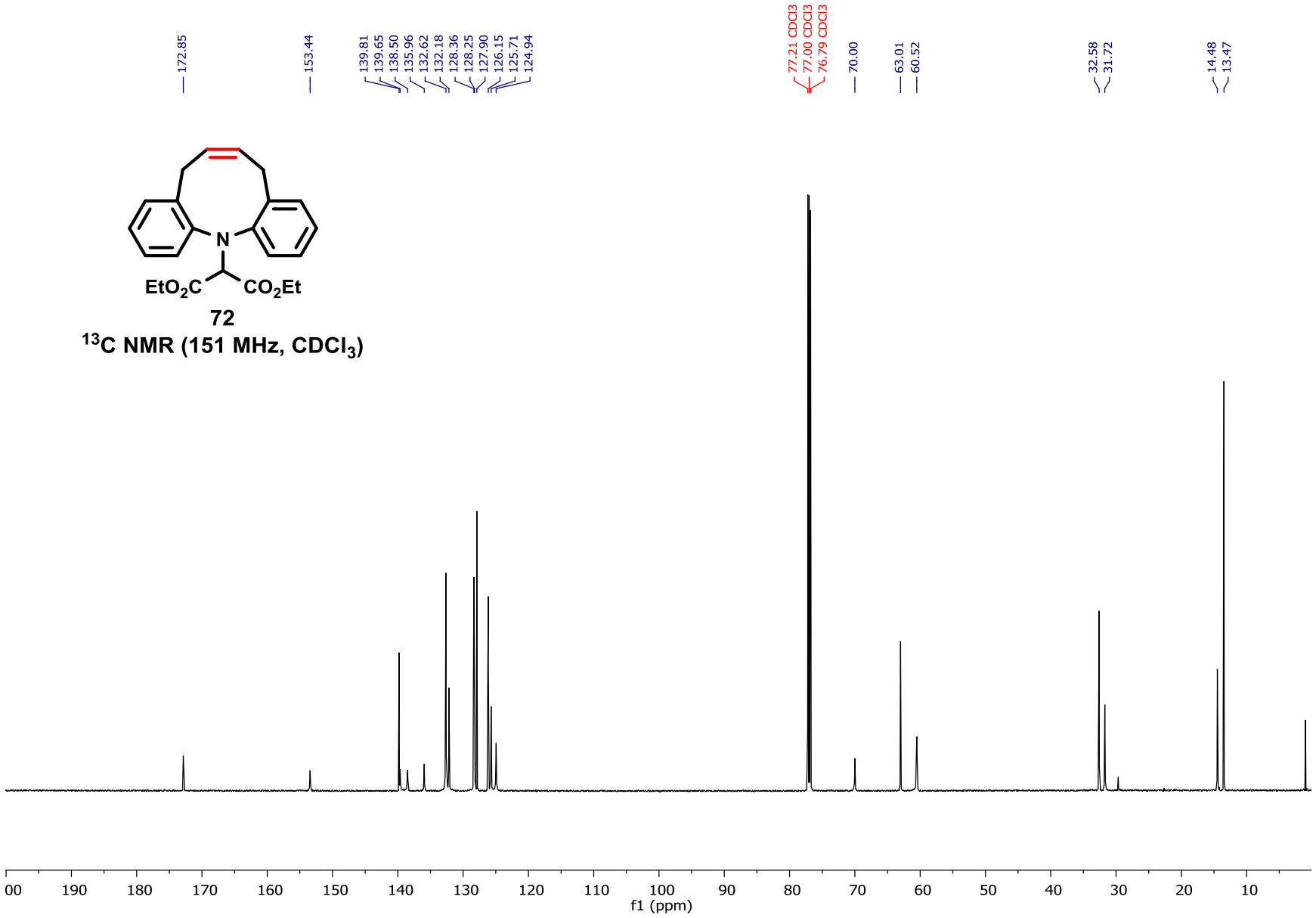
^{1}H NMR (600 MHz, $CDCl_3$)


168.97
154.81
136.70
133.56
131.22
129.08
128.23
126.92
123.09
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
67.28
61.53
61.25
14.46
13.84
N
EtO2C
CO2Et
71
13C NMR (151 MHz, CDCl3)
f1 (ppm)



72

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


172.85
153.44
139.81
139.65
138.50
135.96
132.62
132.18
128.36
128.25
127.90
126.15
125.71
124.94
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
70.00
63.01
60.52
32.58
31.72
14.48
13.47
N
EtO2C
CO2Et
72
13C NMR (151 MHz, CDCl3)
f1 (ppm)