Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Recent Advances in the Synthesis of Analogues of Phytohormones Strigolactones with Ring-Closing Metathesis as a Key Step

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Supporting Information

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Synthetic procedures

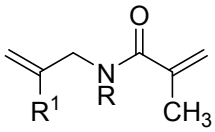
General details

All solvents were purchased by Sigma-Aldrich and used without further purification unless specified. Anhydrous THF and anhydrous toluene were prepared by distillation from Na and benzophenon. The persistent blue-violet color of the solution, due to the benzophenone ketyl, confirmed anhydrous conditions. Anhydrous CH_2Cl_2, DME and ethyl formate were obtained by distillation from CaH_2. Anhydrous CCl_4 was prepared by drying for 24h over 4A activated molecular sieves. *t*BuOK was sublimated immediately before using. NBS was recrystallized from water. All the other reagents were used as received if not otherwise specified. Glassware for moisture-sensitive reactions were oven-dried at 150 °C and assembled under nitrogen. Reactions involving air-sensitive reagents were performed under a dry nitrogen atmosphere. Reactions were monitored by TLC carried out on 0.25-mm silica gel plates (Merck F254). Chromatographic purifications were carried out on silica gel (Merck grade 7734, pore size 60 Å, 70−230 mesh) using flash-column or classical techniques; *R*f values refer to TLC carried out on 0.25 mm silica gel plates (Merck F254), with the same eluent indicated for the column chromatography. ^{1}H-NMR, ^{13}C-NMR and COSY spectra were recorded on a Bruker Avance-200 spectromer or on a Jeol JNM-ECZR600 in $CDCl_3$. ^{1}H NMR spectra were recorded at 200 MHz or at 600 MHz; ^{13}C-NMR at 50.2 MHz or 150 MHz with complete proton decoupling. Multiplicity is indicated as following: s (singlet), br (broad signal), d (doublet), t (triplet), dd (doublet-doublet), td (triplet-doublet), m (multiplet). Chemical shifts were reported in ppm from the residual pick solvent as an internal standard. The coupling costants J are expressed in Hz.

HR-MS data were recorded on an LTQ Orbitrap Hybrid mass spectrometer. MS spectra were recorded on an AT 5973N mass selective detector connected to an AT 6890N GC, cross-linked methyl silicone capillary column. MS data were recorded at an ionizing voltage of 70 eV. M abbreviation indicates molecular ion.

Enantiomers were separated on either a semipreparative or an analytical Chiralpak IC column (particle size 5μm, Daicel, Osaka, Japan). Dimensions: analytical column 4.6ⓘ×250 mmL; semipreparative column 10ⓘ×250 mmL. A Jasco P-2000 polarimeter was used for the determination of optical rotations.

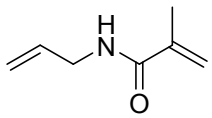
Synthesis of compounds 4a-g



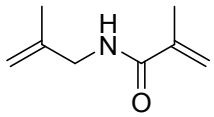
4a: R=H, R^1=H
4b: R=H R^1=CH_3
4c: R=Boc, R^1=H
4d: R=Boc, R^1=CH_3
4e: R=Cbz, R^1=H
4f: R=Cbz, R^1=CH_3
4g: R=CH_3, R^1=H

General procedure for the synthesis of *N*-allylmethacrylamides 4a, 4b, 4g.

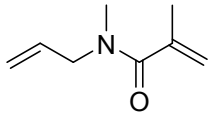
In an oven-dried round bottom flask, a solution of freshly distilled allylamine (1.00 eq) in anhydrous CH_2Cl_2 (57 mL) was cooled to 0°C. K_2CO_3 (3.00 eq) was added and the mixture was stirred at 0 °C for 2h. Then, methacryloyl chloride (1.20 eq) was added dropwise. The mixture was further stirred at 0°C for 3h, then it was warmed up to room temperature and stirred overnight (12h). Afterwards, the reaction mixture was poured into iced water and the aqueous phase was extracted with CH_2Cl_2 (3x20 mL). Then the combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. Evaporation of the solvent gave a colourless liquid which was purified by silica gel chromatography.



***N*-allylmethacrylamide (4a)**. The crude product was purified by flash chromatography on silica gel using a gradient elution from PE/EtOA 4:1 v/v to PE/EtOA 1:1 v/v. Colourless liquid (yield: 91%). TLC Rf = 0.15 (PE/EtOAc 8:2 v/v). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.29 (br s, 1 H, NH), 5.80 (ddt, *J* = 17.1 Hz, J=10.2 Hz, J=5.6 Hz, 1H, CH_2=C<u>H</u>CH_2NH), 5.66–5.65 (m, 1H, (CH_3)C=C<u>H_2</u>), 5.28-5.26 (m, 1H, (CH_3)C=C<u>H_2</u>), 5.18−5.02 (m, 2H, <u>CH_2</u>=CHCH_2NH), 3.86 (tt, J= 5.7 Hz, J=1.5 Hz, 2H, CH_2=CH<u>CH_2</u>NH), 1.91–1.90 (m, 3H, CH_3). Spectral data correspond to those previously reported in literature.[1]



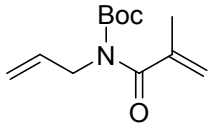
***N*-(2-methyl)allylmethacrylamide (4b)**. Starting from 2-methylallylamine (1.00 eq), compound **4b** was obtained after chromatography (petroleum ether/ethyl acetate 8:2 v/v, Rf=0.37) as a colourless liquid in 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.32 (br s, 1H, NH), 5.64 (s, 1H, $CO(CH_3)C=\underline{CH_2}$), 5.25 (s, 1H, $CO(CH_3)C=\underline{CH_2}$), 4.74 (s, 2H, $\underline{CH_2}NH$), 3.76 (s, 2H, $\underline{CH_2}=C(CH_3)CH_2$), 1.89 (s, 3H, CH_3), 1.65 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.55 (CO), 141.99 (Cq), 140.06 (Cq), 119.49 ($=CH_2$), 110.74 ($=CH_2$), 45.05 (CH_2), 20.38 (CH_3), 18.75 (CH_3). MS: (EI, 70 eV): m/z (%) = 41 (64), 69 (100), 96 (44), 124 (55), 139 (15) [M].



***N*-allyl-*N*-methylmethacrylamide (4g)**. Starting from *N*-methylprop-2-en-1-amine (1.00 eq), compound **4e** was obtained after chromatography (petroleum ether/ethyl acetate/ Et_3N 1:1:0.03 v/v/v ,Rf=0.45) as a colourless liquid in 83% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 18.4 Hz, J=10.6 Hz, J=5.3 Hz, 1H, $CH_2=\underline{CH}CH_2N(CH_3)$), 5.23−5.13 (m, 3H, $3xCH_2=$), 5.06−5.04 (m, 1H, $CH_2=$), 3.98 (br s, 2H, $CH_2=CH\underline{CH_2}N(CH_3)$), 2.87 (s, 3H, CH_3), 1.96−1.95 (m, 3H, CH_3). Spectral data were in agreement with literature values.[2]

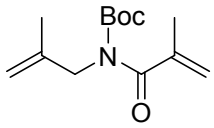
General procedure for the synthesis of compounds 4c and 4d.

To a solution of the corresponding *N*-allylmethacrylamide **4a** or **4b** (1.00 eq) in anhydrous THF (380 mL), $(t\text{-Boc})_2O$ (2.00 eq) and few milligrams of DMAP were added. The reaction mixture was stirred at 80°C overnight. Then, the reaction was quenched with water and extracted with CH_2Cl_2 (3x100 mL). The collected organic phases were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography.



***tert*-Butyl allyl(methacryloyl)carbamate (4c)**. The crude product was purified by chromatography (PE/EtOAc 9:1 v/v, Rf=0.88) to give the final product as a colourless liquid in 91% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.86 (ddt, *J* = 17.1 Hz, J=10.2 Hz, J=5.7 Hz, 1H, $CH_2=\underline{CH}CH_2NBoc$), 5.18–5.05 (m, 4H, 2x $=CH_2$), 4.18 (dt, J= 5.8 Hz, J=1.4 Hz, 2H, $CH_2=CH\underline{CH_2}NBoc$), 1.94–1.93 (m, 3H, CH_3), 1,41 (s, 9H,

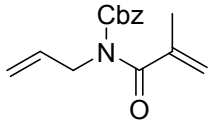
Boc); ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 173.82 (CON), 153.17 (COO Boc), 143.35 (<u>C</u>=CH_2), 133.06 (CH_2=<u>CH</u>CH_2NBoc), 117.08 (=CH_2), 116.11 (=CH_2), 83.30 (<u>C</u>(CH_3)$_3$), 47.03 (CH_2), 27.81 (3CH_3), 19.30 (CH_3); MS (EI): *m/z* (%) = 28 (45), 41 (73), 57 (100), 69 (96), 82 (20), 169 (62) . HRMS (ESI) for $C_{12}H_{19}NO_3$ Calcd 226.1443 $[M + H]^+$; Found 226.1501 $[M + H]^+$.



***tert*-Butyl methacryloyl(2-methylallyl)carbamate (4d)**. The crude product was purified by chromatography (PE/EtOAc) 9:1, Rf=0.60) to give the final product as a colourless liquid in 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.18 (br s, 1H, (CH_3)C=<u>CH_2</u>), 5.14 (br s, 1H, (CH_3)C=<u>CH_2</u>), 4.80 (br s, 1H, <u>CH_2</u>=C(CH_3)CH_2N), 4.73 (br s, 1H, <u>CH_2</u>=C(CH_3)CH_2N), 4.16 (s, 2H, CH_2), 1.98 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.42 (s, 9H, Boc); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 173.85 (CON), 153.44 (CO Boc), 143.34 (Cq), 140.84 (Cq), 116.05 (CH_2), 110.67 (CH_2), 83.35 (Cq), 49.81 (CH_2), 27.78 (3xCH_3), 20.42 (CH_3), 19.49 (CH_3); MS: (EI, 70 eV): m/z (%) = 41 (49), 57 (100), 69 (84), 183 (94) [M].

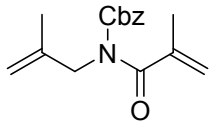
General procedure for the synthesis of compounds 4e and 4f.

A solution of the corresponding *N*-allylmethacrylamide (1.00 eq) in THF (20 ml) was cooled to -78 °C, then *n*-BuLi (1.20 eq) was added dropwise. The reaction mixture was stirred for 1h at the same temperature, then, CbzCl (1.00 eq) was added and the reaction mixture was slowly warmed to rt for 3h. The mixture was quenched with aqueous NH_4Cl and extracted CH_2Cl_2 (3x20 mL). Then the combined organic layers were dried over Na_2SO_4, filtered and concentrated in reduced pressure. The residue was purified by column chromatography.



Benzyl allyl(methacryloyl)carbamate (4e). Eluent used for the column chromatography: petroleum ether/ethyl acetate 9:1 v/v, Rf=0.65. Yield: 83%, colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39−7.34 (m, 5H, ArH), 5.86 (ddt, *J* = 17.1 Hz, J=10.3 Hz, J=5.8 Hz, 1H, CH_2=<u>CH</u>CH_2NCbz), 5.21–5.13 (m, 6H, 2x=<u>CH_2</u> + CH_2Cbz), 4.31 (dt, J=5.8 Hz, J=1.4 Hz, 2H, CH_2=CH<u>CH_2</u>NCbz), 1.93–1.92 (m, 3H, CH_3). ^{13}C NMR (50.2 MHz, $CDCl_3$): δ 173.88 (CON), 154.58 (CO Cbz), 142.85 (ArC), 134.72 (<u>C</u>=CH_2), 132.72 (CH_2=<u>CH</u>CH_2NCbz), 128.78 (ArCH), 128.70 (2xArCH), 128.66 (2xArCH), 117.89 (=CH_2), 116.88 (=CH_2),

68.76 (CH_2Cbz), 47.37 (CH_2), 19.13 (CH_3). HRMS (ESI) for $C_{15}H_{17}NO_3$ Calcd 282.1106 $[M + Na]^+$; Found 282.1152 $[M + Na]^+$.



Benzyl methacryloyl(2-methylallyl)carbamate (4f). Eluent used for the column chromatography: petroleum ether/ethyl acetate 9:1, Rf=0.55). Yield: 85%, colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (s, 5H, ArH), 5.21–5.14 (m, 4H, CH_2Cbz + $(CH_3)C=\underline{CH_2}$), 4.86–4.85 (m, 1H, $\underline{CH_2}=C(CH_3)CH_2NCbz$), 4.78–4.77 (m, 1H, $\underline{CH_2}=C(CH_3)CH_2NCbz$), 4.27 (s, 2H, $CH_2=C(CH_3)\underline{CH_2}NCbz$), 1.95 (s, 3H, CH_3), 1.75 (s, 3H, CH_3); ^{13}C-NMR (50.2 MHz, $CDCl_3$): δ 173.63 (CON), 154.78 (CO Cbz), 142.90 (Cq), 140.48 (ArC), 134.78 (Cq), 128.68 (CH), 128.60 (2xArCH), 128.56 (2xArCH), 116.59 (CH_2), 111.11 (CH_2), 68.83 (CH_2 Cbz), 49.89 (CH_2), 20.45 (CH_3), 19.30 (CH_3); MS: (EI, 70 eV): m/z (%) = 69 (12), 91 (100), 144 (8), 169 (4), 273 (1) [M].

References

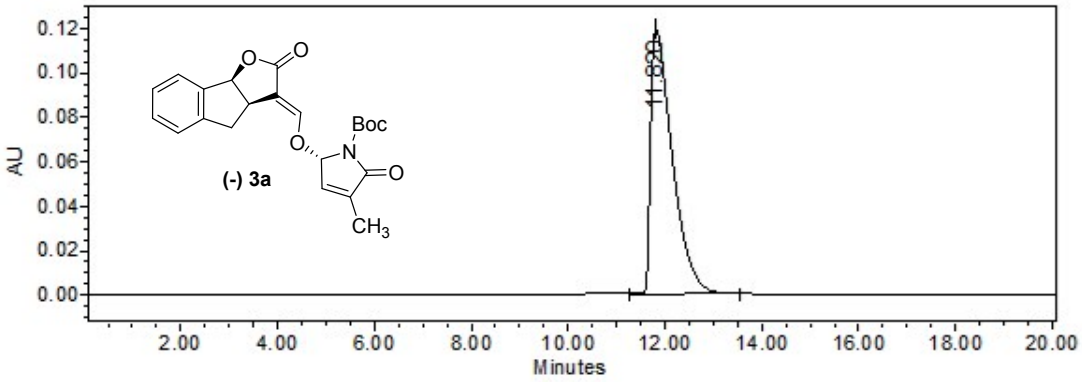
(1) Fuerstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.;Nolan, S. P. *J. Org. Chem.*, 2000, **65 (7)**, 2204-2207

(2) Netz, N.; Opatz, T. *J. Org. Chem.*, 2016, **81 (4)**, 1723–1730

Optical rotations for enantiomers

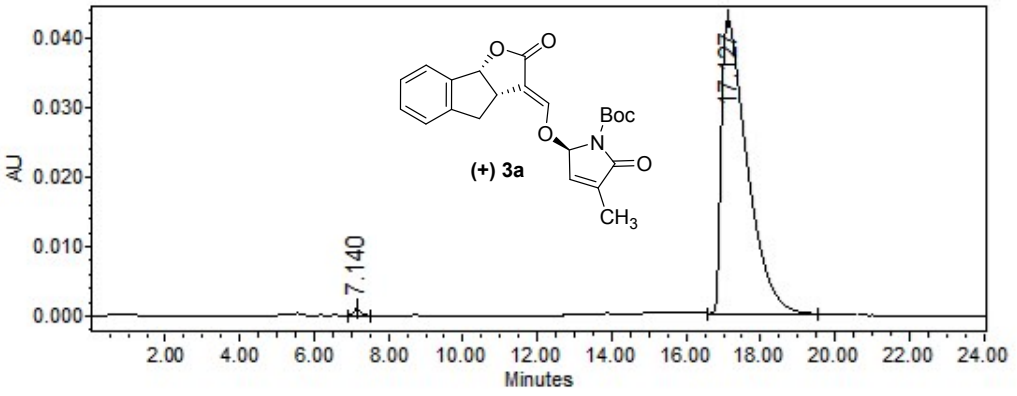
Compound	Stereochemistry	$[\alpha]_D^{25}$
(−) **3a**	3a*R*, 8b*S*, 2'*S*	− 234.7 (*c* 0.17, $CHCl_3$)
(+) **3a**	3a*S*, 8b*R*, 2'*R*	+ 200.8 (*c* 0.17, $CHCl_3$)

HPLC chromatograms for enantiomers



Compound	Retention Time (min)	Area (%)
(−) **3a**	11.820	100.00

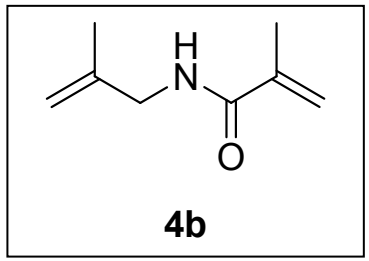
Conditions = Analytical Chiralpak IC column; isocratic, CH_2Cl_2; flow rate: 0.60 ml/min



Compound	Retention Time (min)	Area (%)
(+) **3a**	7.14	0.58
	17.127	99.42

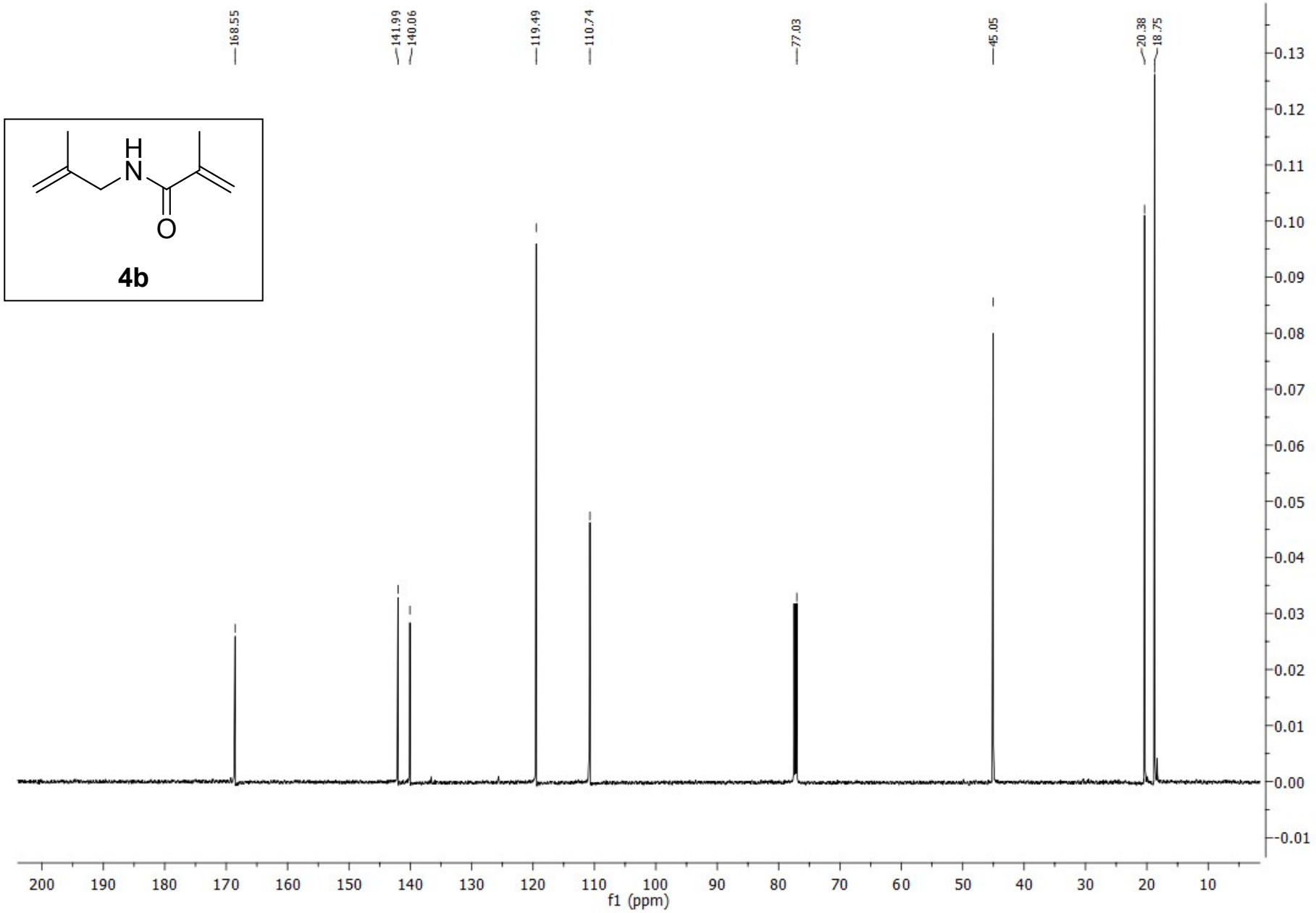
Conditions = Analytical Chiralpak IC column; isocratic, CH_2Cl_2; flow rate: 0.60 ml/min

^{1}H NMR (600 MHz) spectrum of *N*-(2-methyl)allylmethacrylamide (4b) in $CDCl_3$

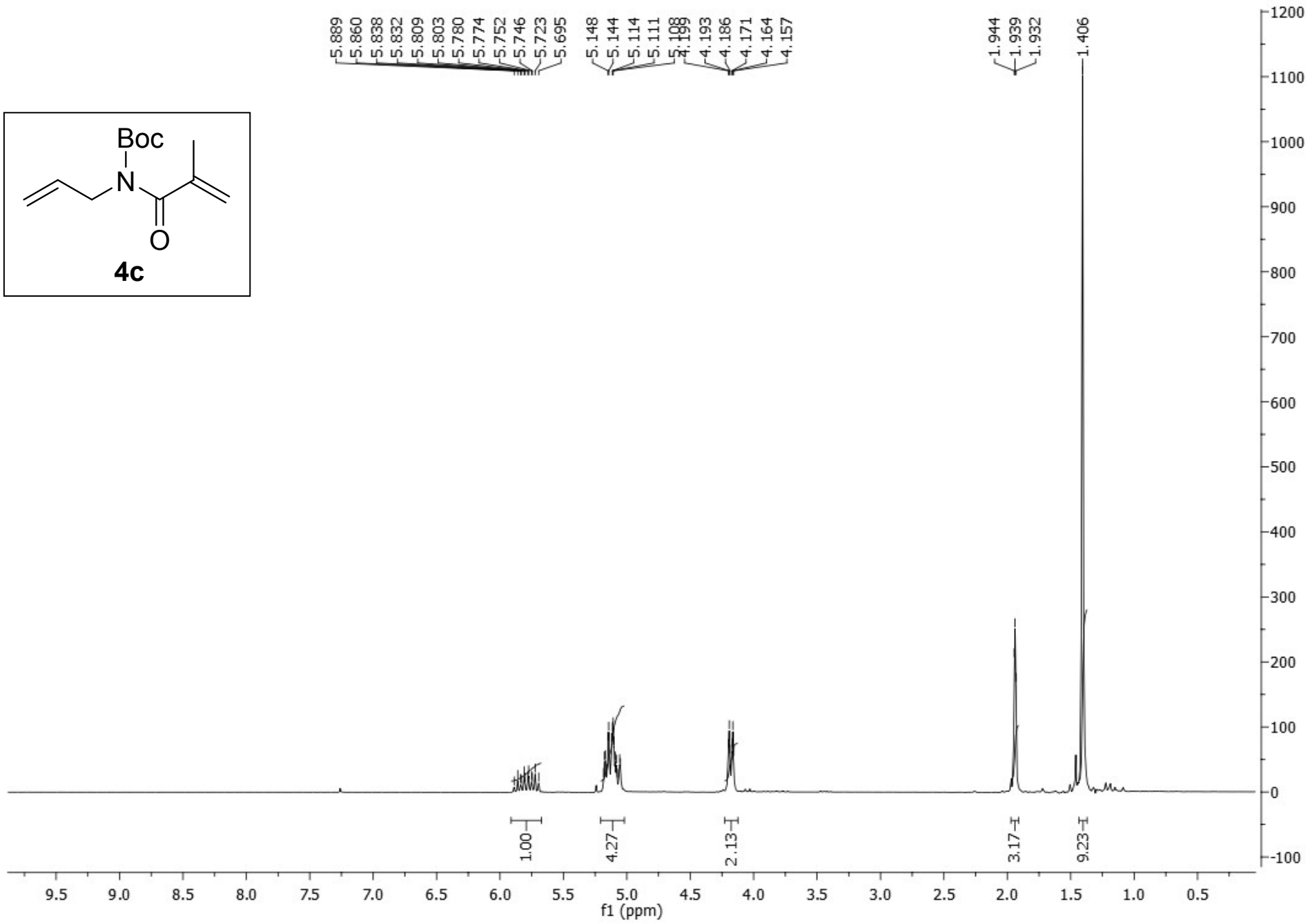


4b

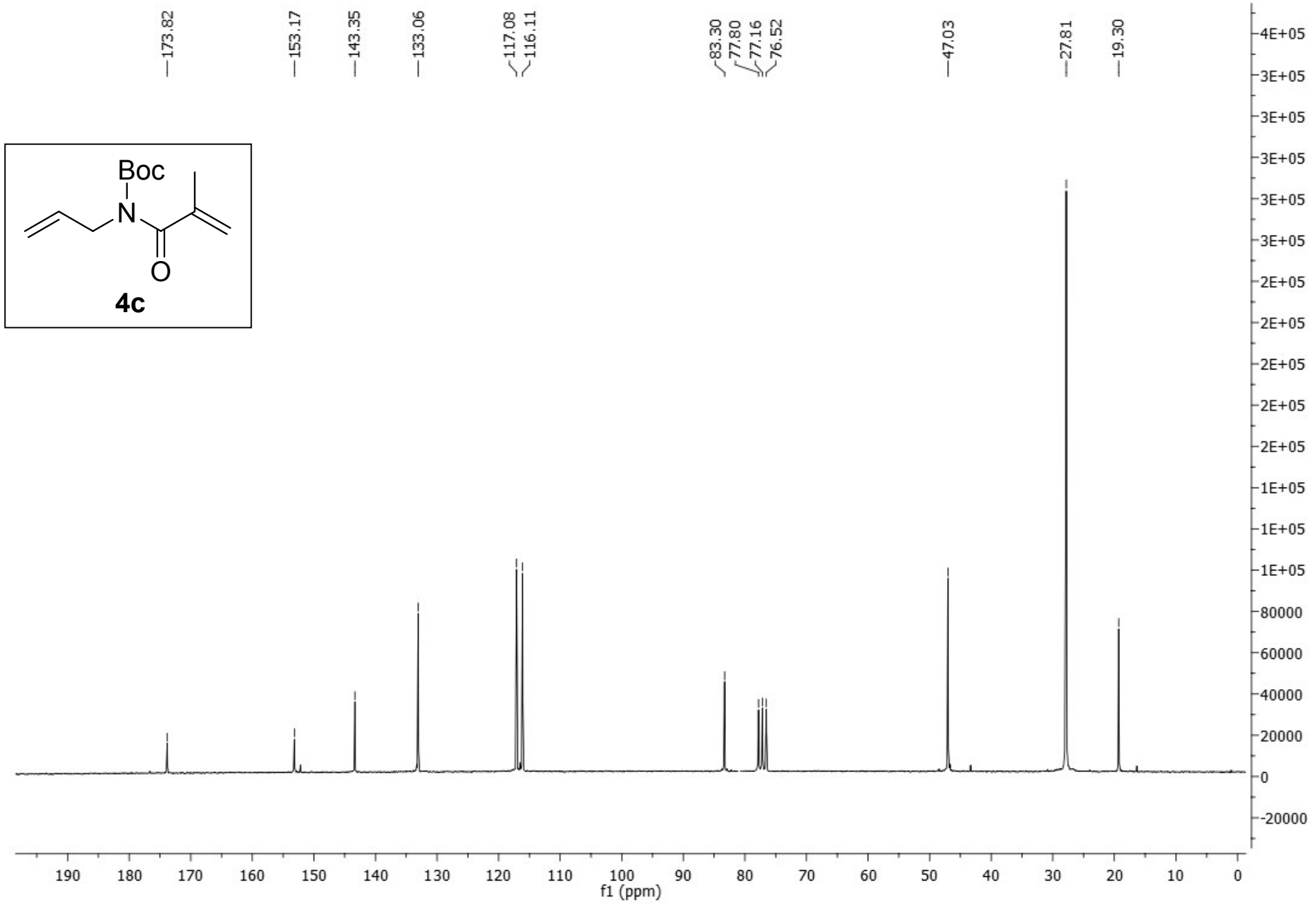
^{13}C NMR (150 MHz) spectrum of *N*-(2-methyl)allylmethacrylamide (4b) in $CDCl_3$



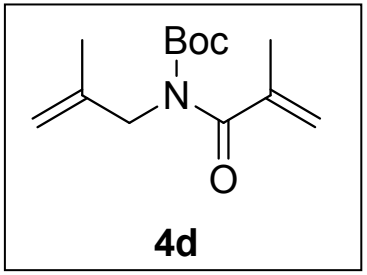
^{1}H NMR (200 MHz) spectrum of *tert*-Butyl allyl(methacryloyl)carbamate (4c) in $CDCl_3$



^{13}C NMR (50.2 MHz) spectrum of *tert*-Butyl allyl(methacryloyl)carbamate (4c) in $CDCl_3$

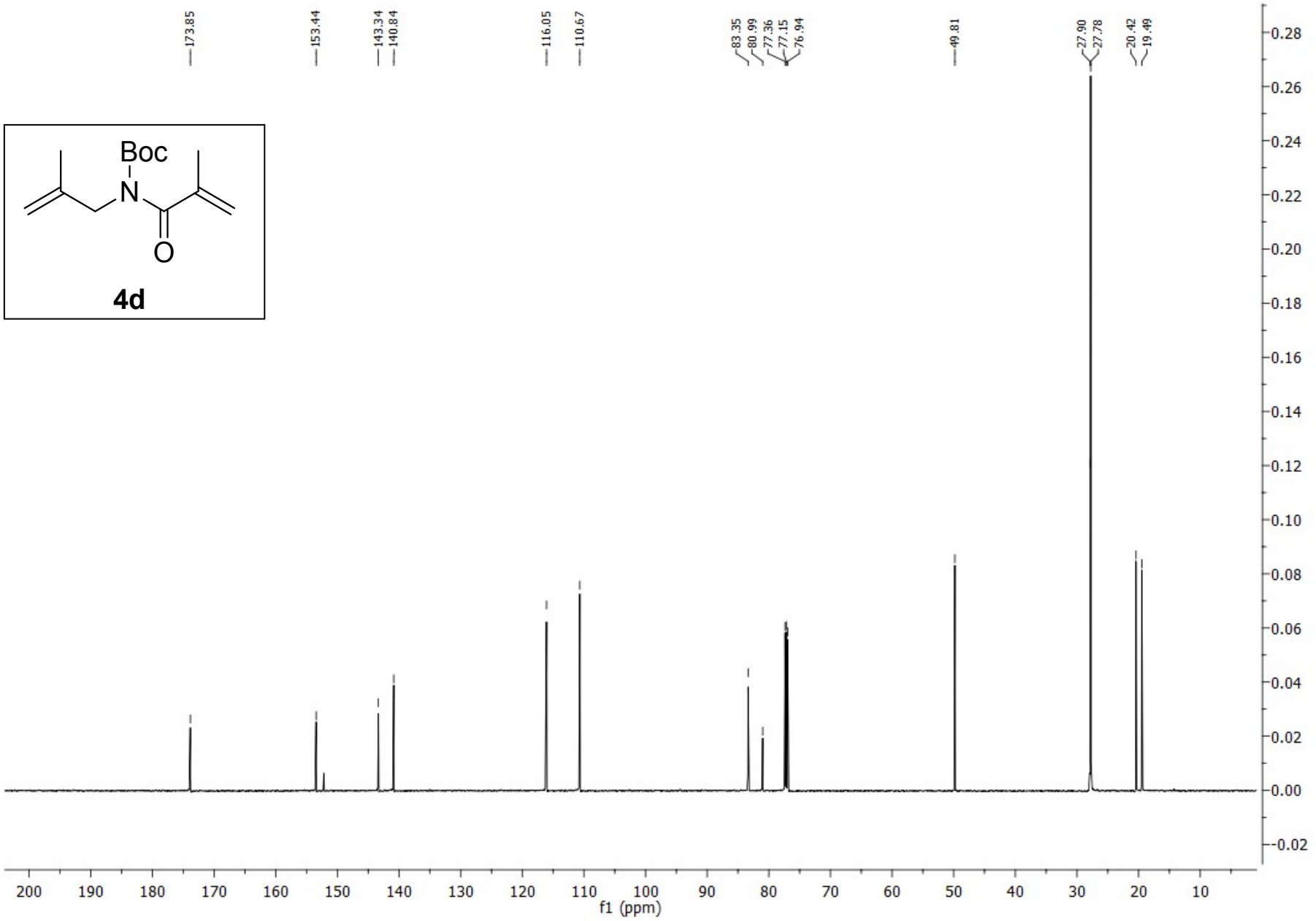


^{1}H NMR (600 MHz) spectrum of *tert*-butyl methacryloyl(2-methylallyl)carbamate (4d) in $CDCl_3$

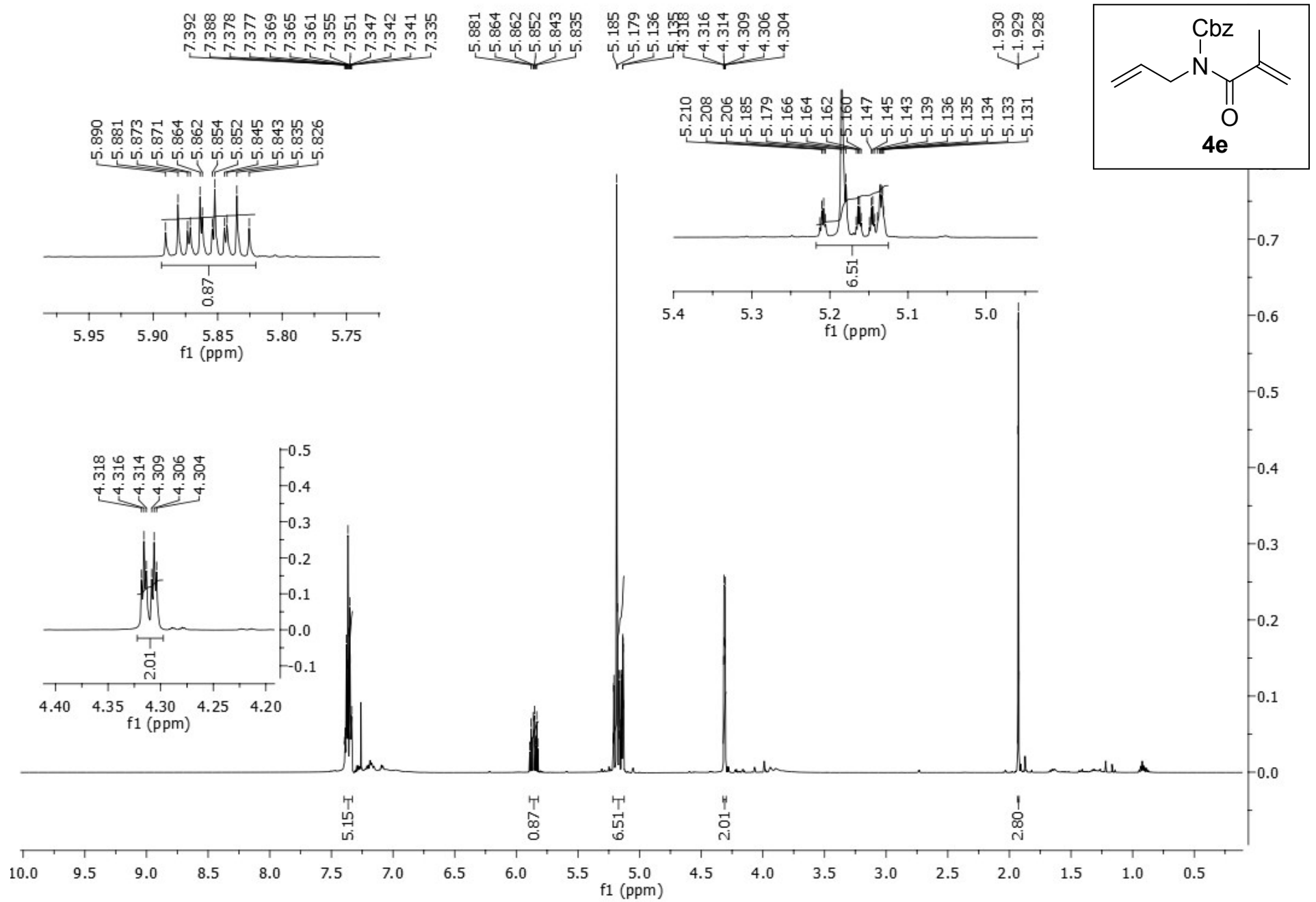


4d

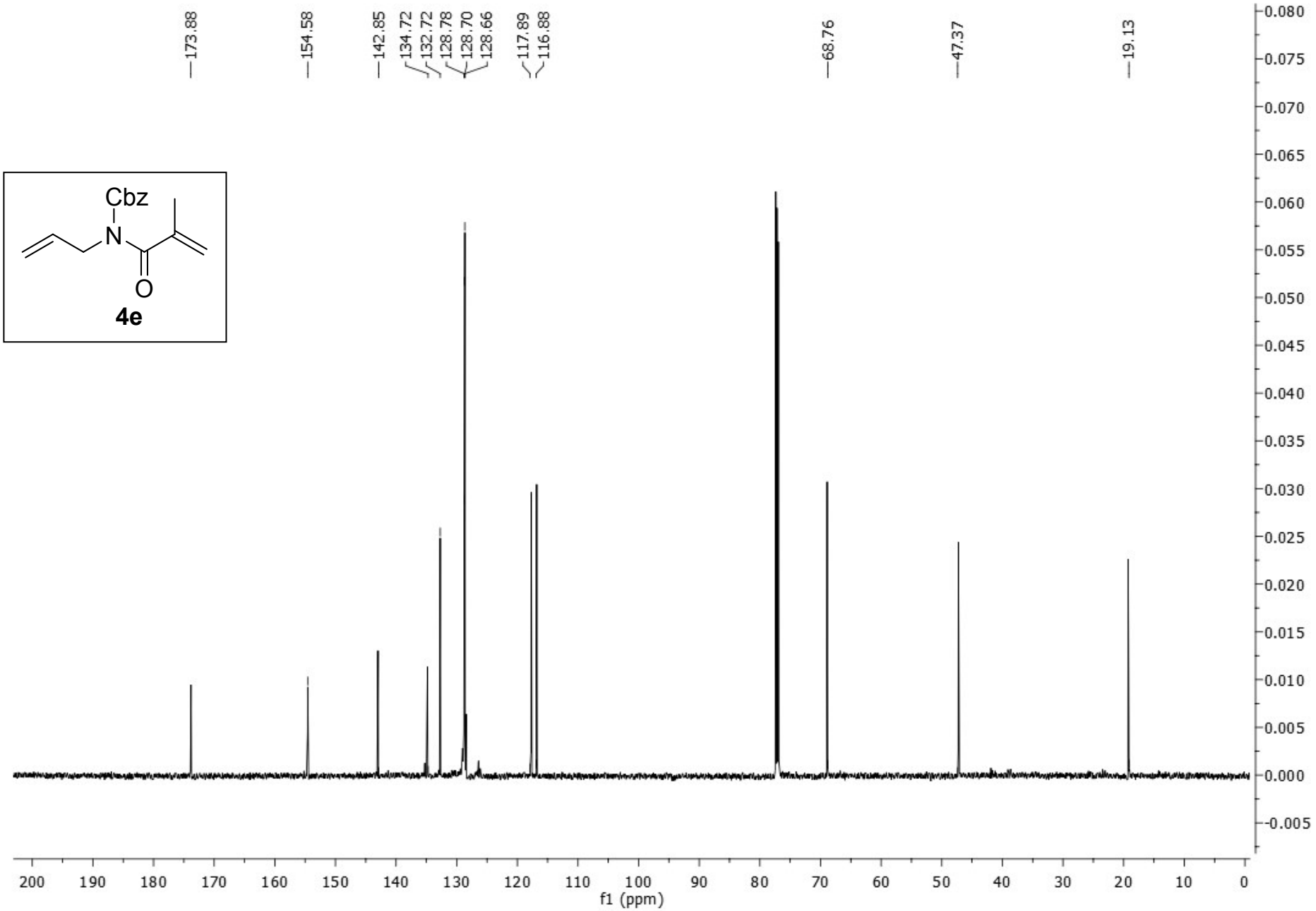
^{13}C NMR (150 MHz) spectrum of *tert*-butyl methacryloyl(2-methylallyl)carbamate (4d) in $CDCl_3$



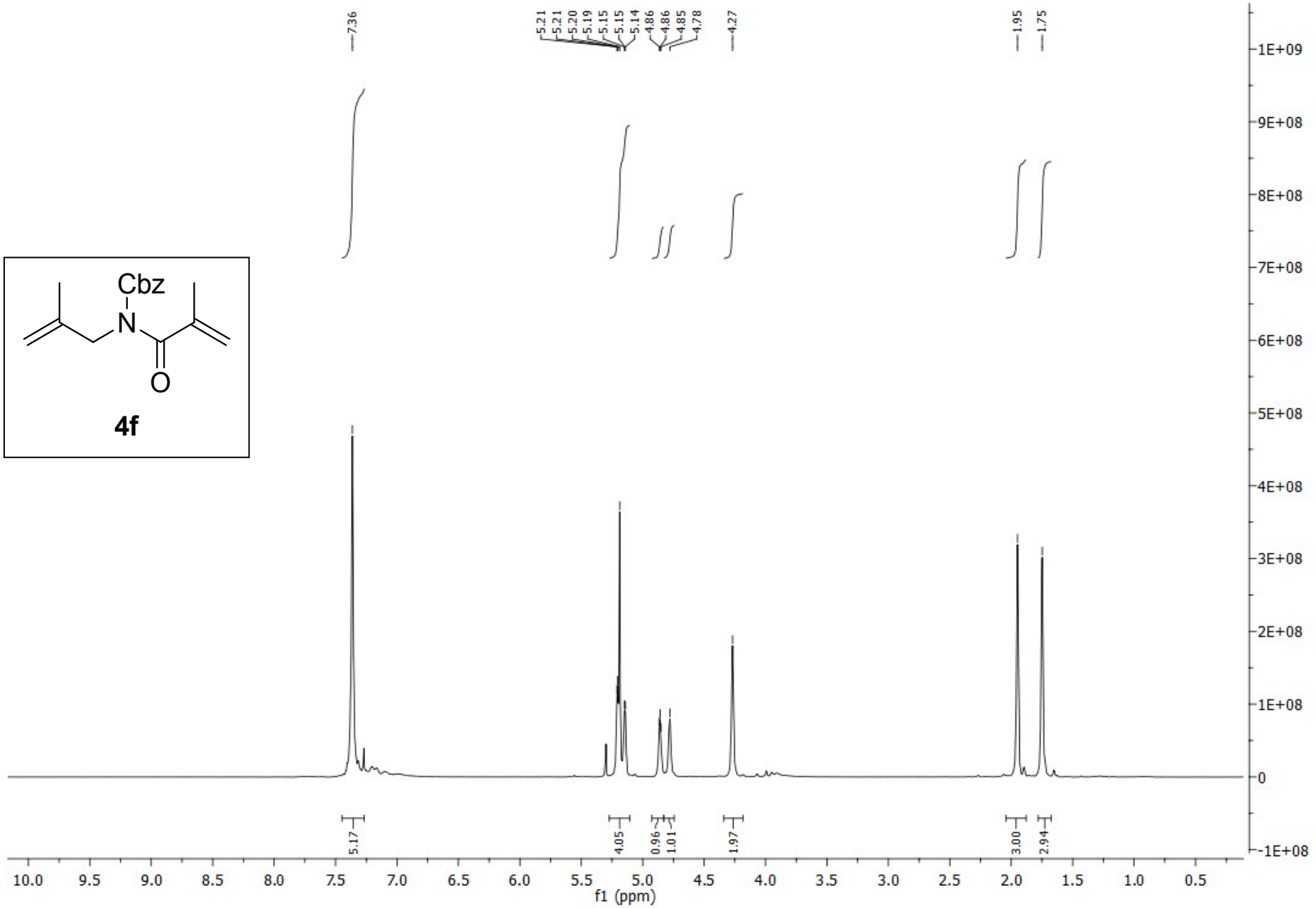
^{1}H NMR (600 MHz) spectrum of Benzyl allyl(methacryloyl)carbamate (4e) in $CDCl_3$



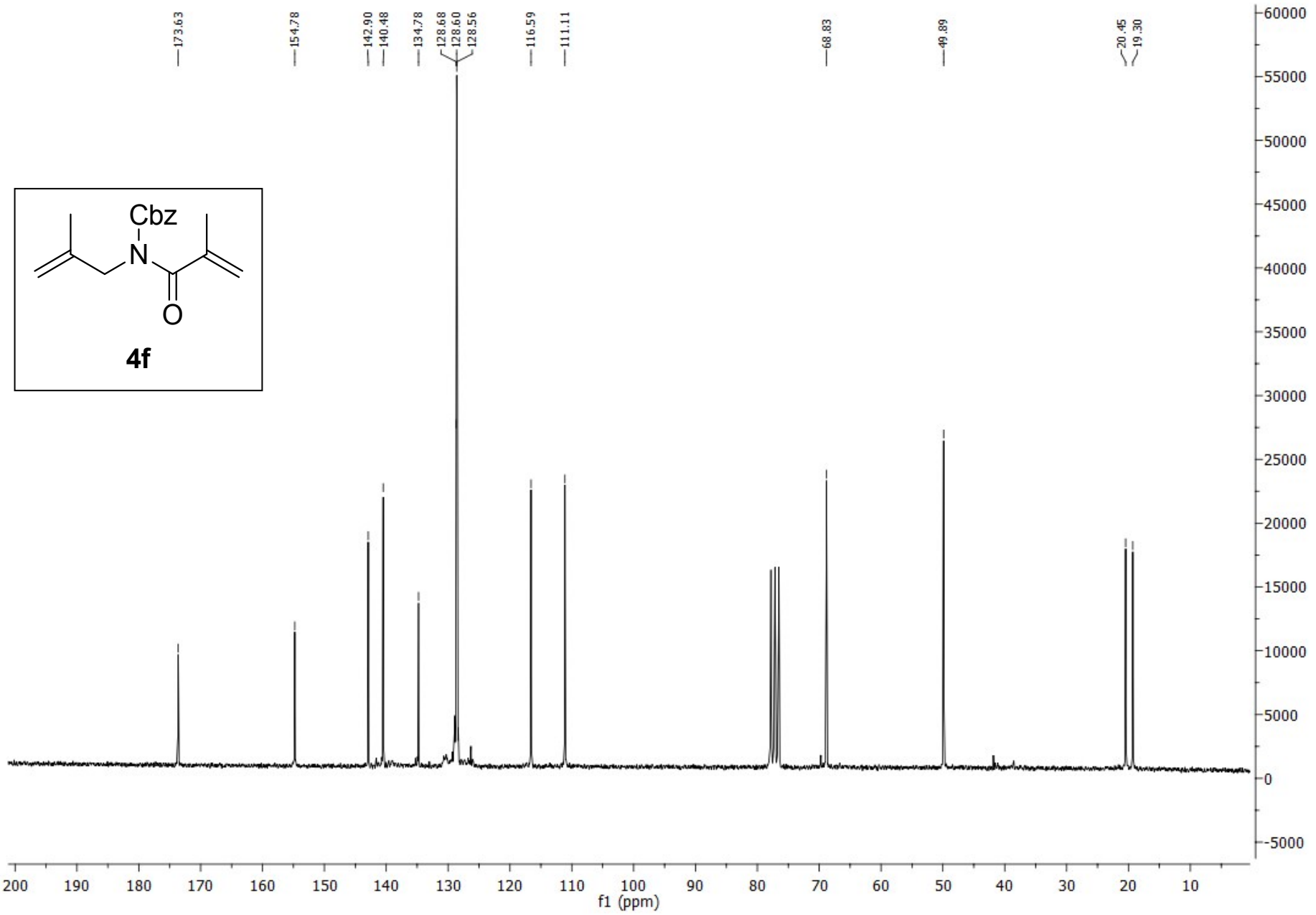
^{13}C NMR (150 MHz) spectrum of Benzyl allyl(methacryloyl)carbamate (4e) in $CDCl_3$



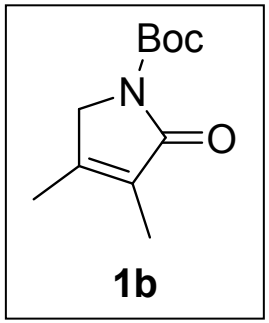
^{1}H NMR (200 MHz) spectrum of benzyl methacryloyl(2-methylallyl)carbamate (4f) in $CDCl_3$



^{13}C NMR (50.2 MHz) spectrum of benzyl methacryloyl(2-methylallyl)carbamate (4f) in $CDCl_3$

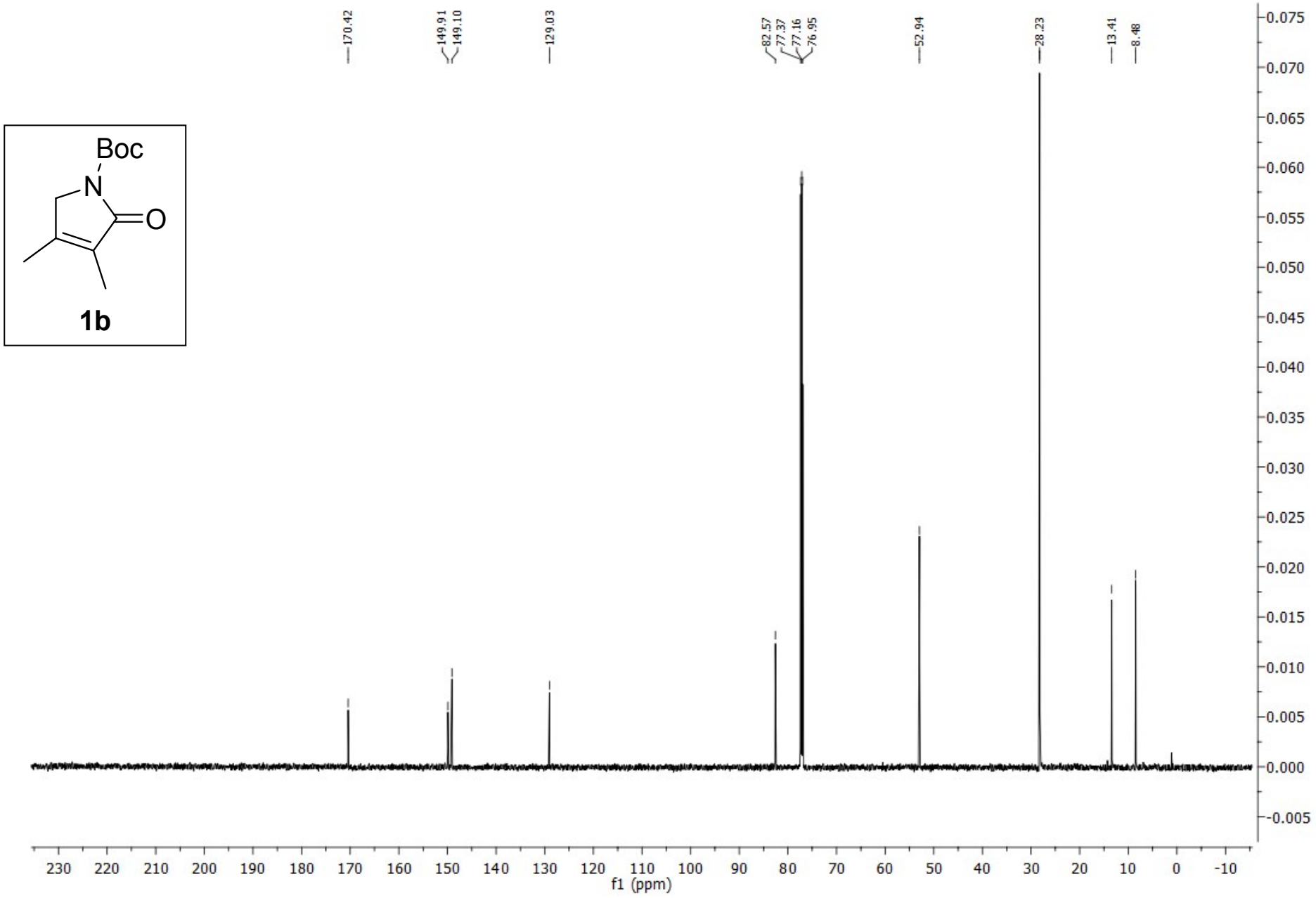


^{1}H NMR spectrum (600 MHZ) of *tert*-butyl 3,4-dimethyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1b) in $CDCl_3$

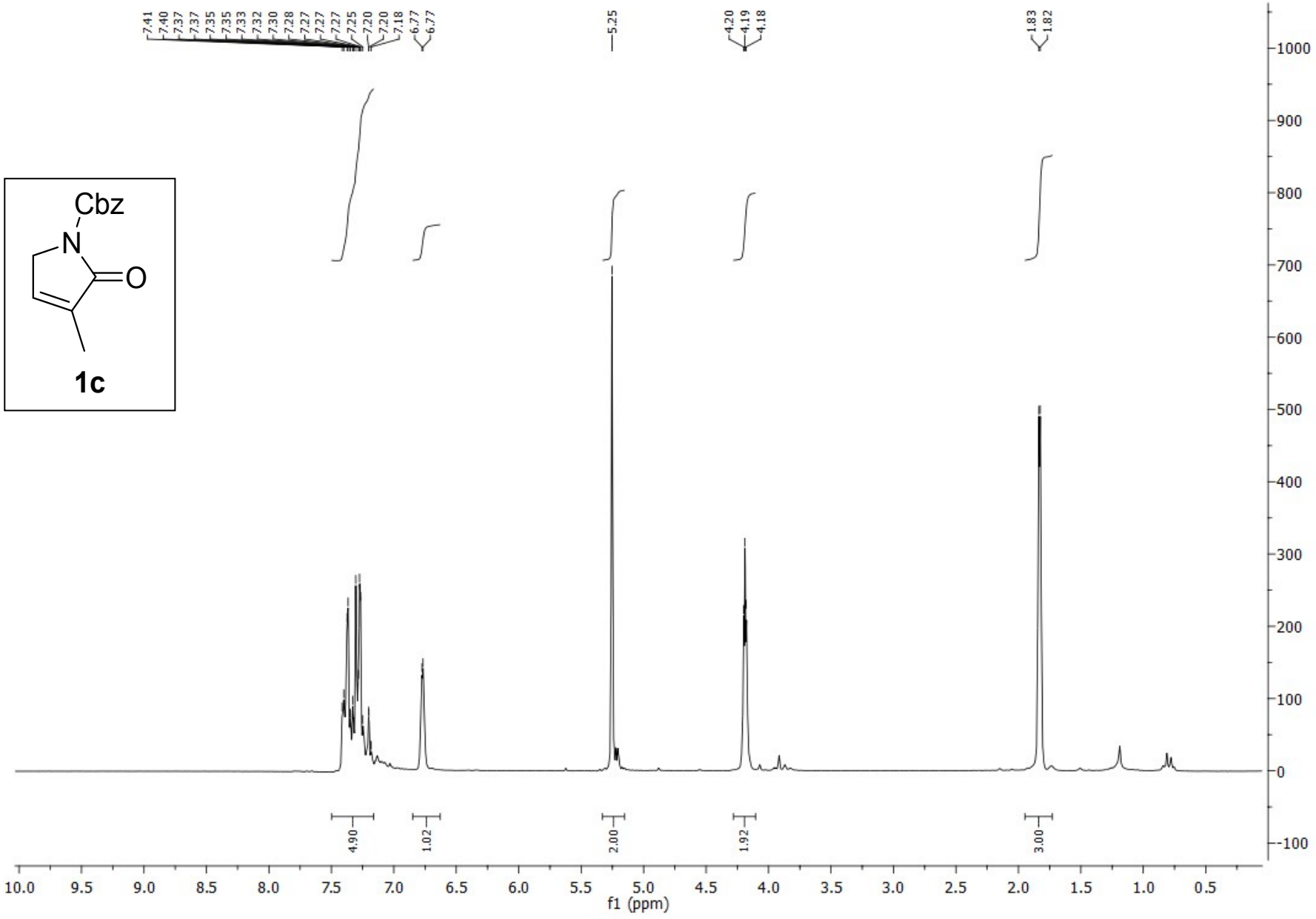


1b

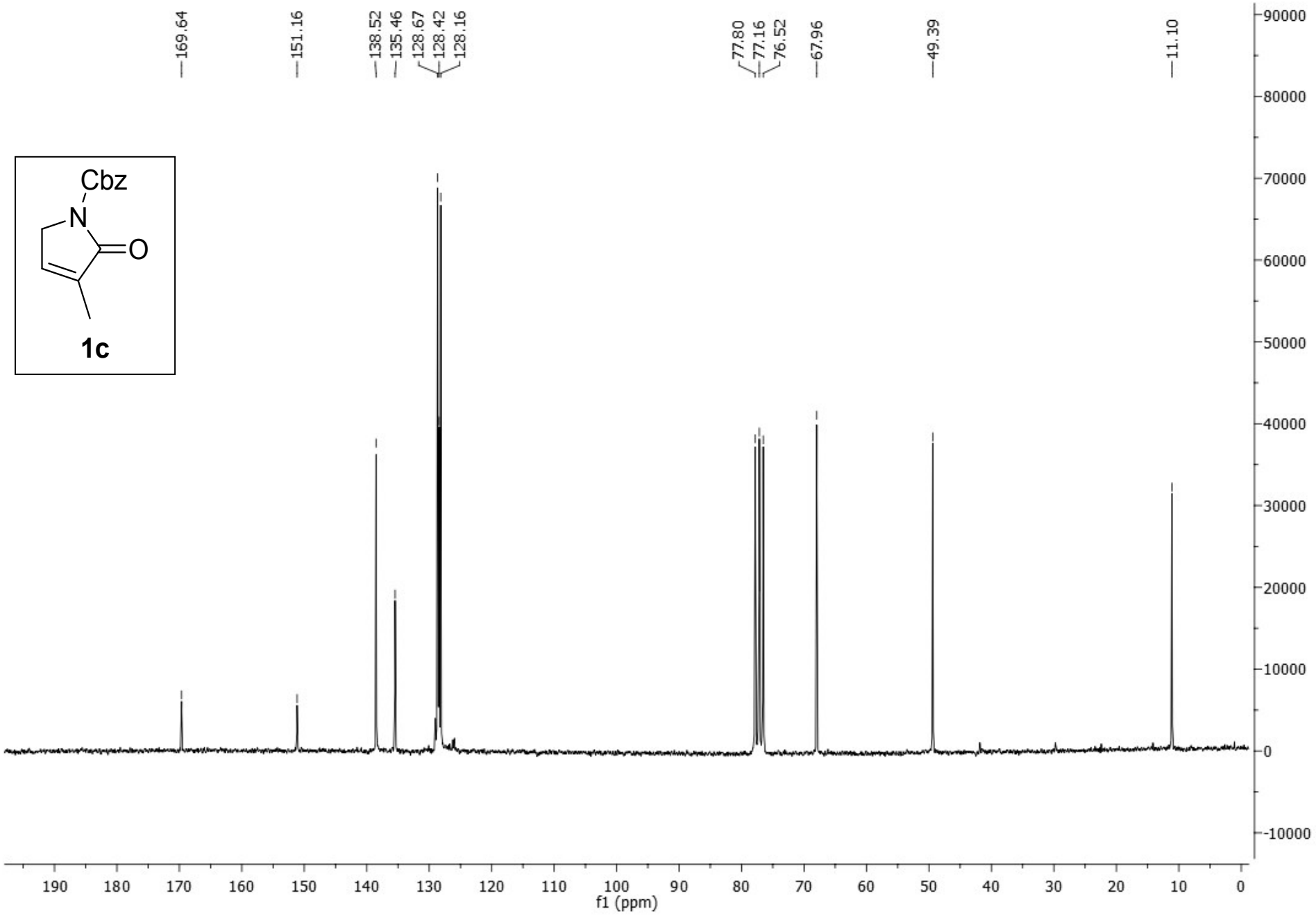
^{13}C NMR spectrum (150 MHz) of *tert*-butyl 3,4-dimethyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1b) in $CDCl_3$



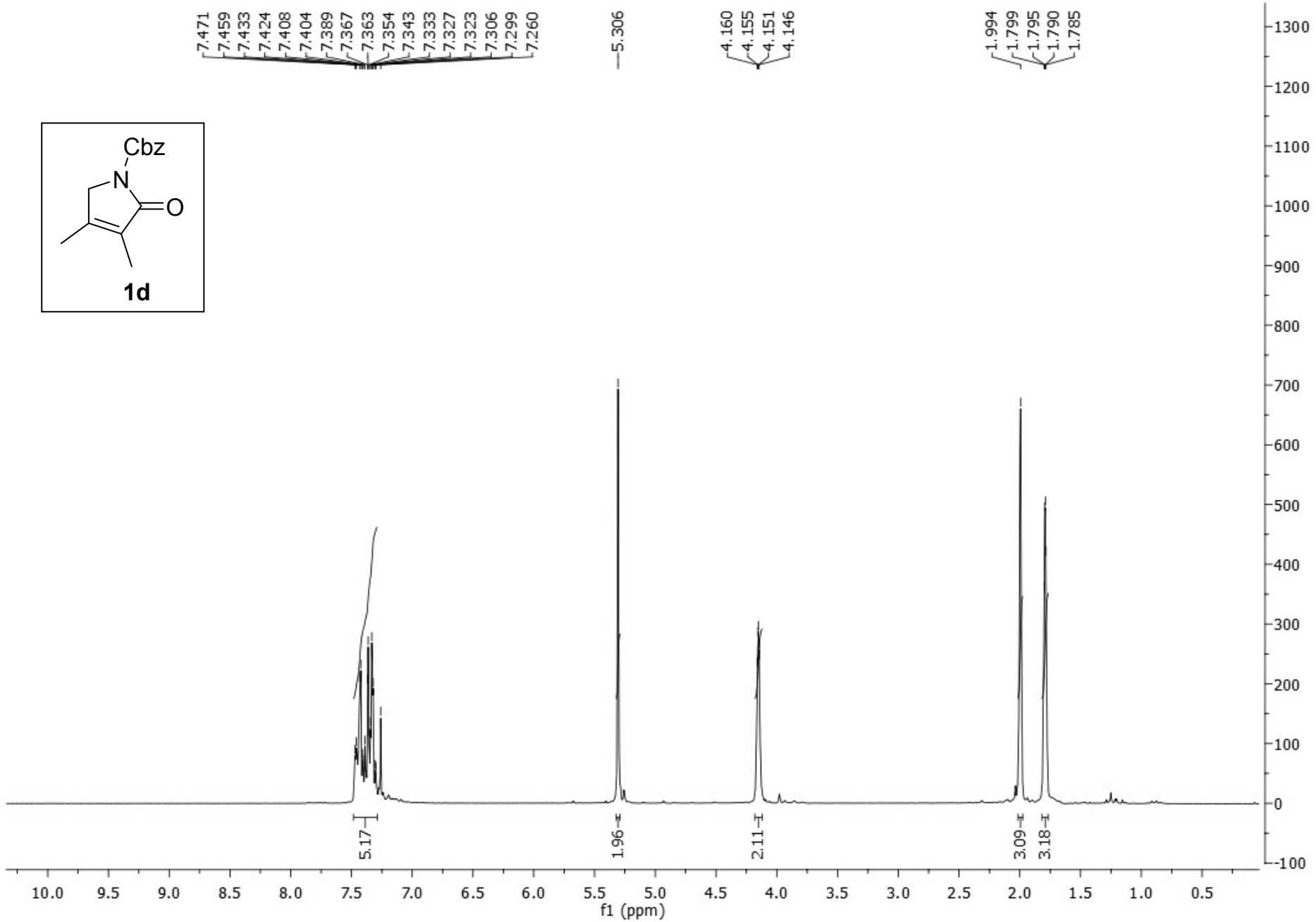
^{1}H NMR spectrum (200 MHz) of benzyl 3-methyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1c) in $CDCl_3$



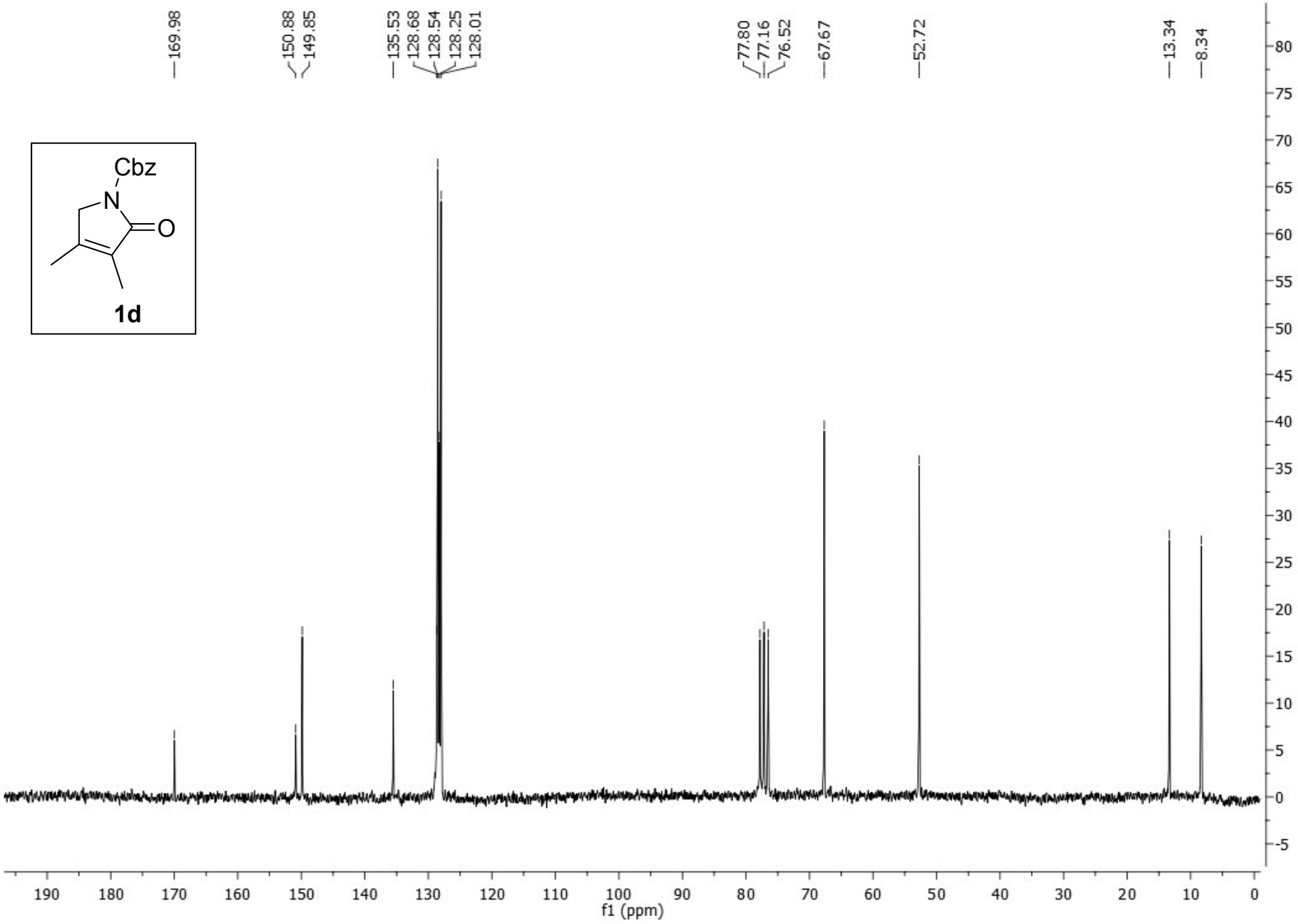
^{13}C NMR spectrum (50.2 MHz) of benzyl 3-methyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1c) in $CDCl_3$



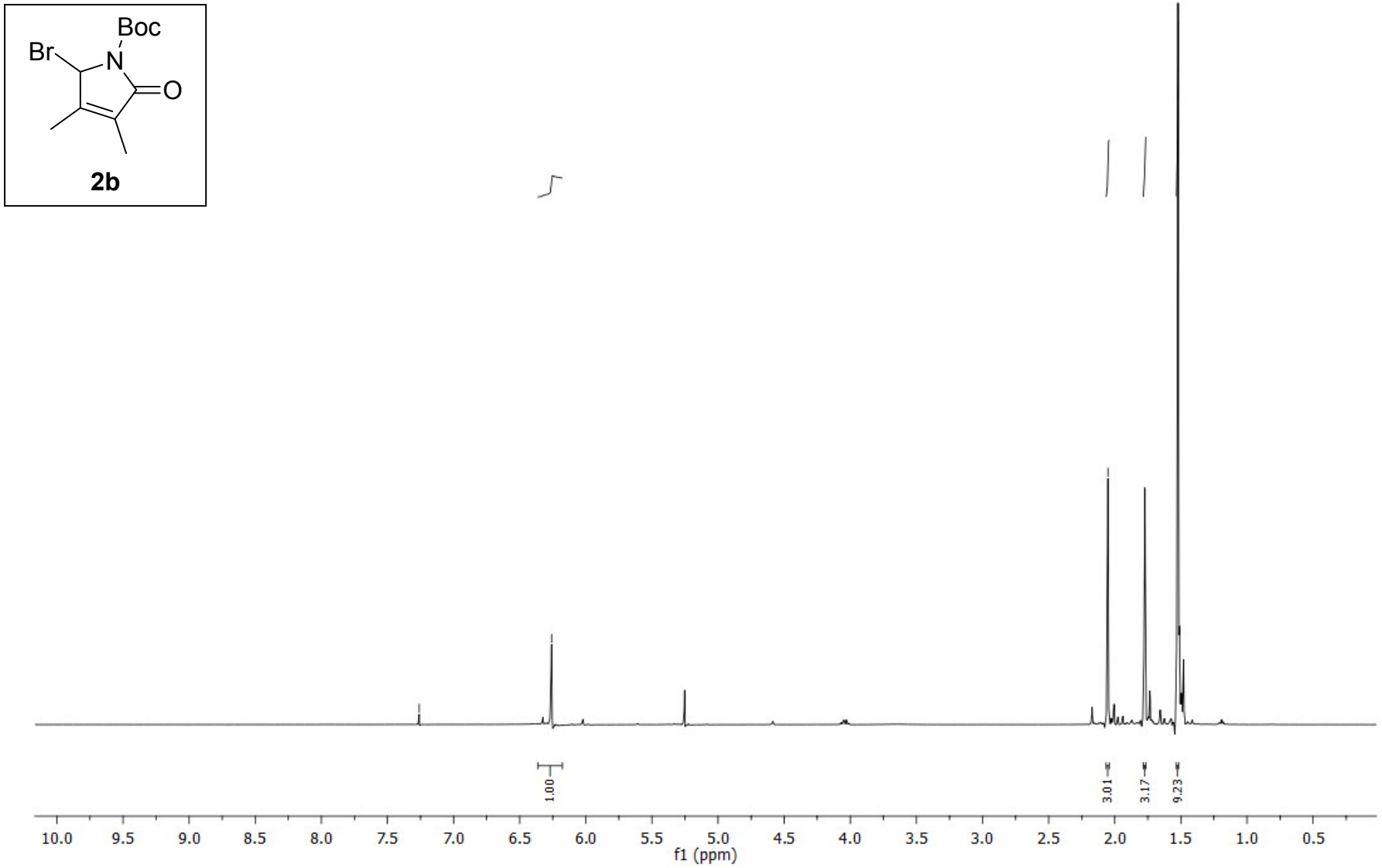
^{1}H NMR spectrum (200 MHz) of benzyl 3,4-dimethyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1d) in $CDCl_3$



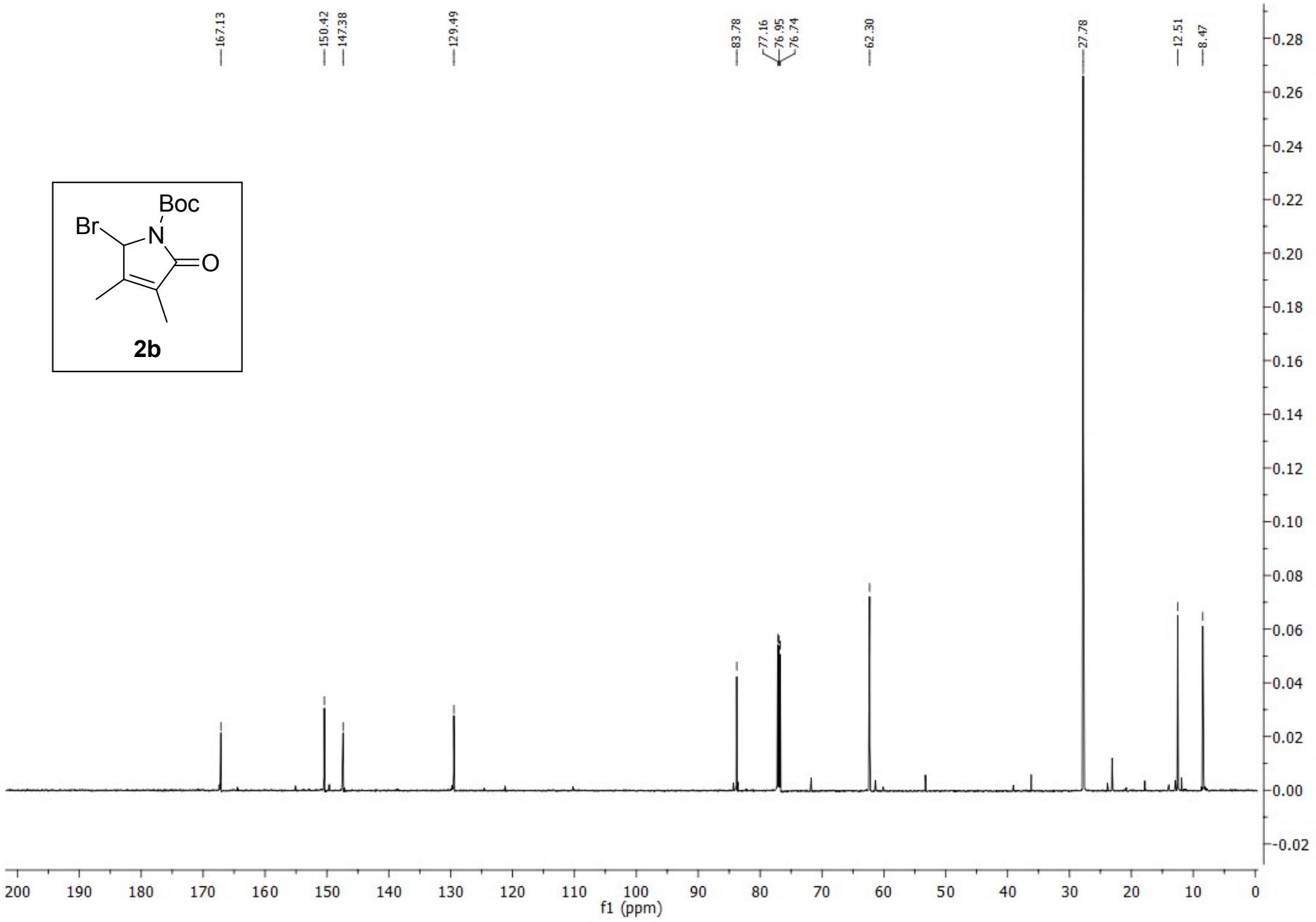
^{13}C NMR spectrum (50.2 MHz) of benzyl 3,4-dimethyl-2-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (1d) in $CDCl_3$



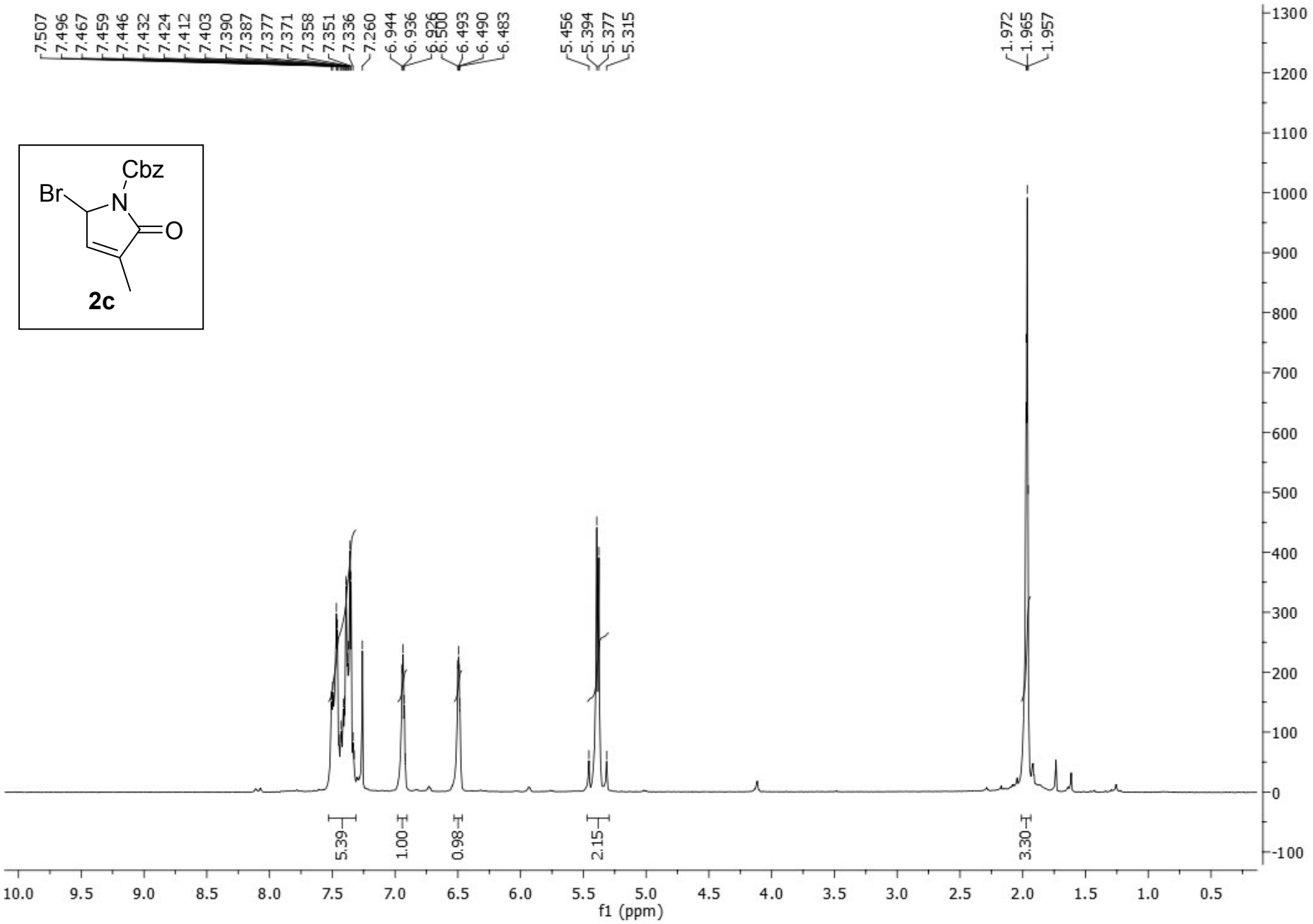
^{1}H NMR spectrum (600 MHz) of *tert*-butyl 2-bromo-3,4-dimethyl-5-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (2b) in $CDCl_3$



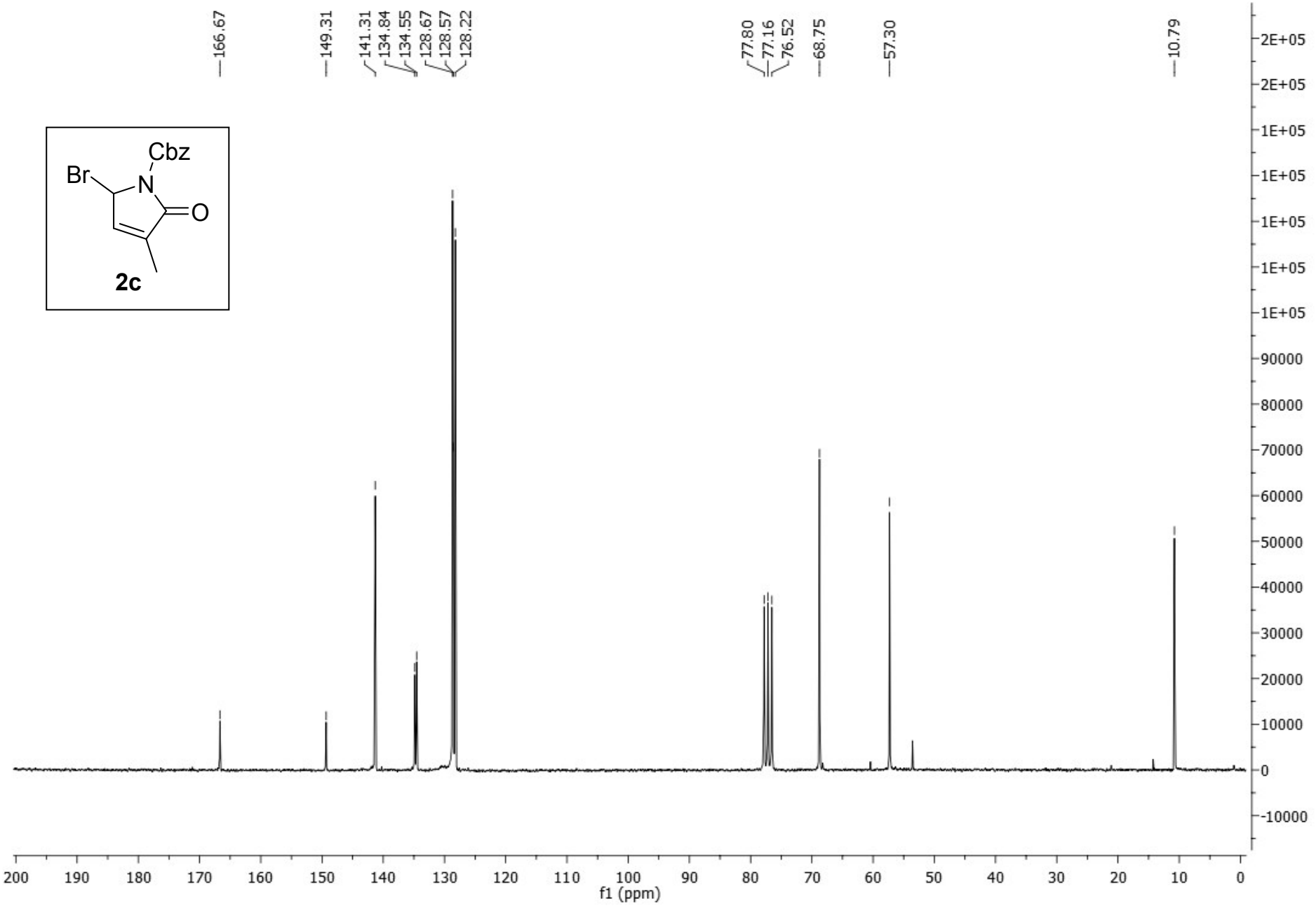
^{13}C NMR spectrum (150 MHz) of *tert*-butyl 2-bromo-3,4-dimethyl-5-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (2b) in $CDCl_3$



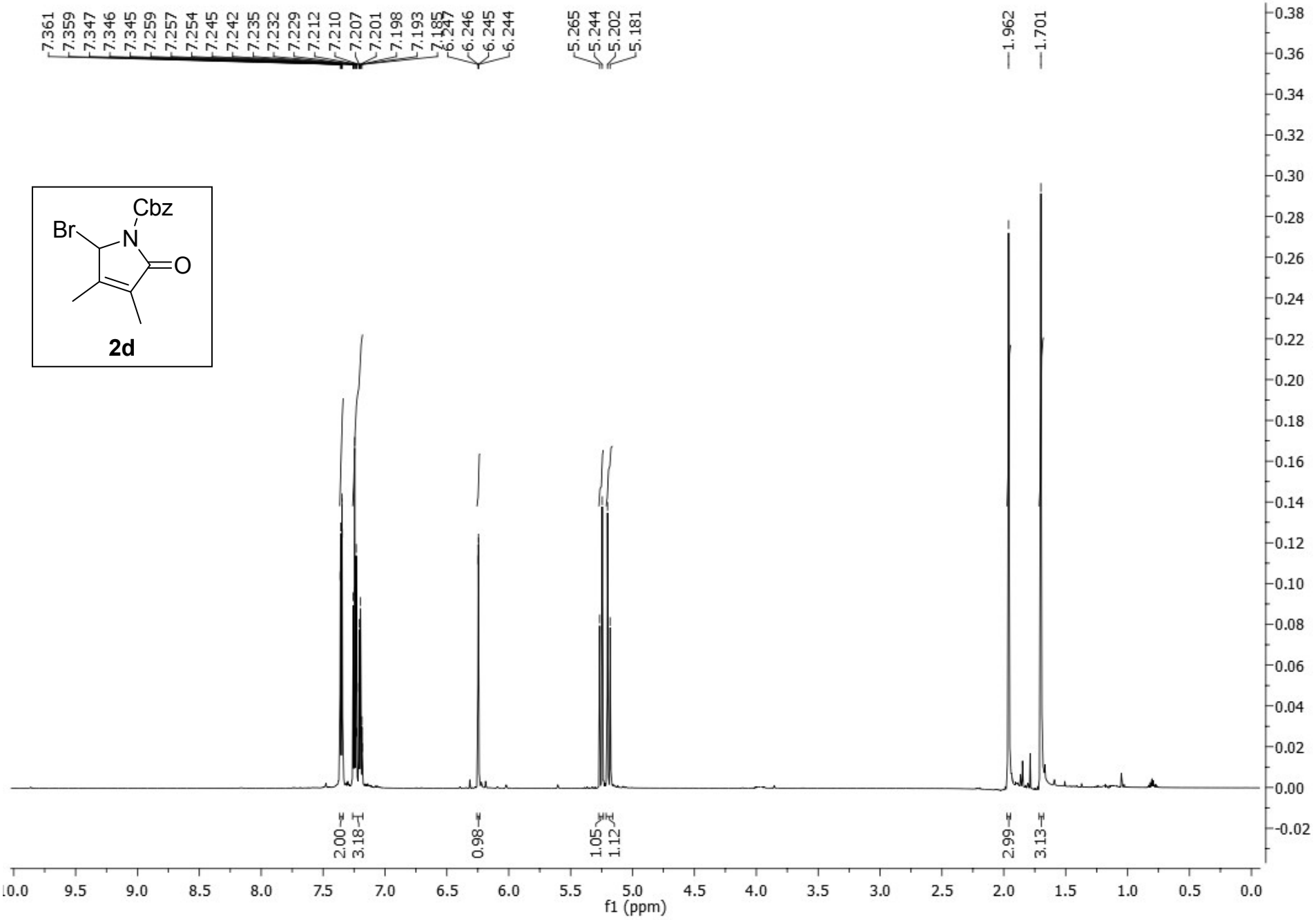
^{1}H NMR spectrum (200 MHz) benzyl 5-bromo-3-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (2c) in $CDCl_3$



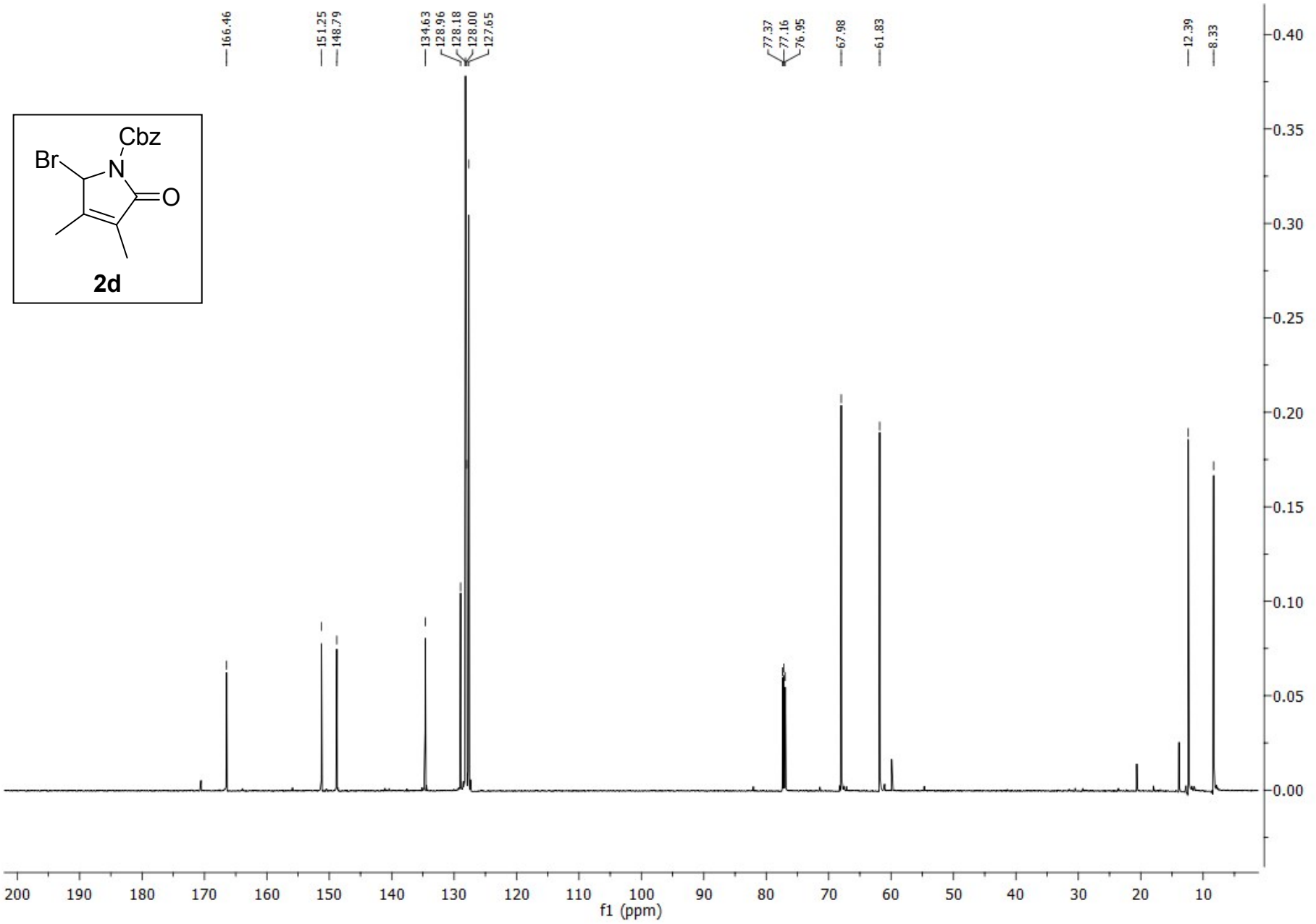
^{13}C NMR spectrum (50.2 MHz) benzyl 5-bromo-3-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (2c) in $CDCl_3$



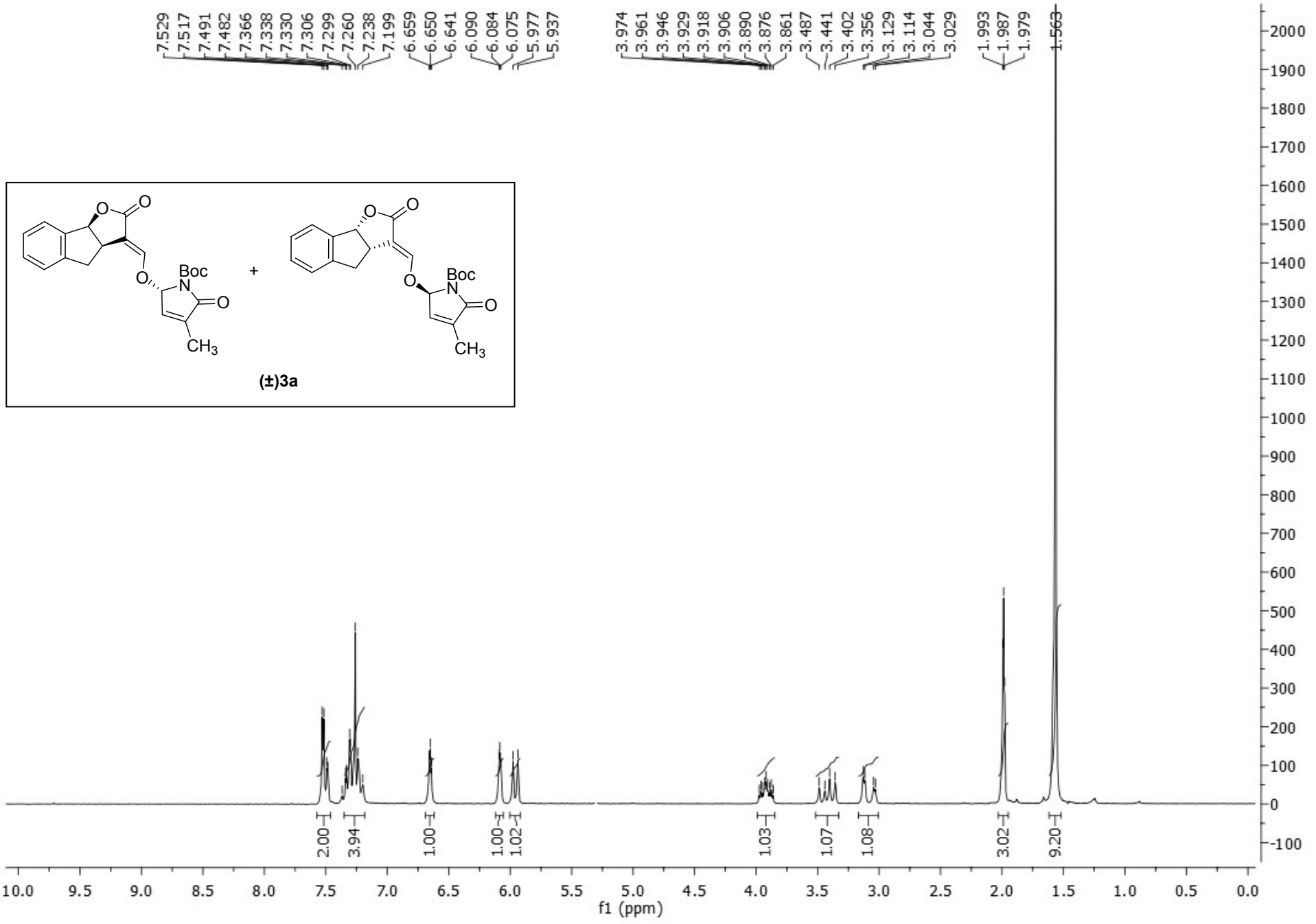
^{1}H NMR spectrum (600 MHz) of benzyl 2-bromo-3,4-dimethyl-5-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (2d) in $CDCl_3$



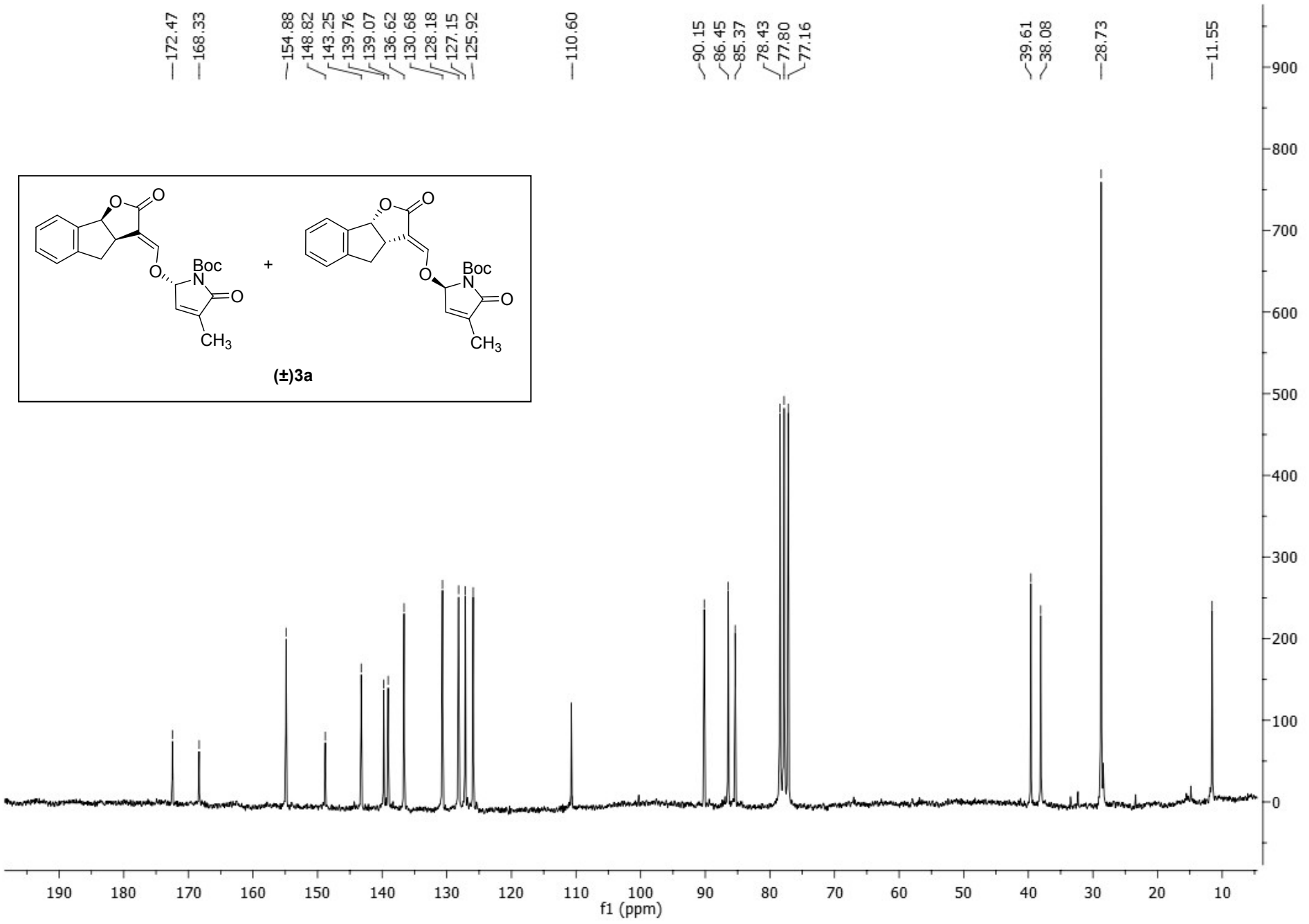
^{13}C NMR spectrum (150 MHz) of benzyl 2-bromo-3,4-dimethyl-5-oxo-2,5-dihydro-1H-pyrrole-1-carboxylate (2d) in $CDCl_3$



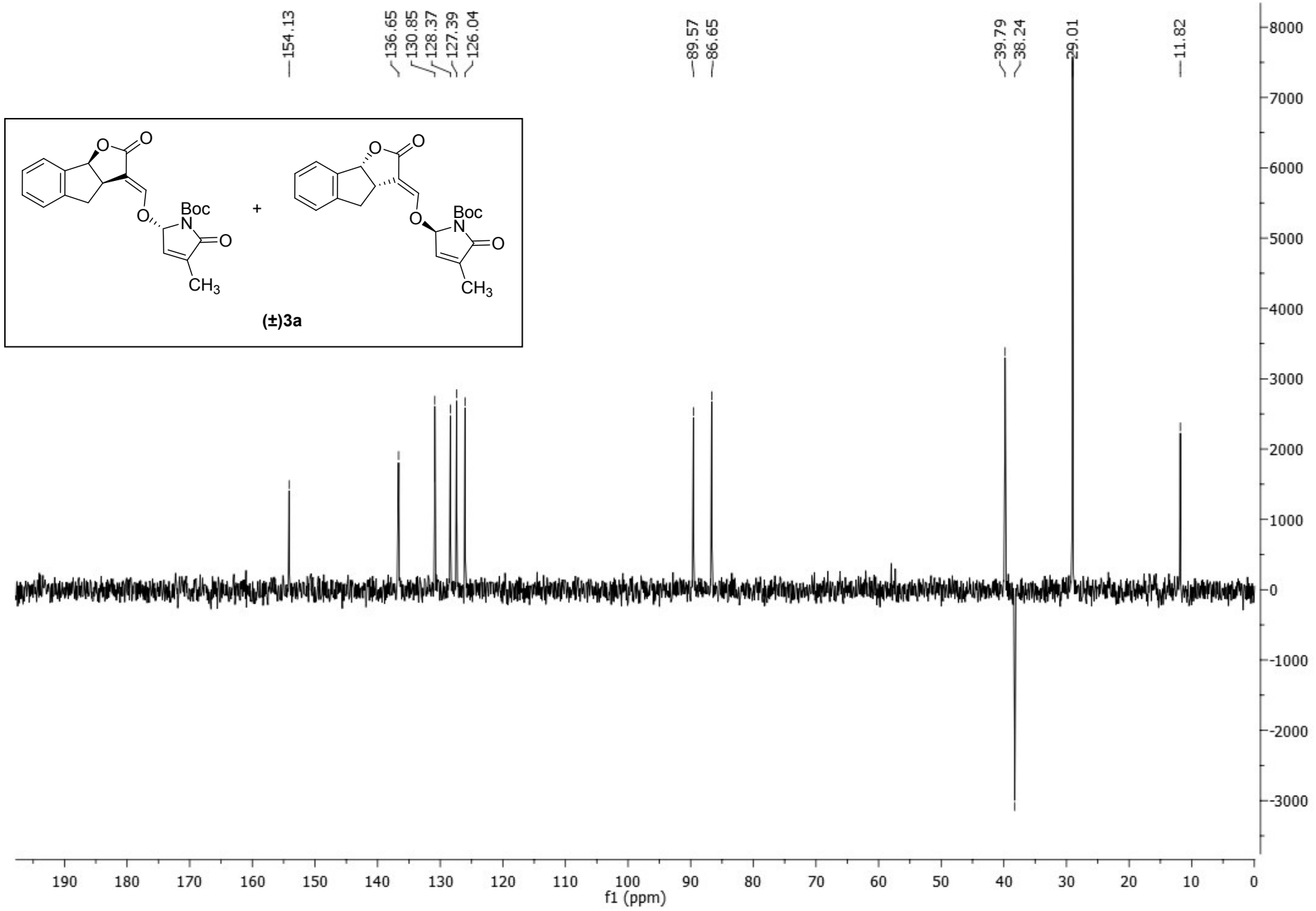
^{1}H NMR (200 MHz) spectrum of (±)3a in $CDCl_3$



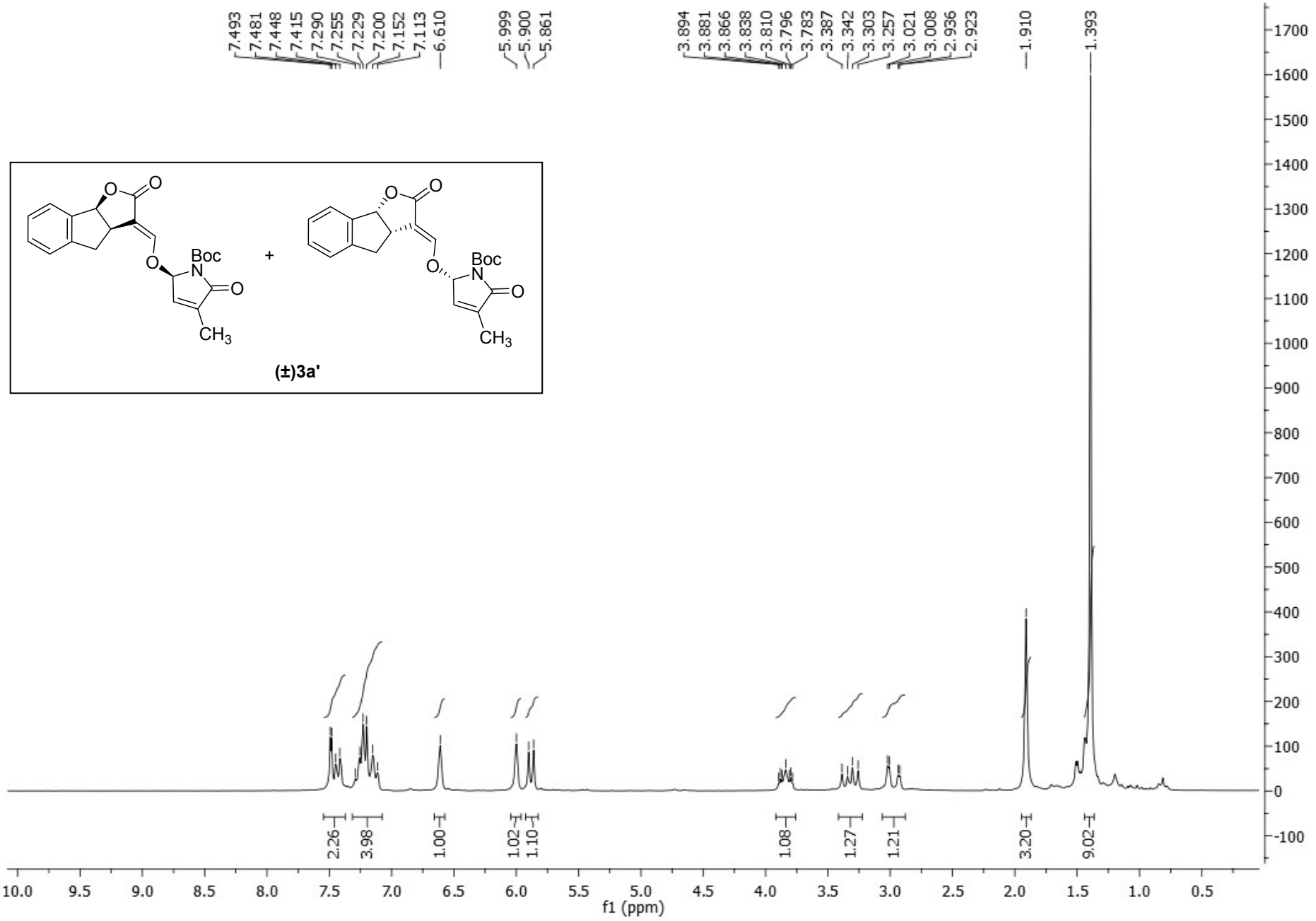
^{13}C NMR (50.2 MHz) spectrum of (±)3a in $CDCl_3$



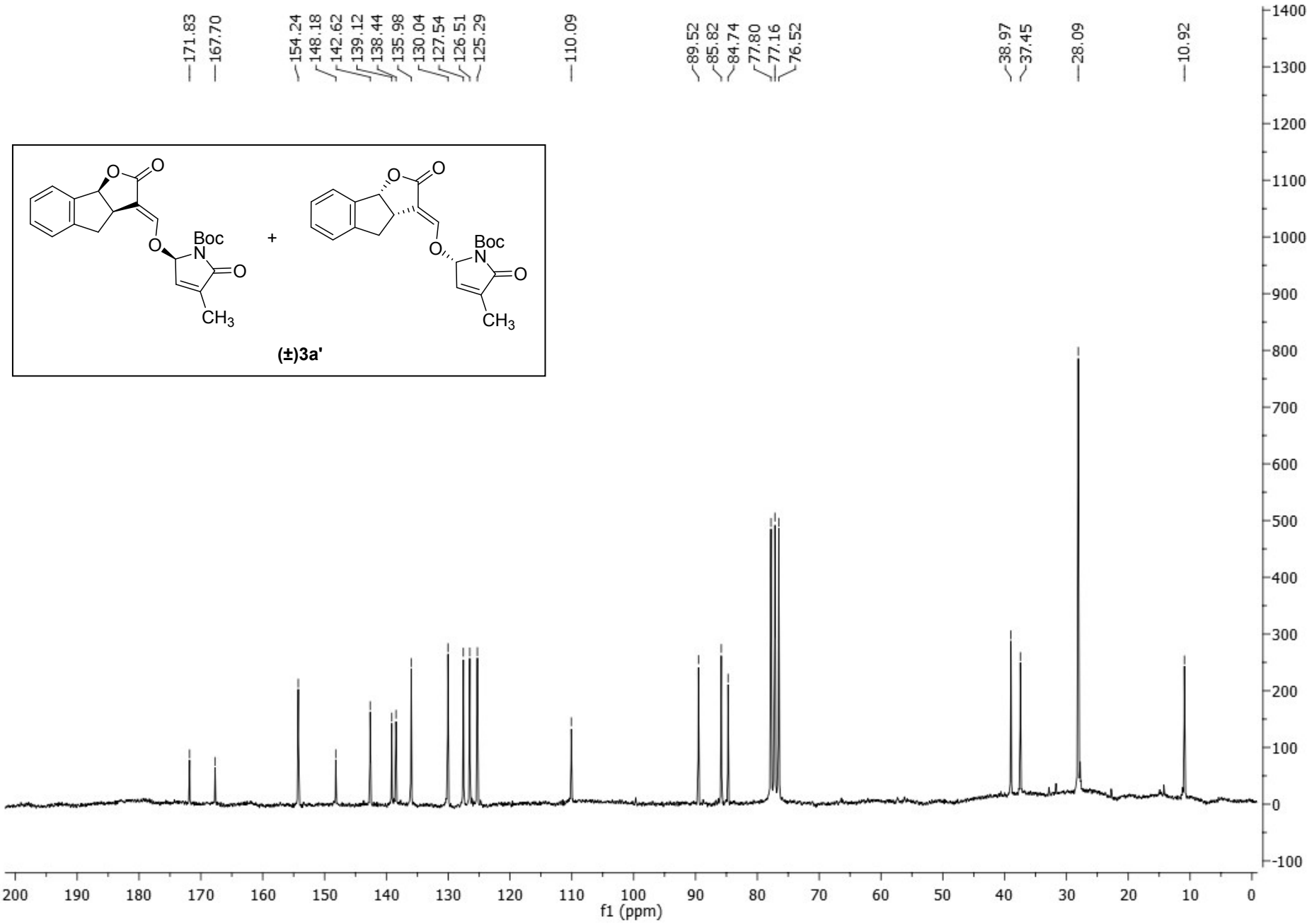
DEPT-135 spectrum of (±)3a in $CDCl_3$



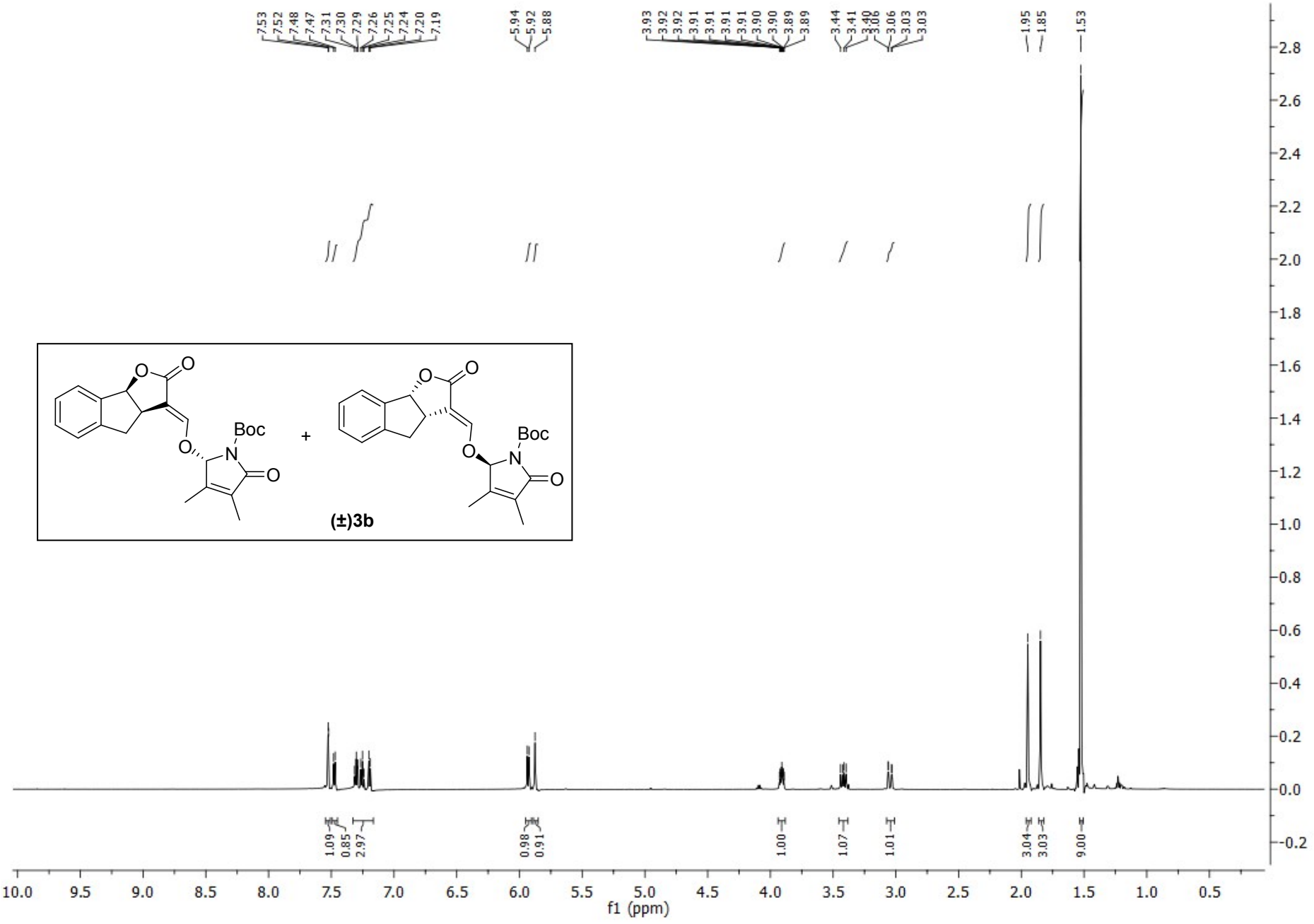
^{1}H NMR (200 MHz) spectrum of (±)3a′ in $CDCl_3$



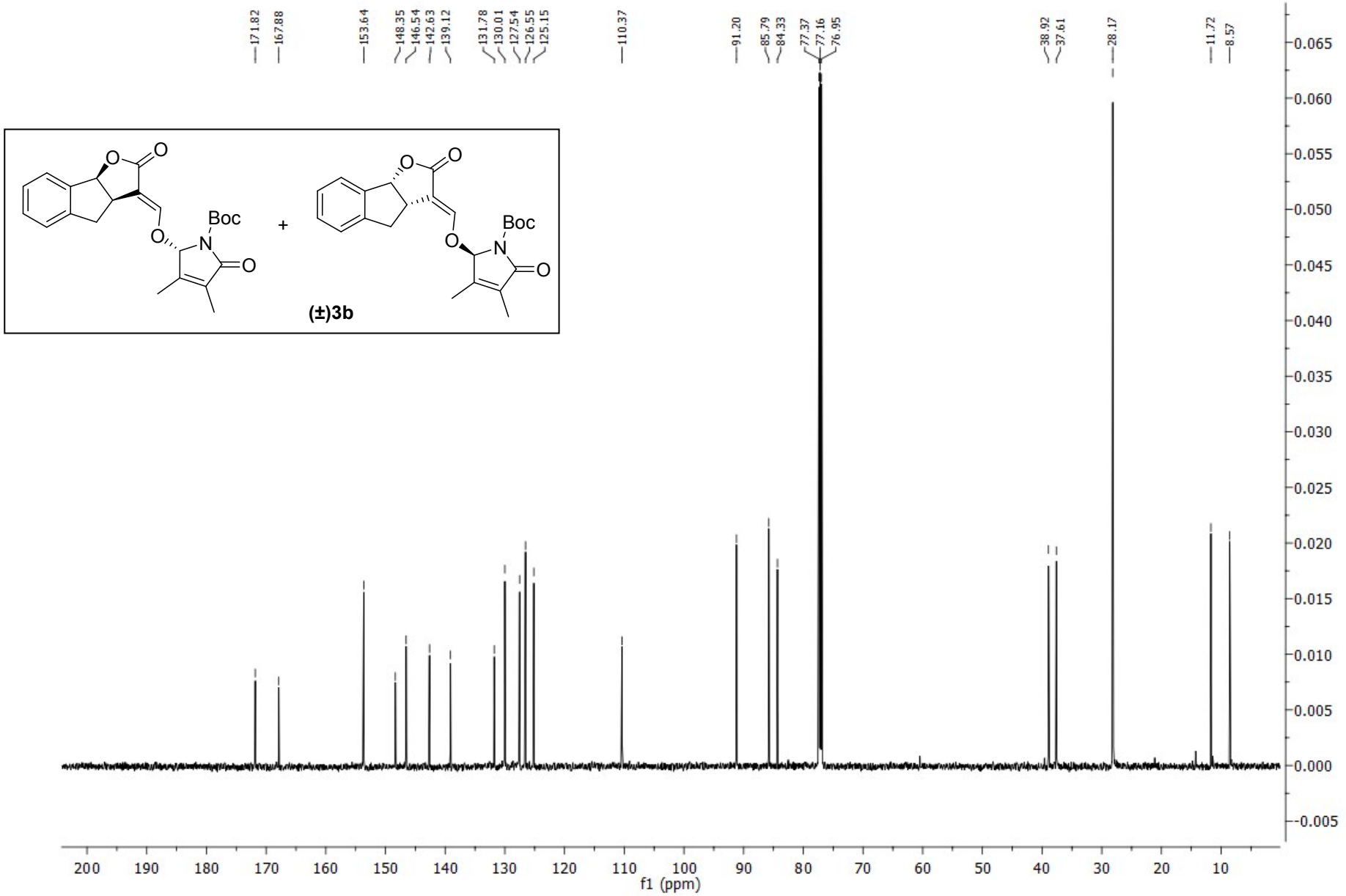
^{13}C NMR (50.2 MHz) spectrum of (±)3a' in $CDCl_3$



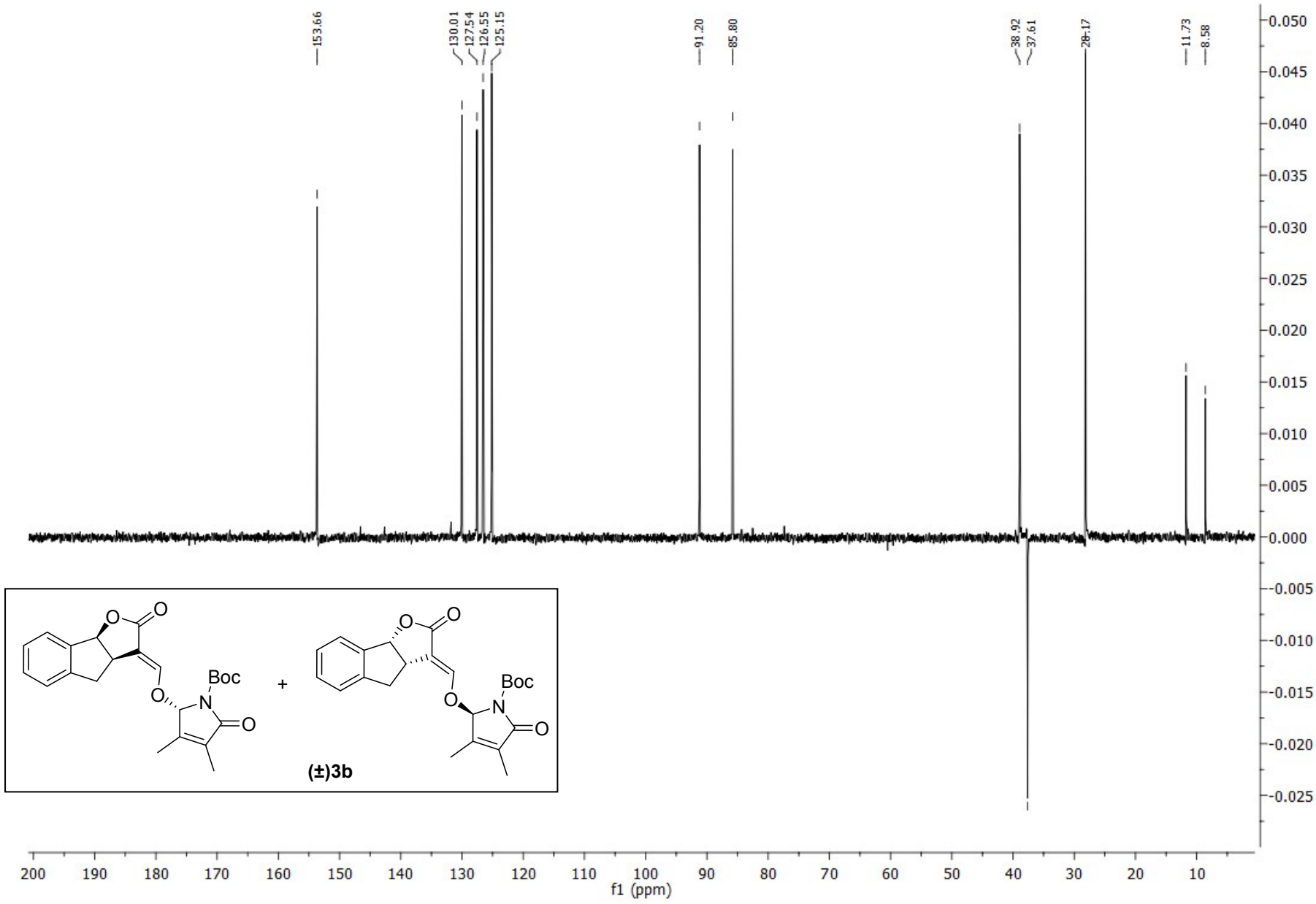
^{1}H NMR (600 MHz) spectrum of (±)3b in $CDCl_3$



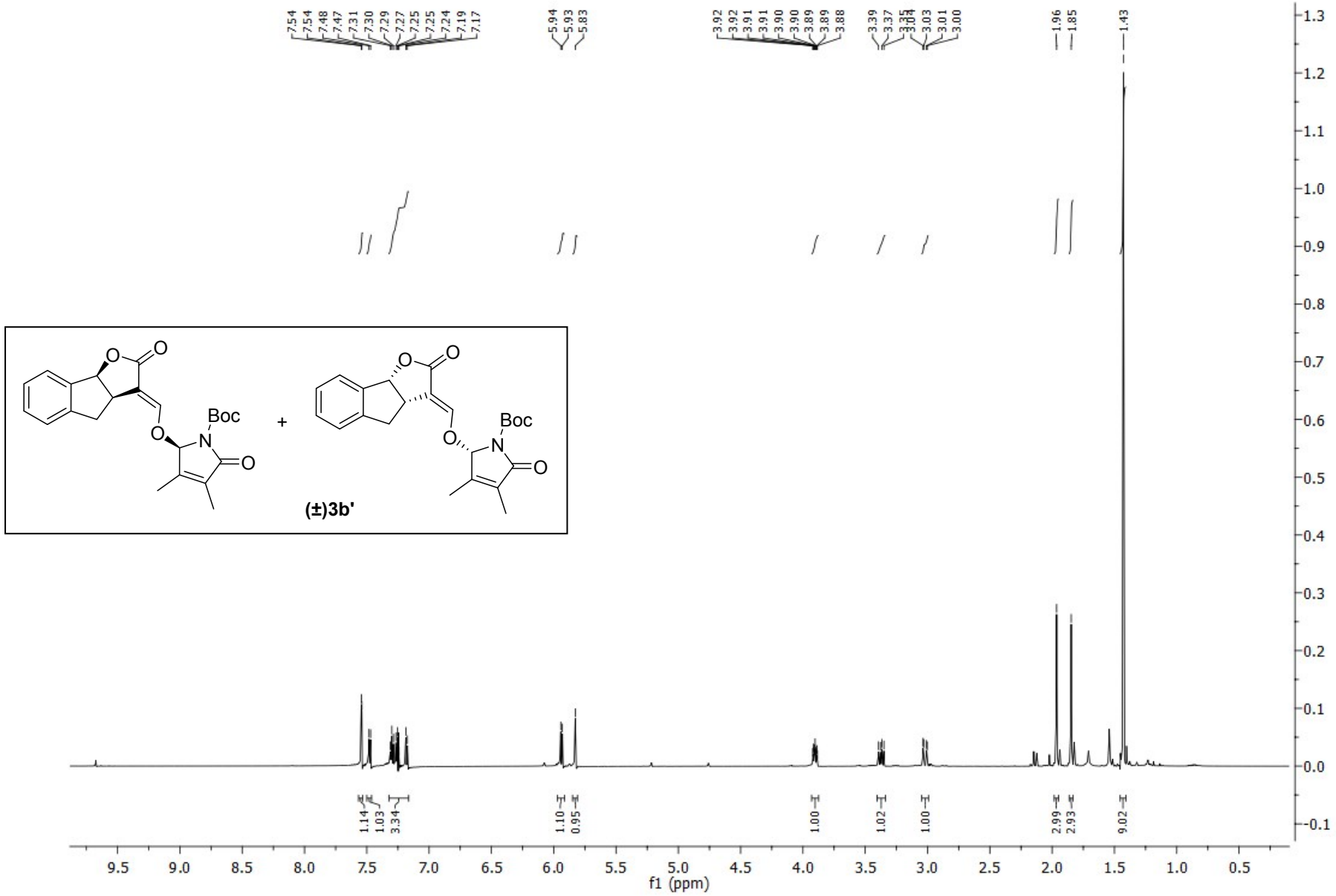
^{13}C NMR (150 MHz) spectrum of (±)3b in $CDCl_3$



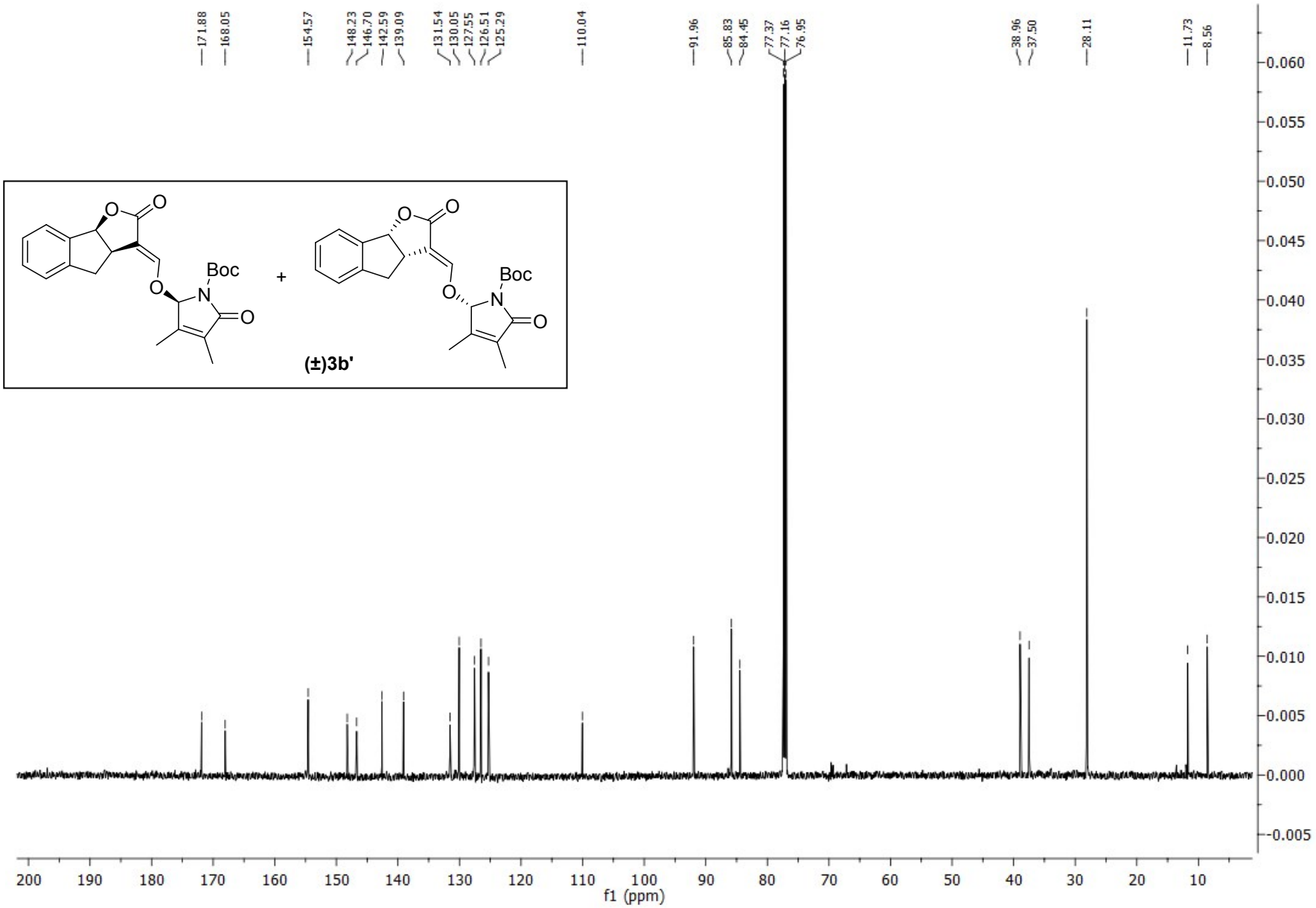
DEPT-135 spectrum of (±)3b in $CDCl_3$



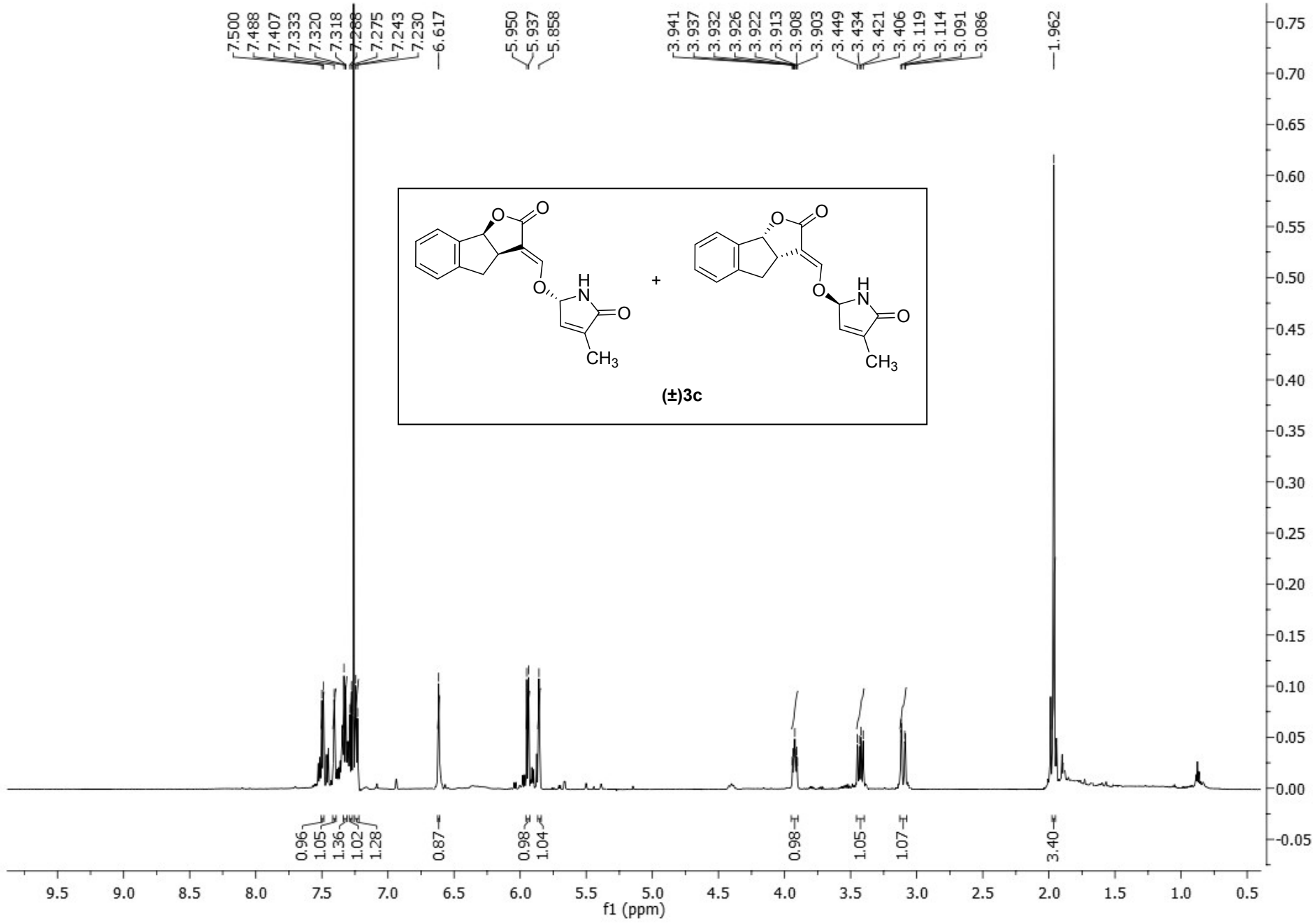
^{1}H NMR (600 MHz) spectrum of (±)3b' in $CDCl_3$



^{13}C NMR (150 MHz) spectrum of (±)3b' in $CDCl_3$

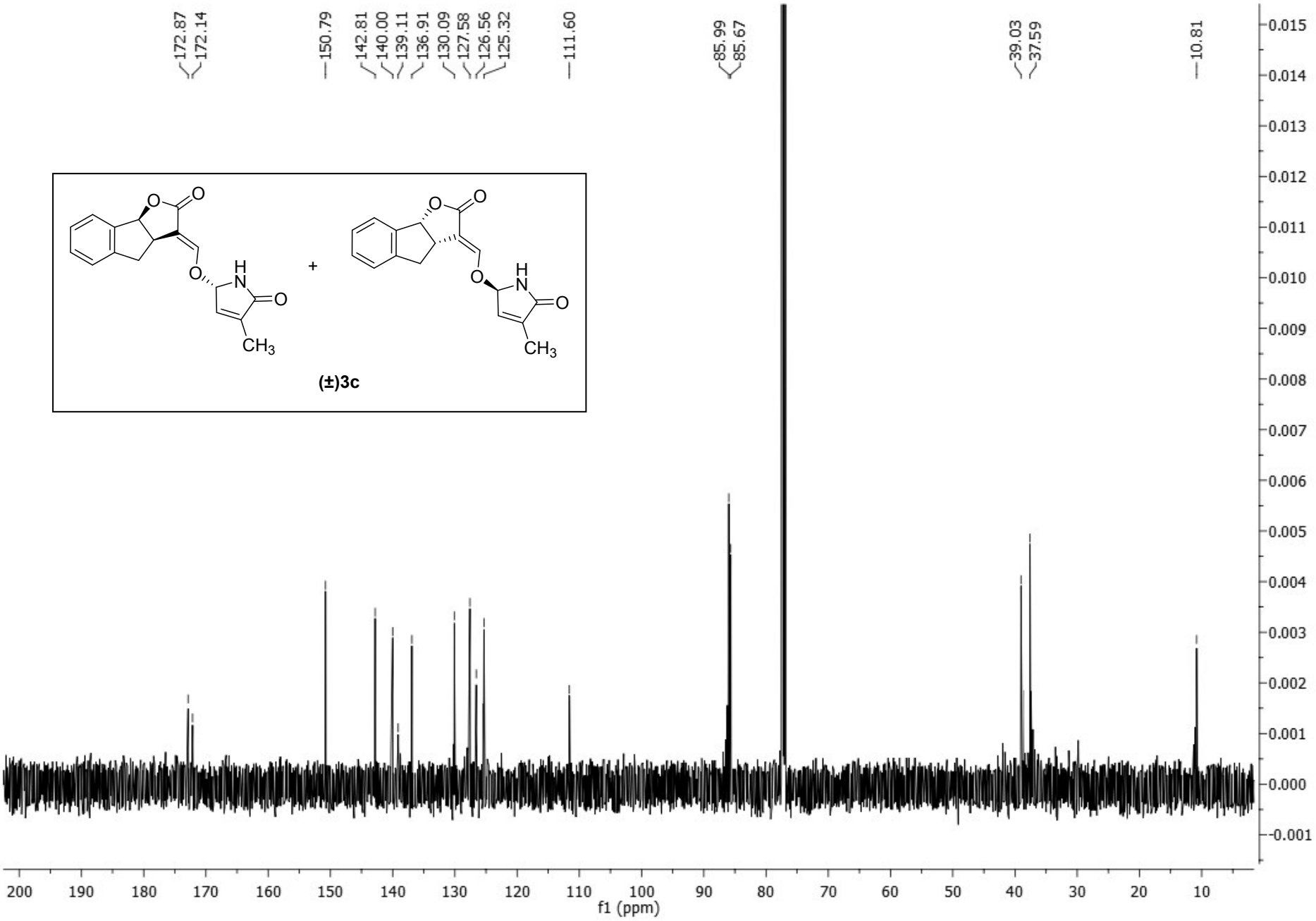


^{1}H NMR (600 MHz) spectrum of (±)3c in $CDCl_3$

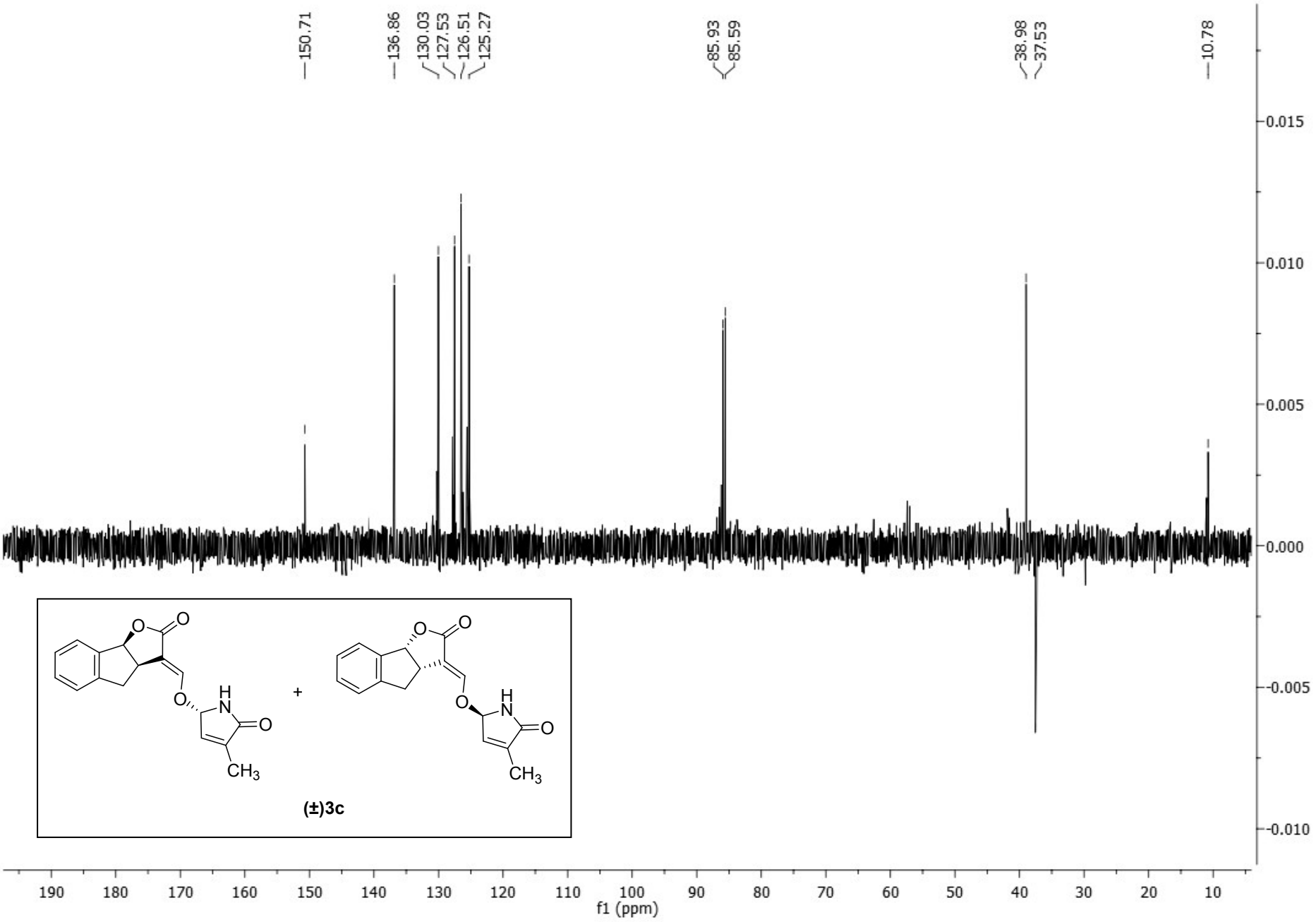


(±)3c

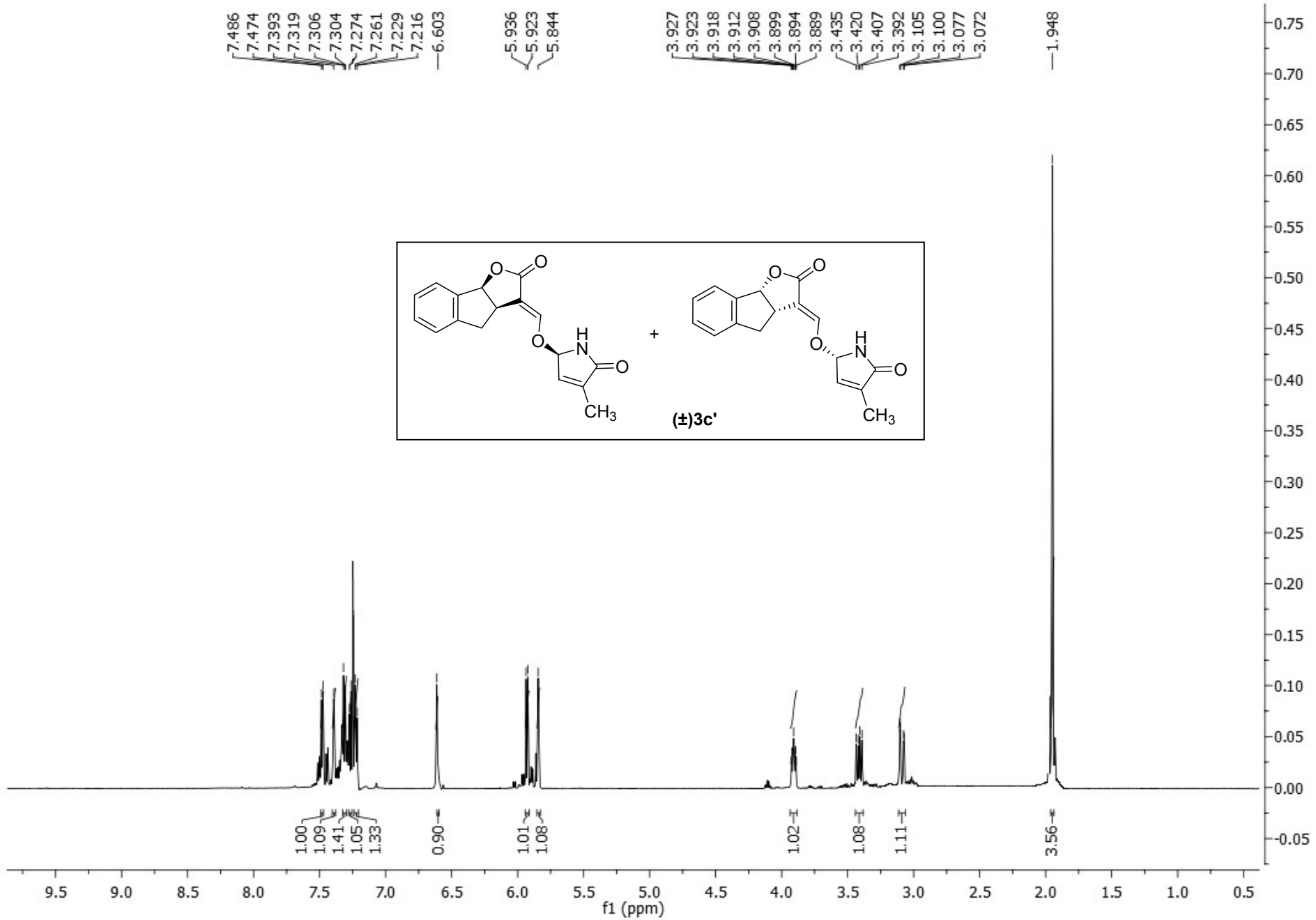
^{13}C NMR (150 MHz) spectrum of (±)3c in $CDCl_3$



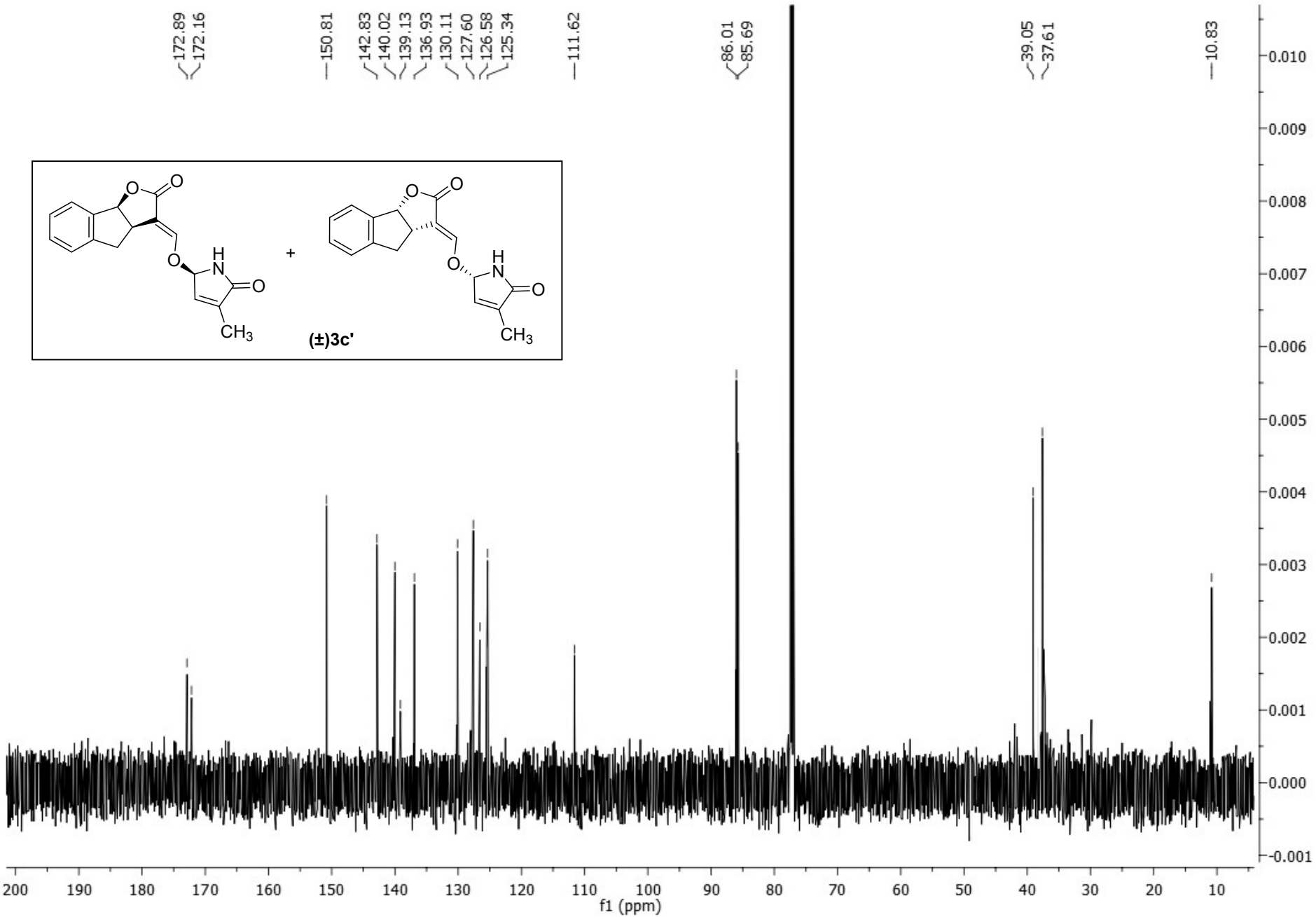
DEPT-135 spectrum of (±)3c in $CDCl_3$



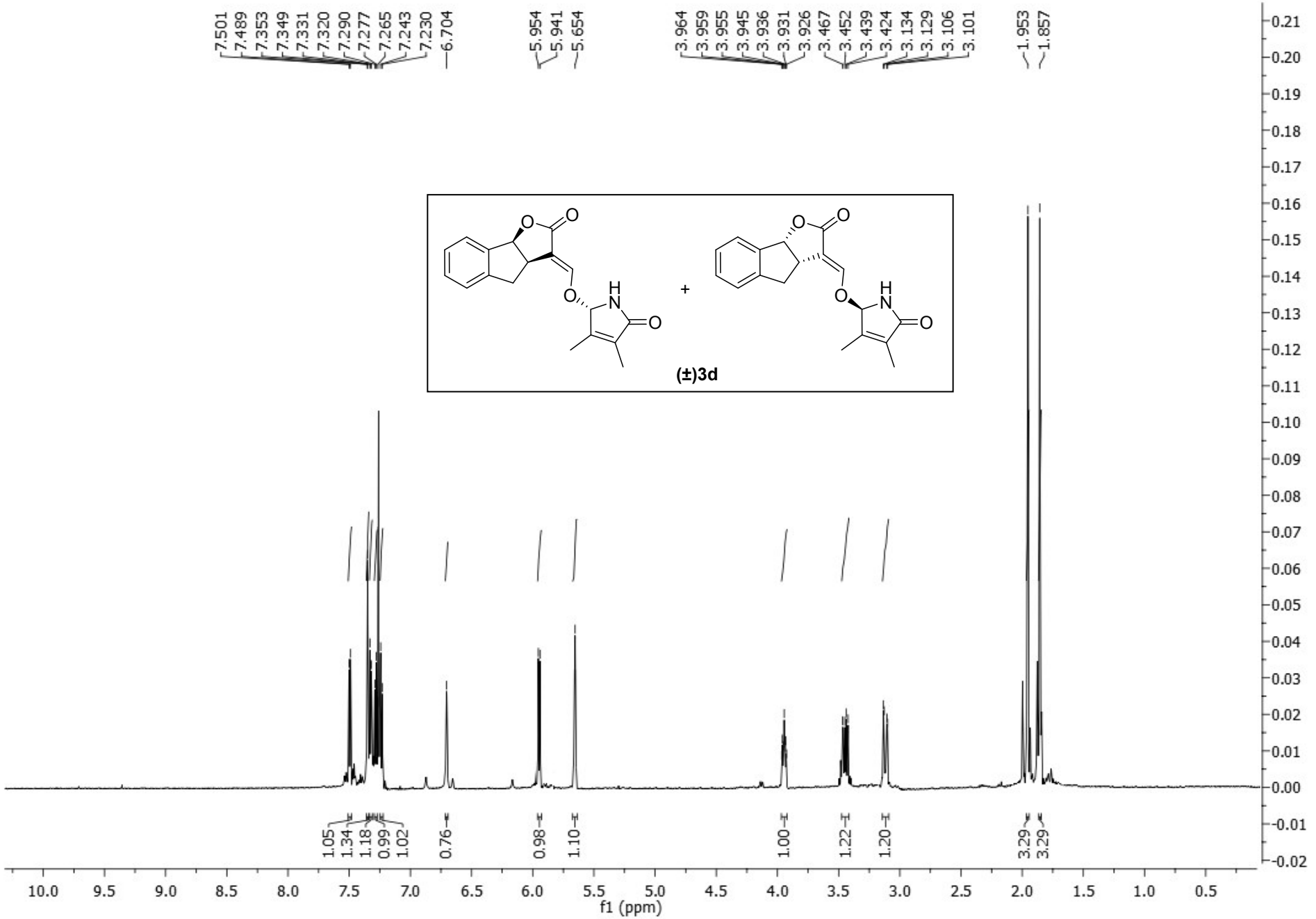
^{1}H NMR (600 MHz) spectrum of (±)3c′ in $CDCl_3$



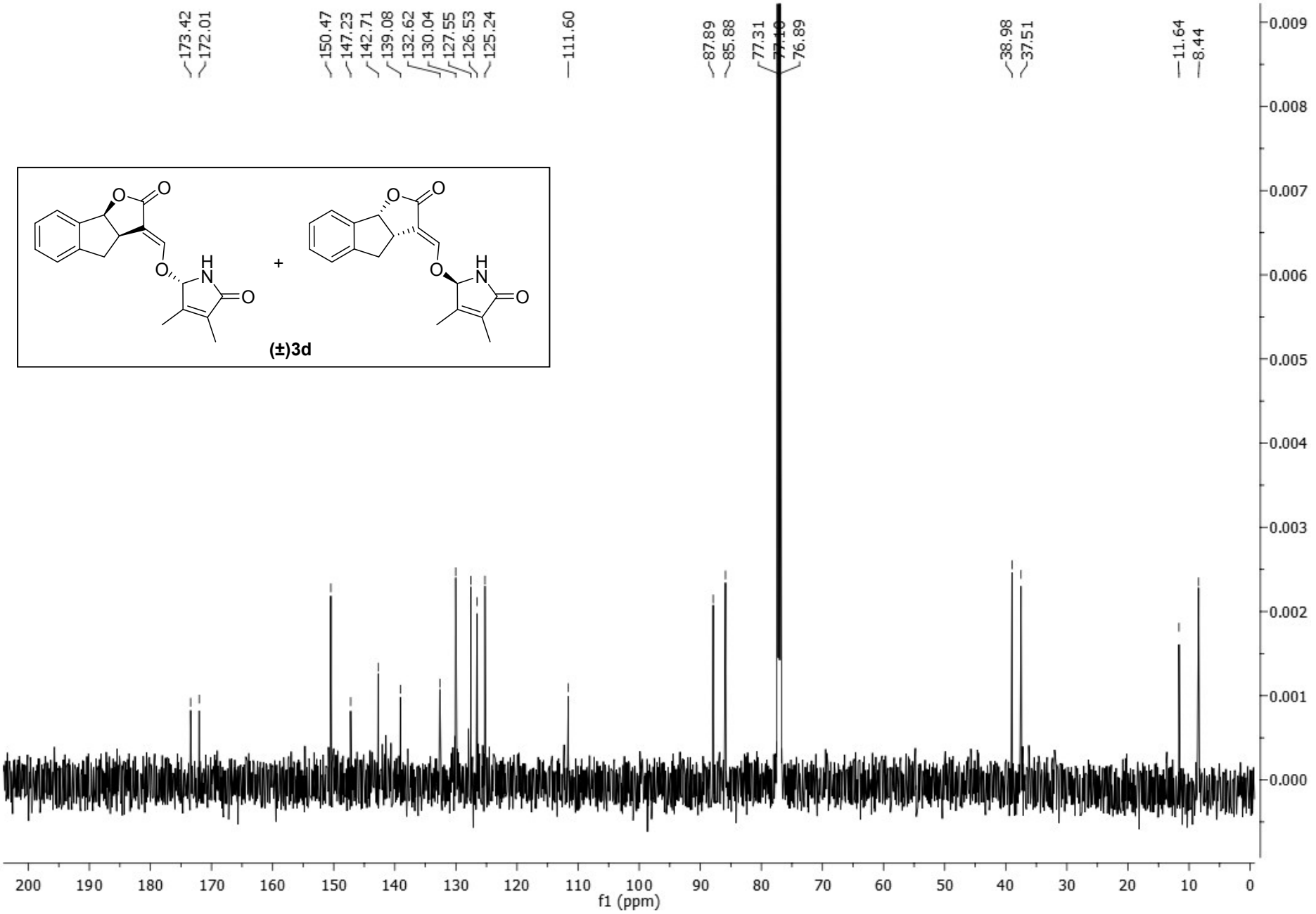
^{13}C NMR (150 MHz) spectrum of (±)3c′ in $CDCl_3$



^{1}H NMR (600 MHz) spectrum of (±)3d in $CDCl_3$

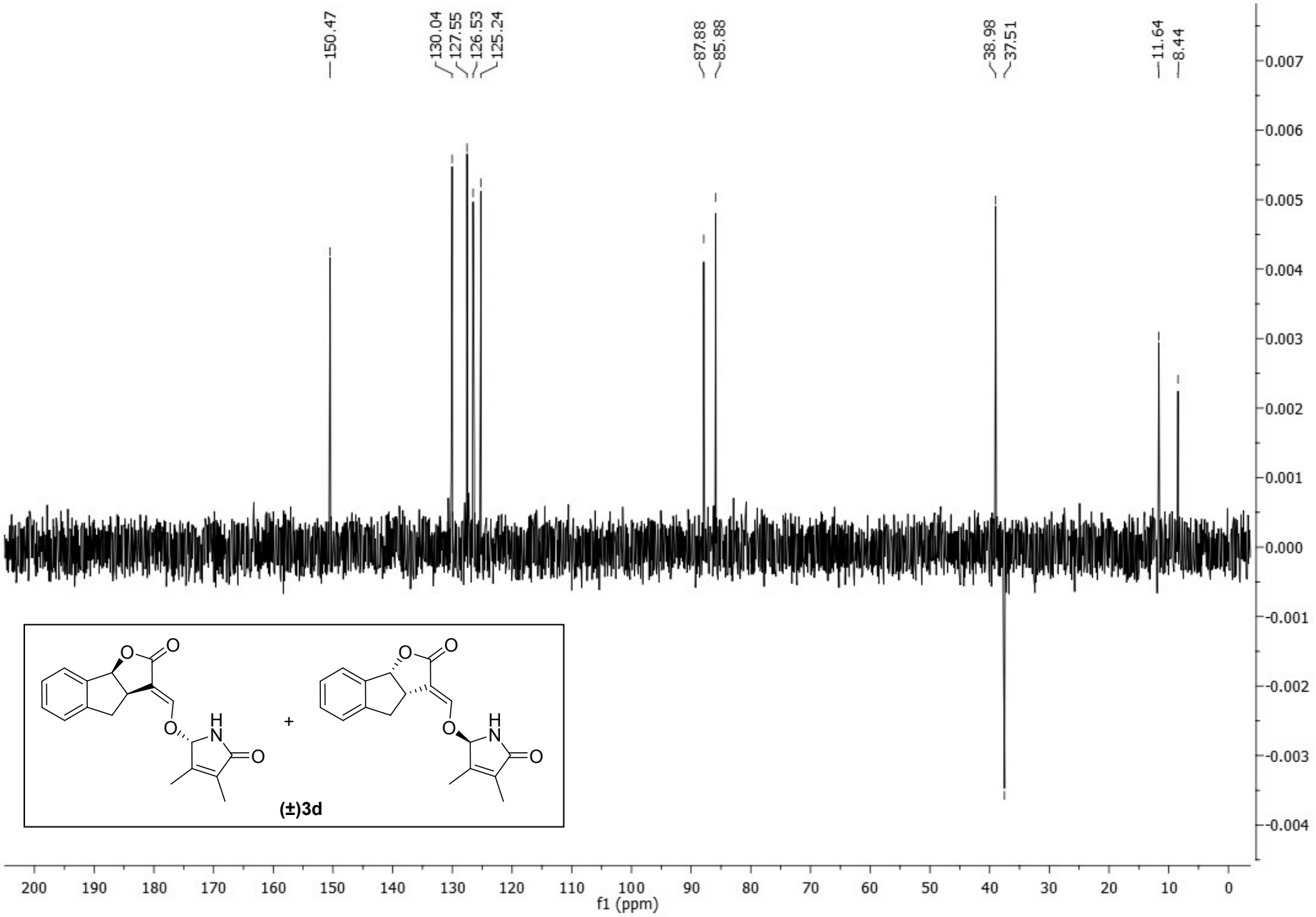


^{13}C NMR (150 MHz) spectrum of (±)3d in $CDCl_3$

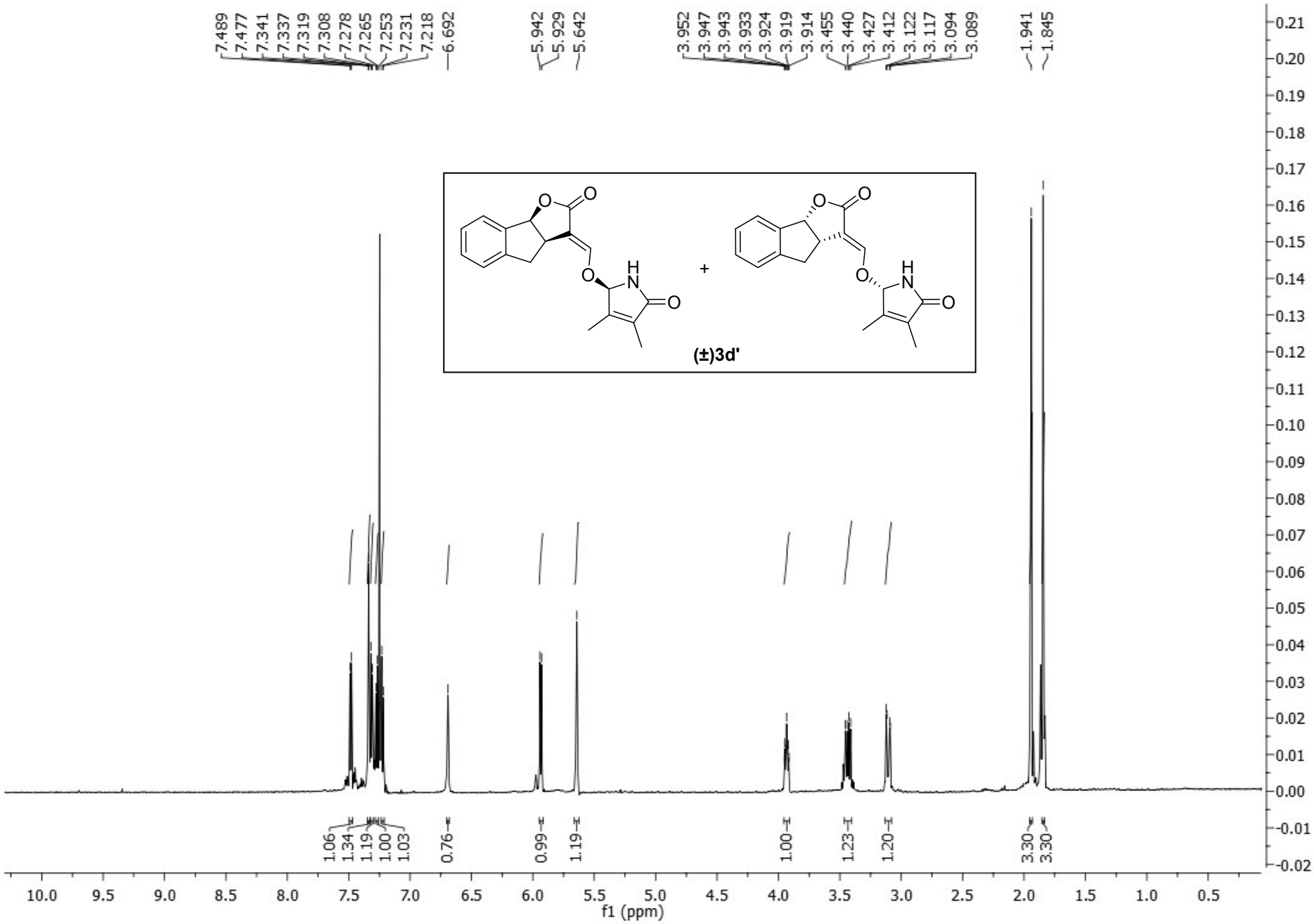


(±)3d

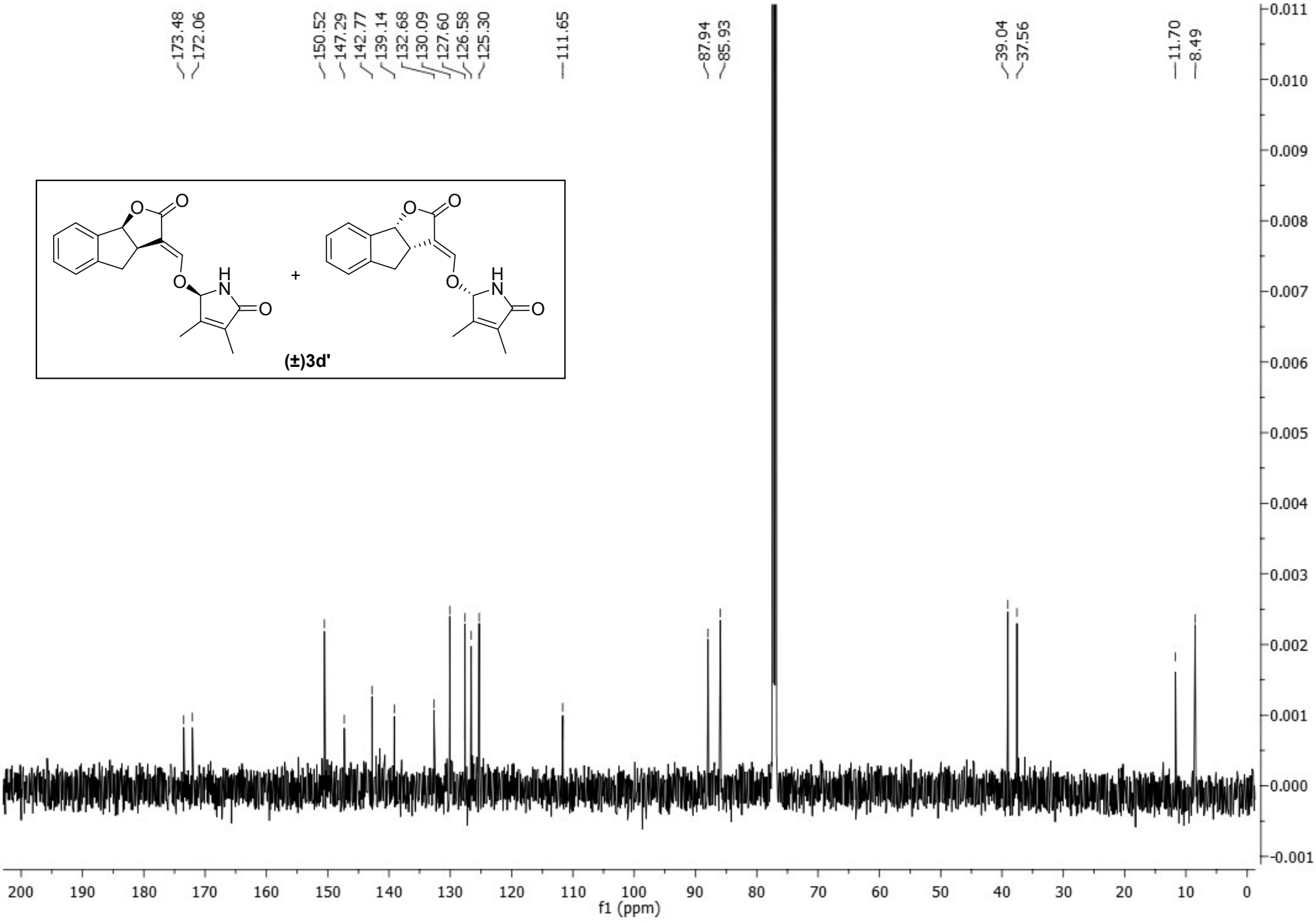
DEPT-135 spectrum of (±)3d in $CDCl_3$



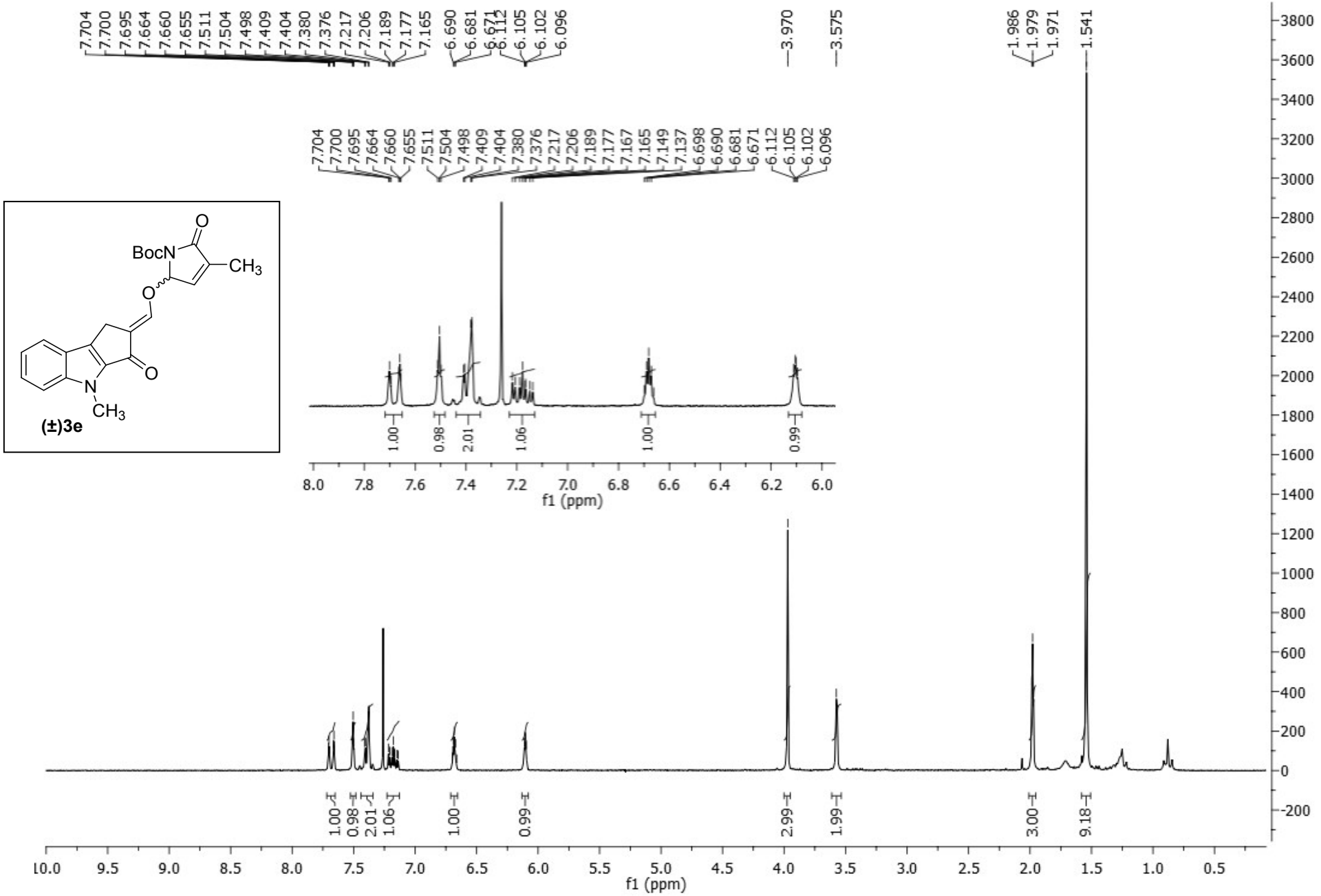
^{1}H NMR (600 MHz) spectrum of (±)3d' in $CDCl_3$



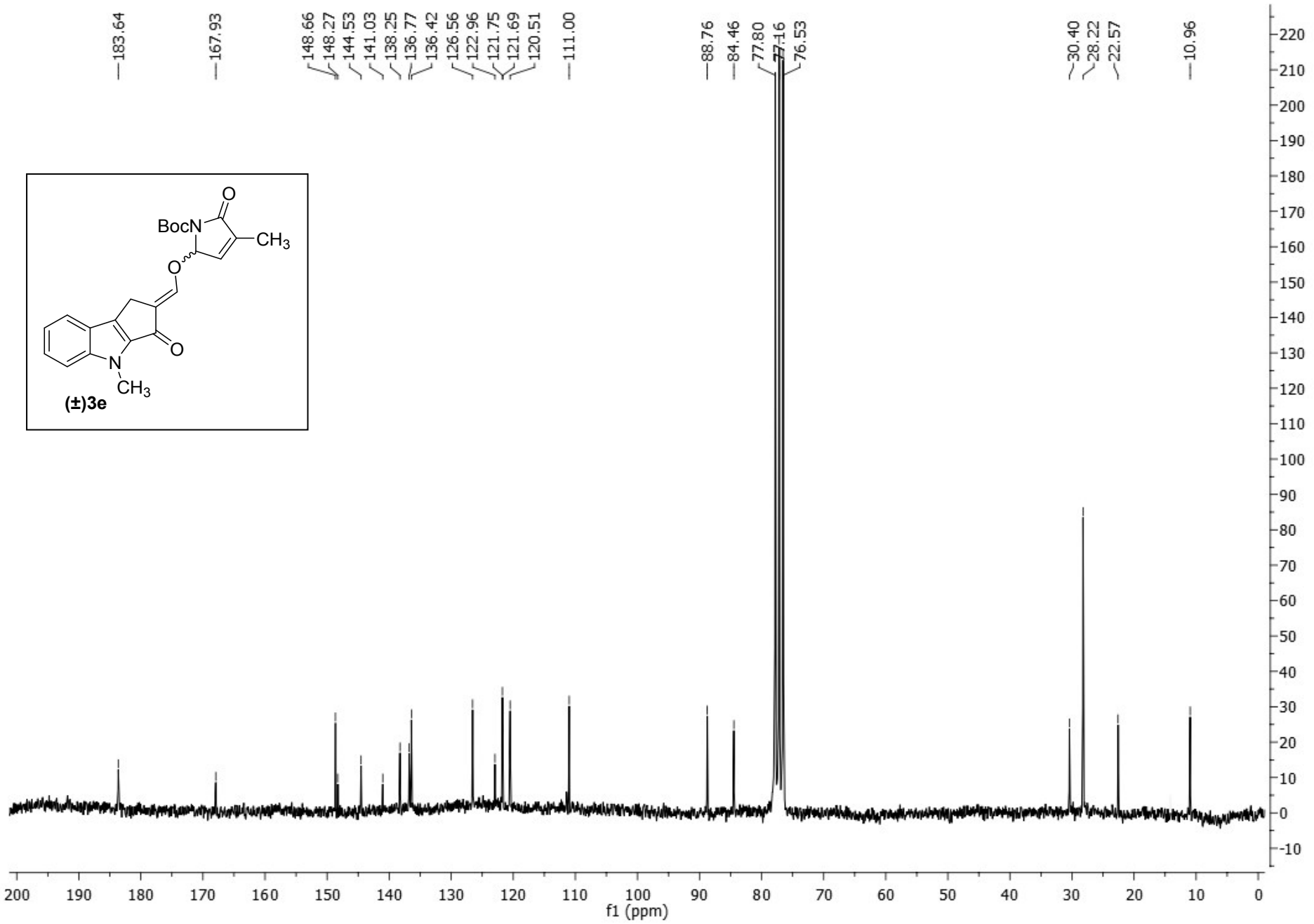
^{13}C NMR (150 MHz) spectrum of (±)3d′ in $CDCl_3$



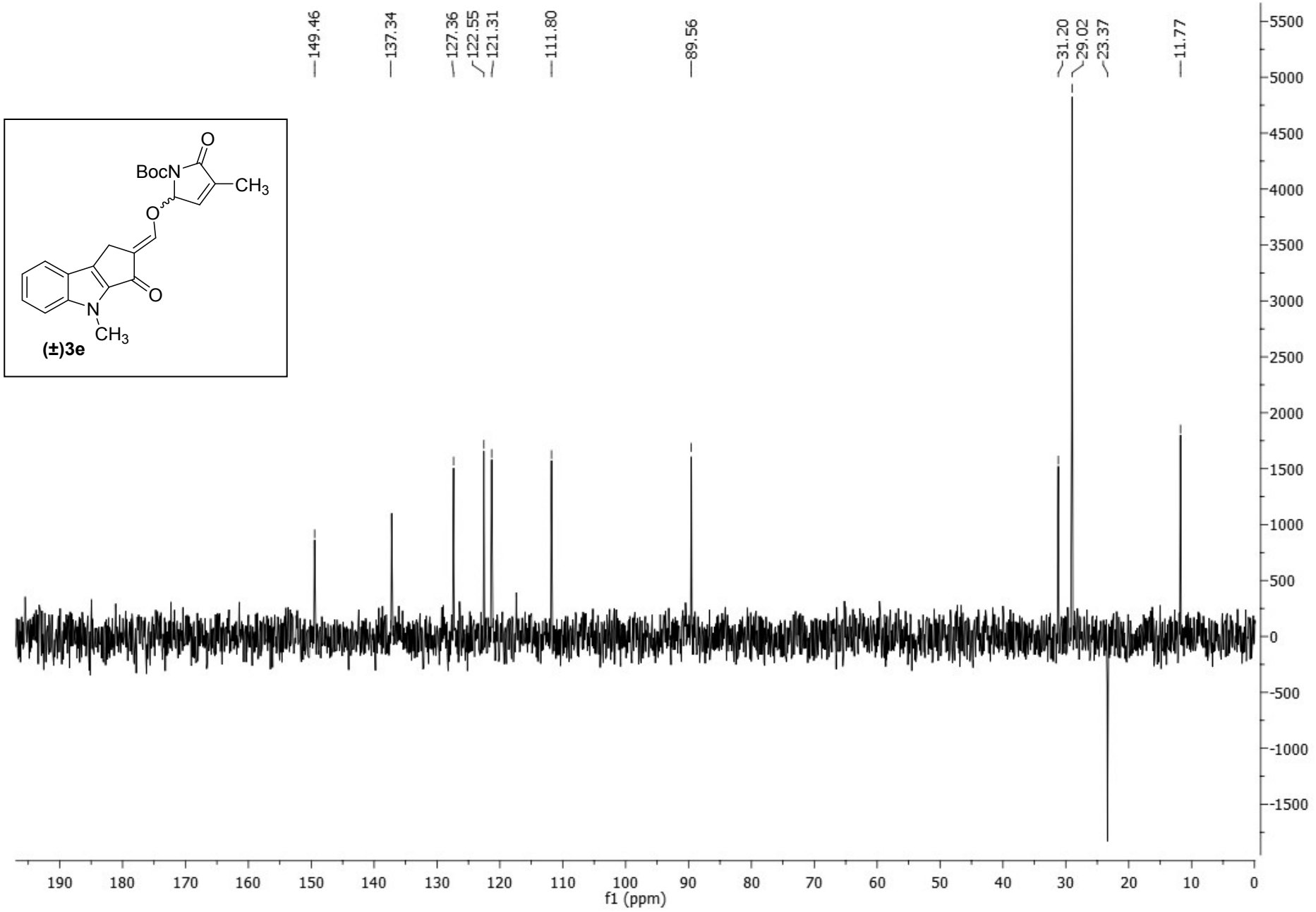
^{1}H NMR (200 MHz) spectrum of (±)3e in $CDCl_3$



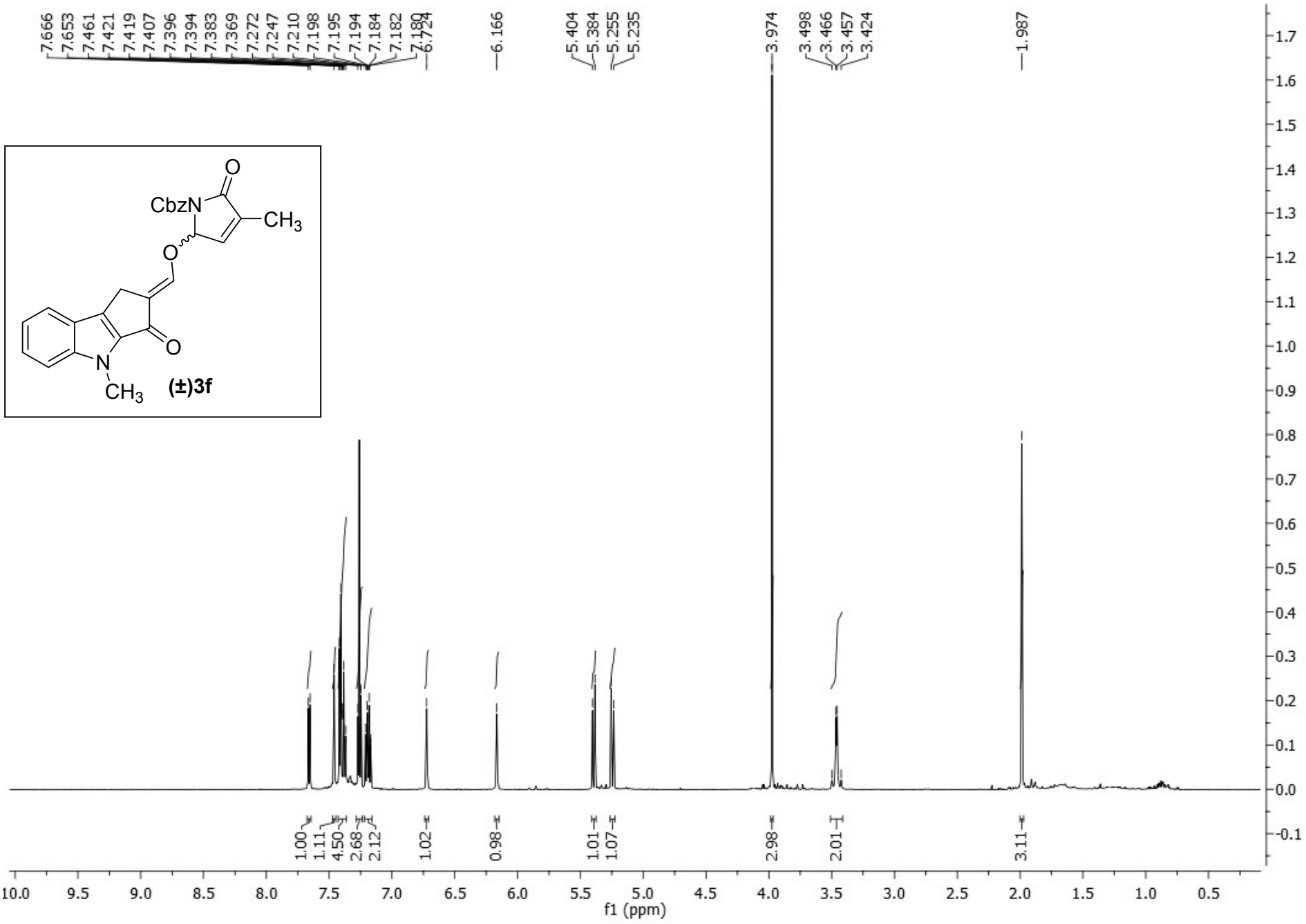
^{13}C NMR (50.2 MHz) spectrum of (±)3e in $CDCl_3$



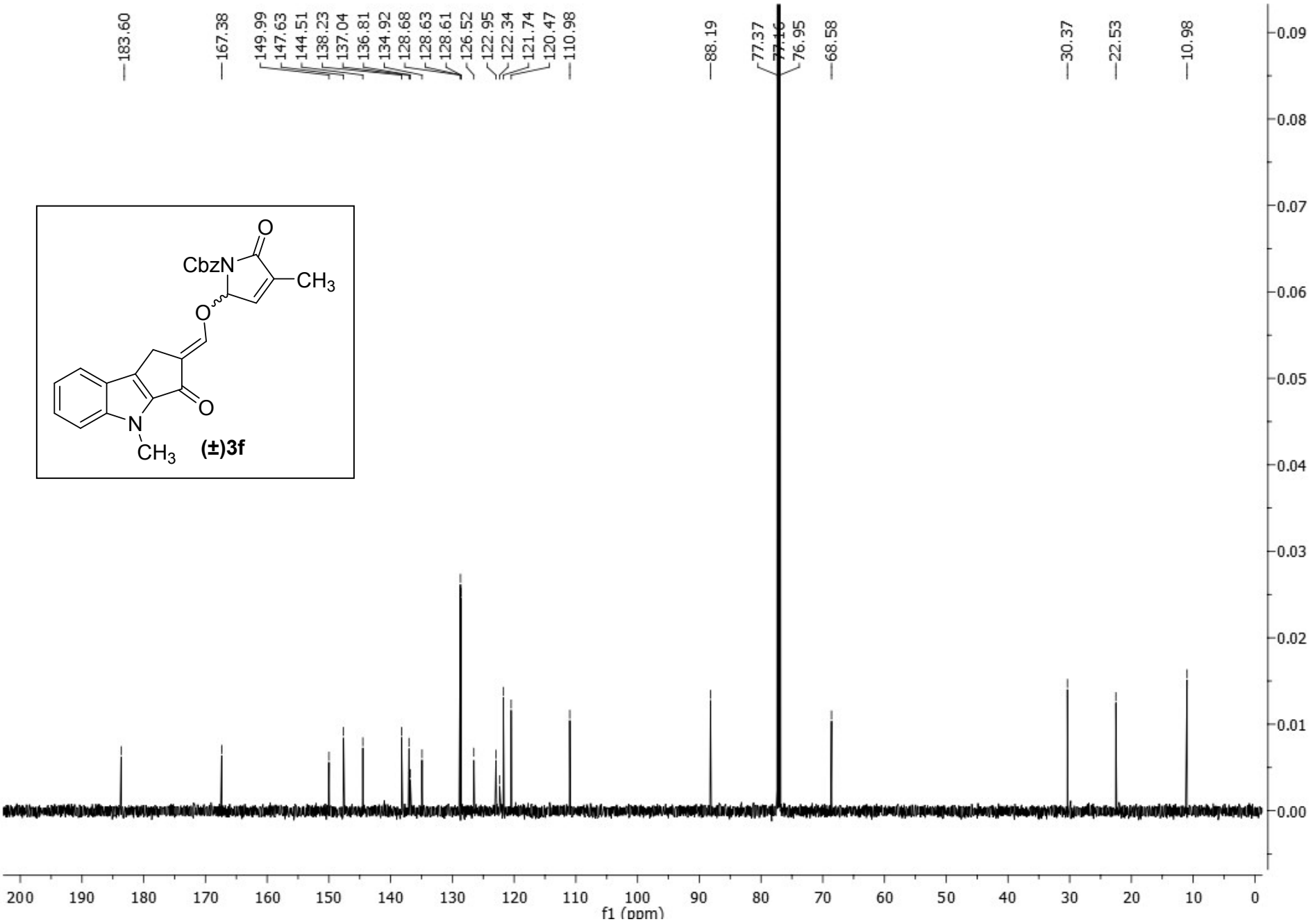
DEPT-135 spectrum of (±)3e in $CDCl_3$

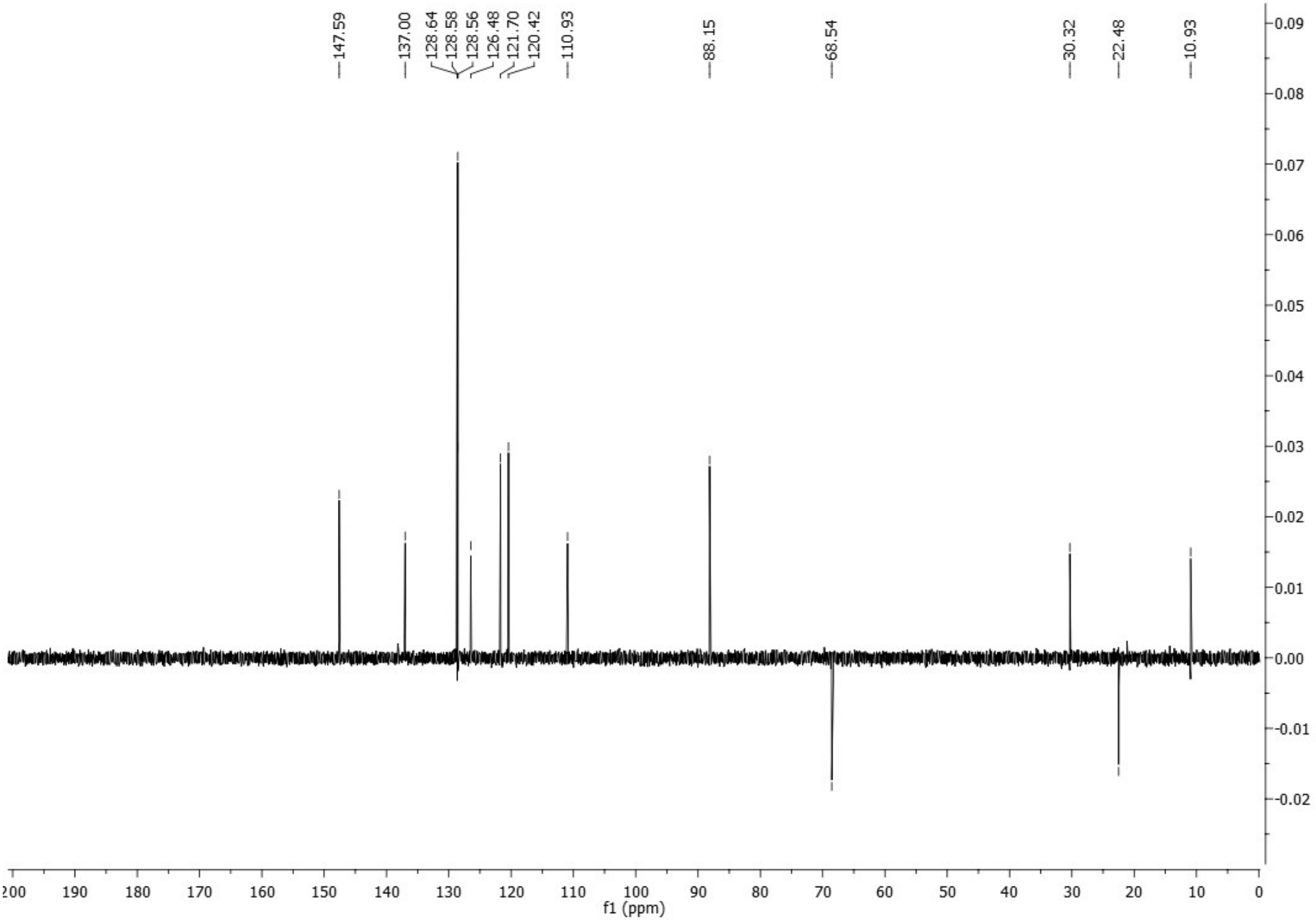


^{1}H NMR (600 MHz) spectrum of (±)3f in $CDCl_3$

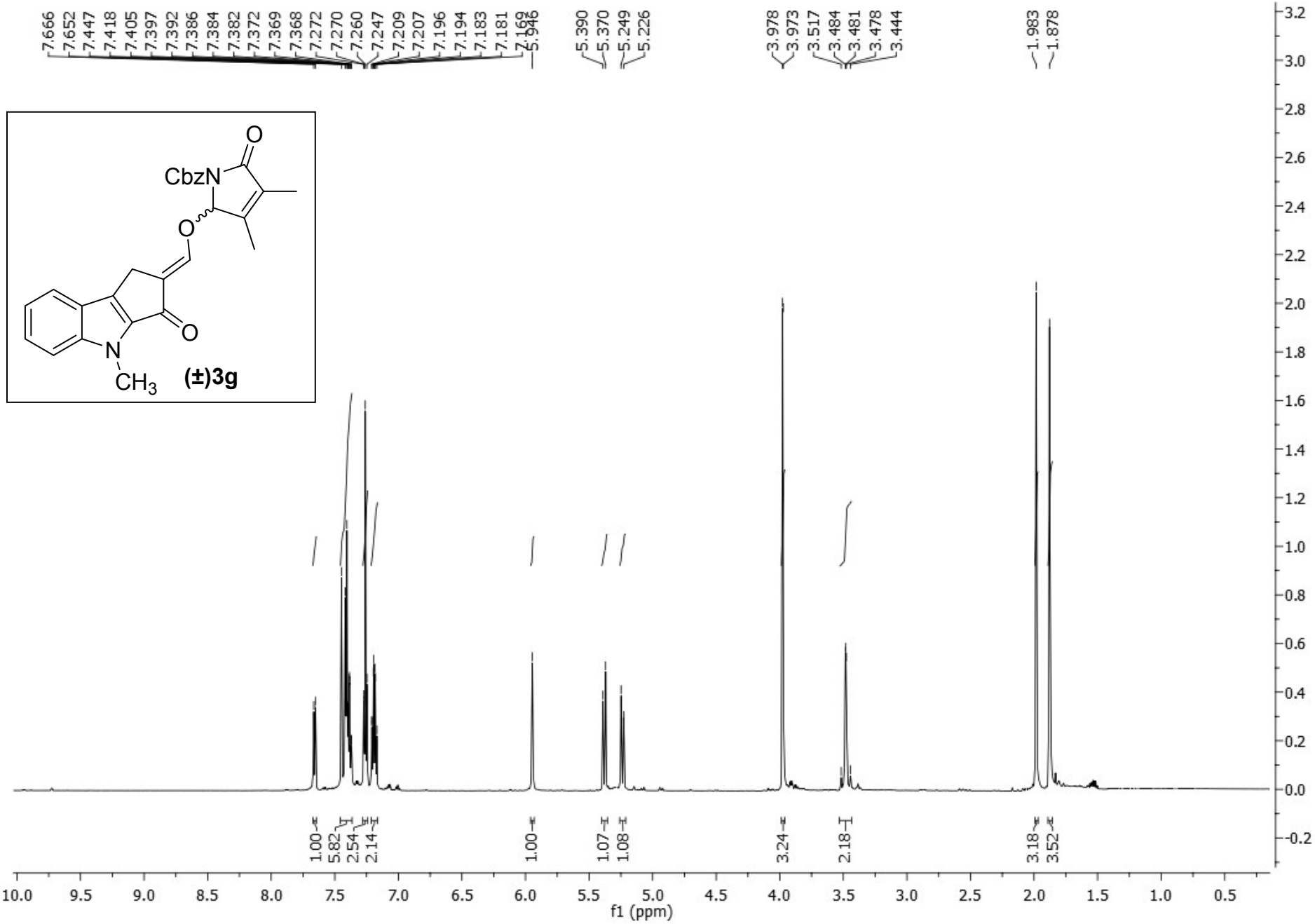


^{13}C NMR (150 MHz) spectrum of (±)3f in $CDCl_3$

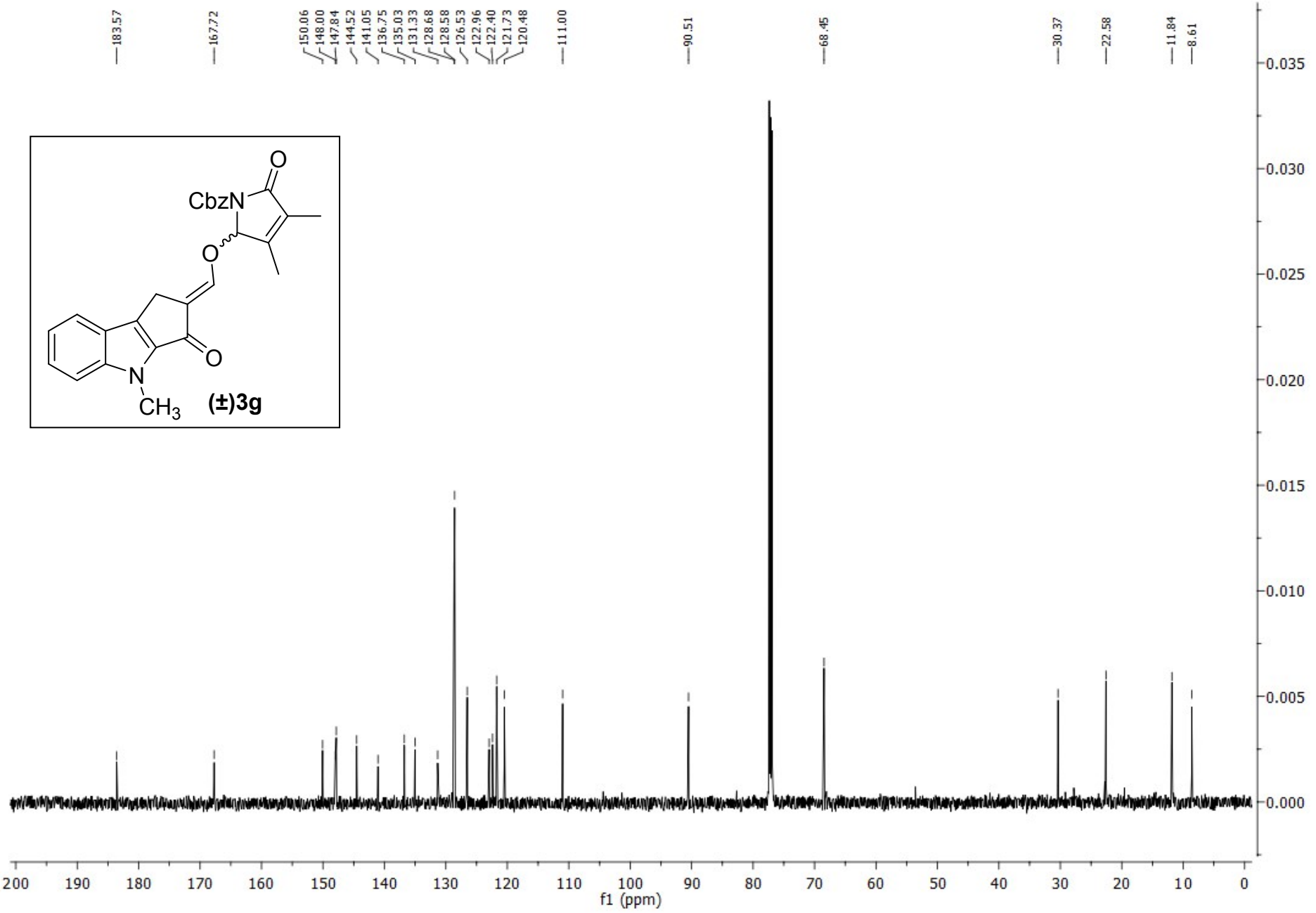



147.59
137.00
128.64
128.58
128.56
126.48
121.70
120.42
110.93
88.15
68.54
30.32
22.48
10.93
f1 (ppm)

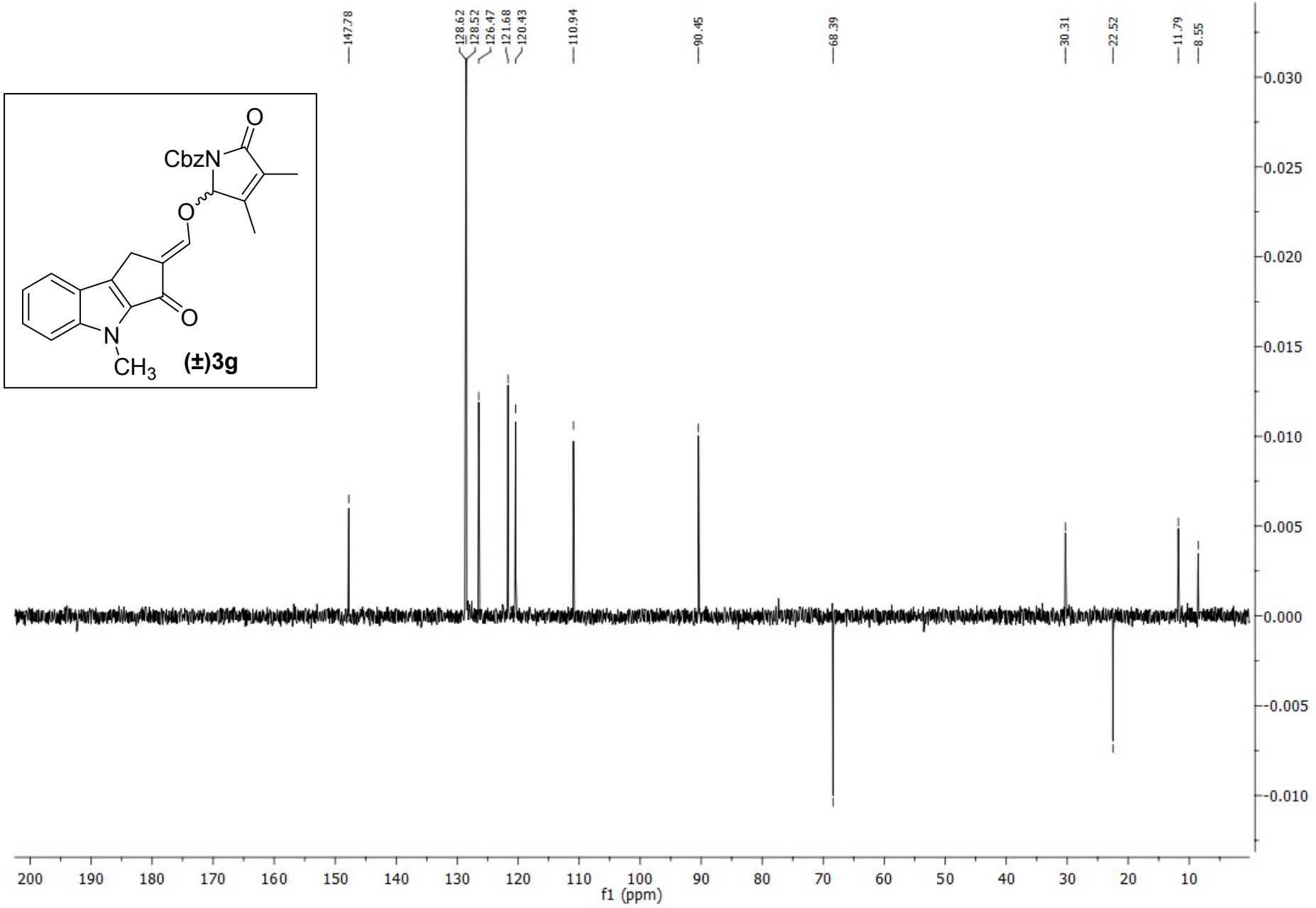
^{1}H NMR (600 MHz) spectrum of (±)3g in $CDCl_3$



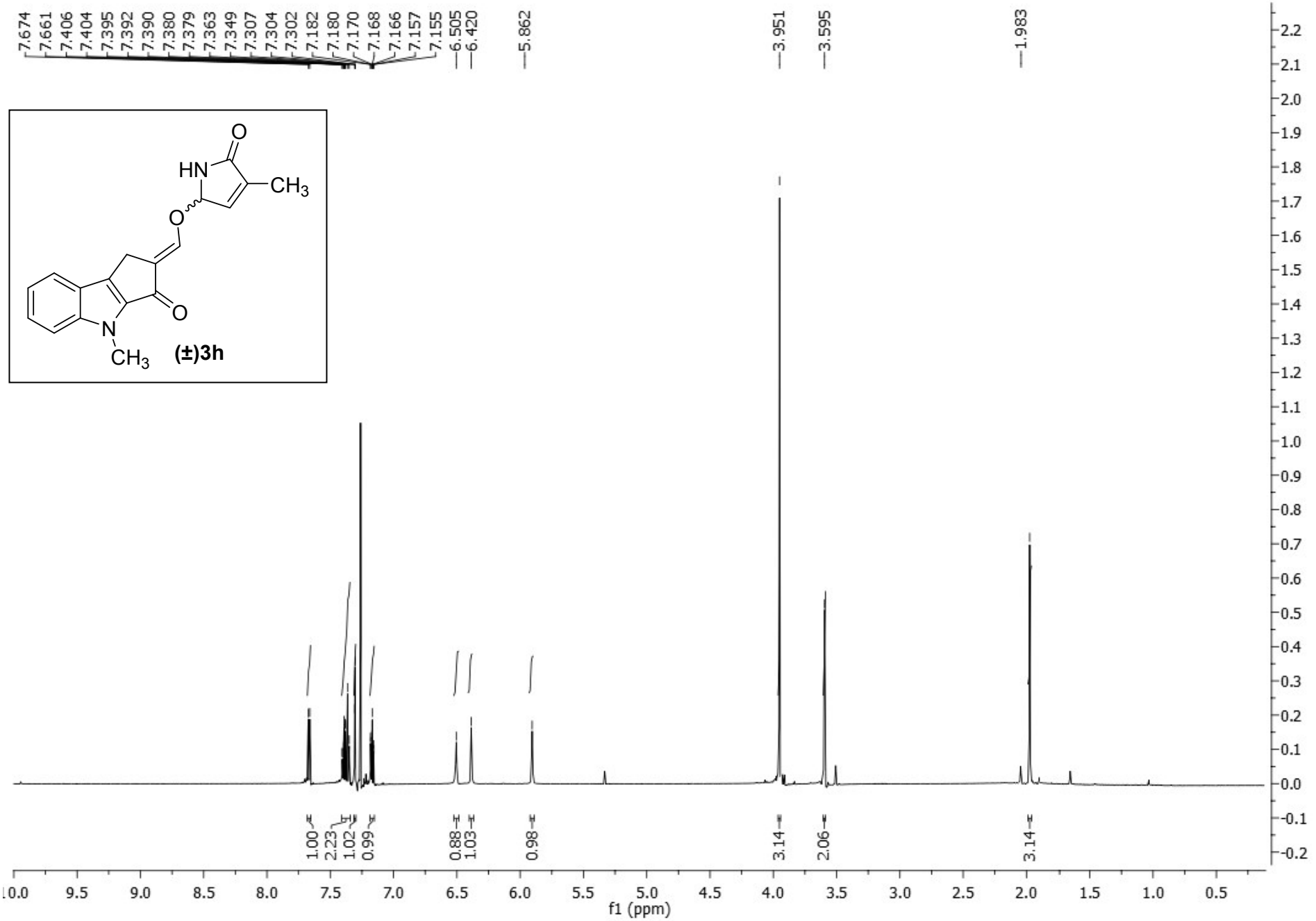
^{13}C NMR (150 MHz) spectrum of (±)3g in $CDCl_3$



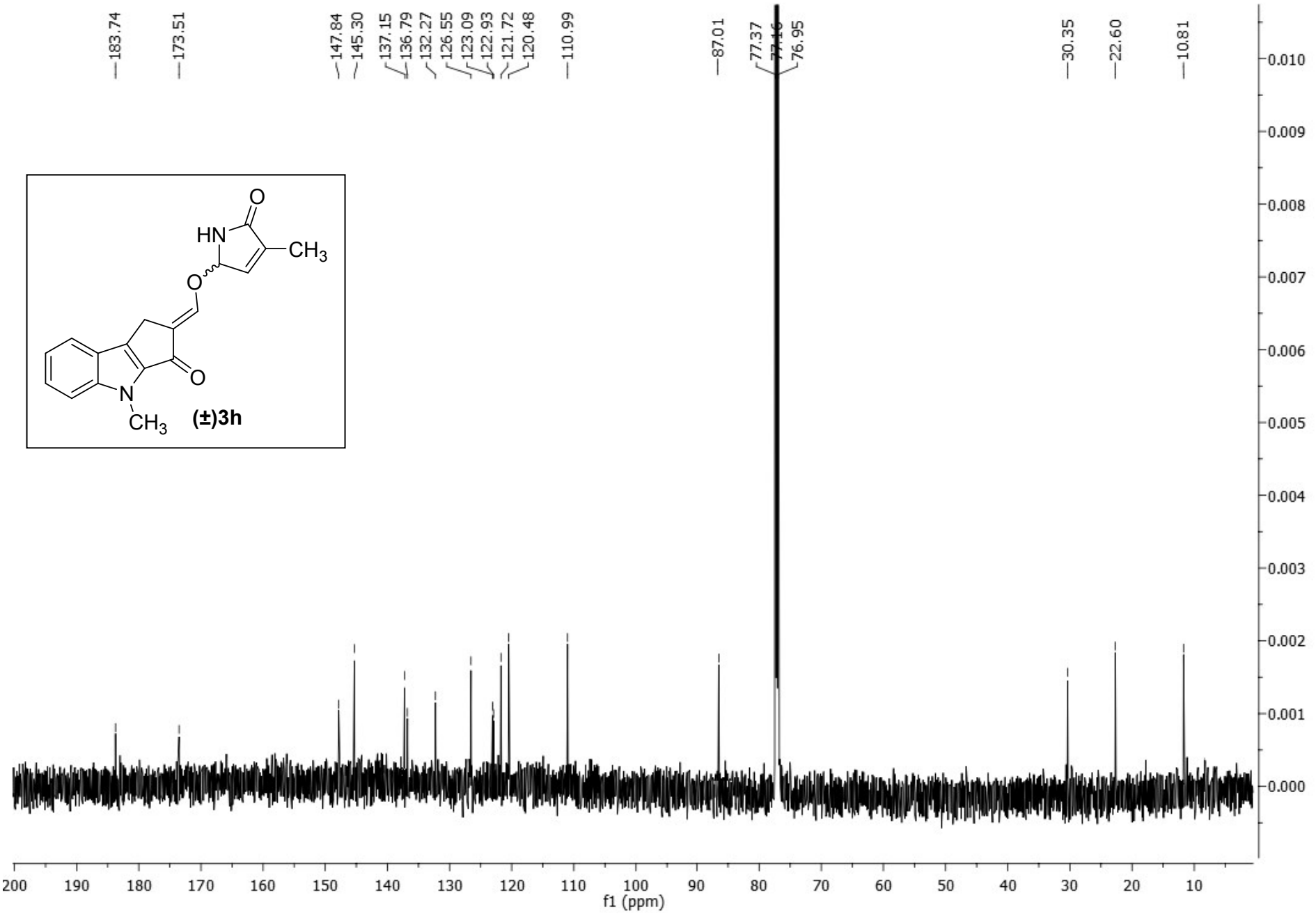
DEPT-135 spectrum of (±)3g in $CDCl_3$



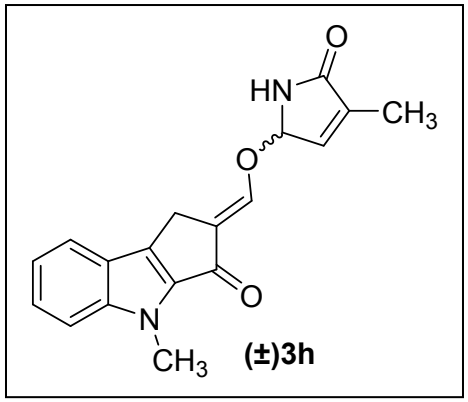
^{1}H NMR (600 MHz) spectrum of (±)3h in $CDCl_3$



^{13}C NMR (150 MHz) spectrum of (±)3h in $CDCl_3$

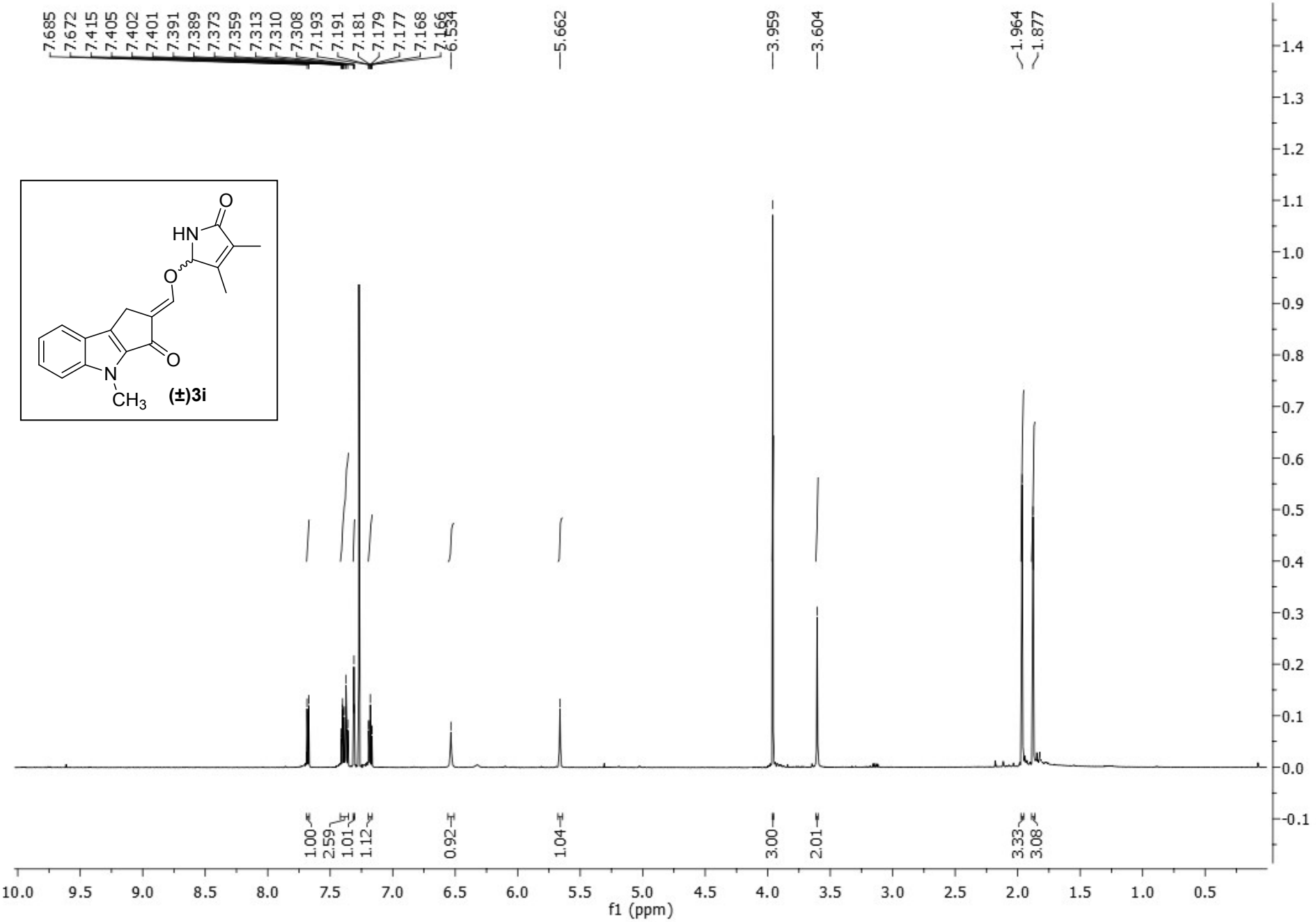


DEPT-135 spectrum of (±)3i in $CDCl_3$

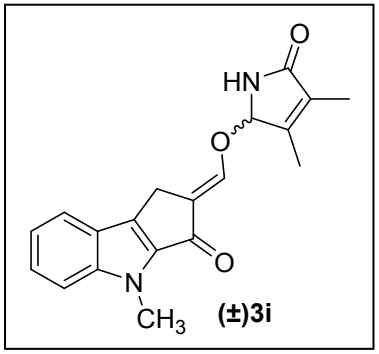


(±)3h

^{1}H NMR (600 MHz) spectrum of (±)3i in $CDCl_3$

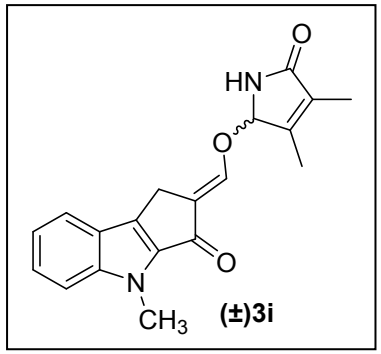


^{13}C NMR (150 MHz) spectrum of (±)3i in $CDCl_3$



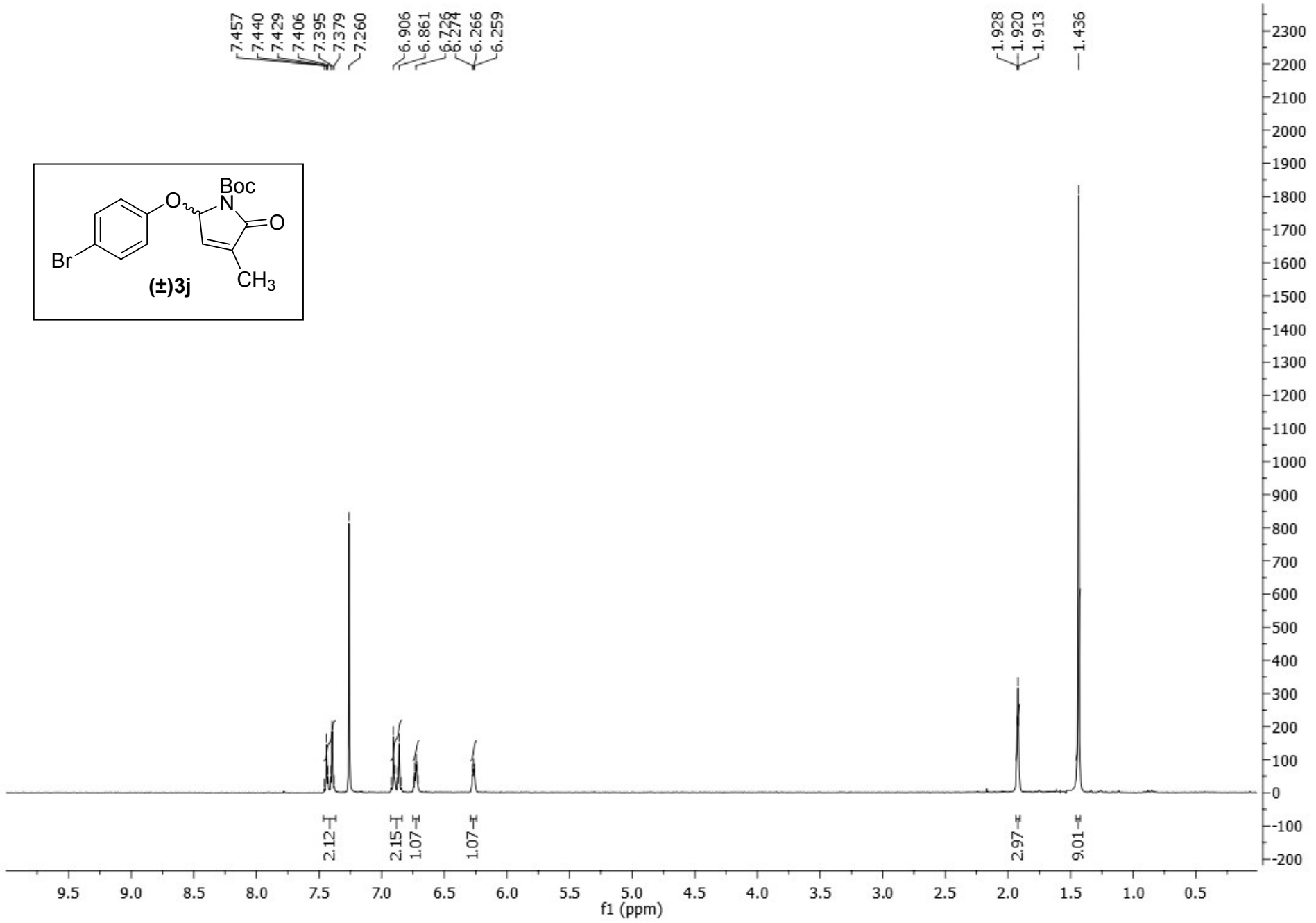
(±)3i

DEPT-135 spectrum of (±)3i in $CDCl_3$

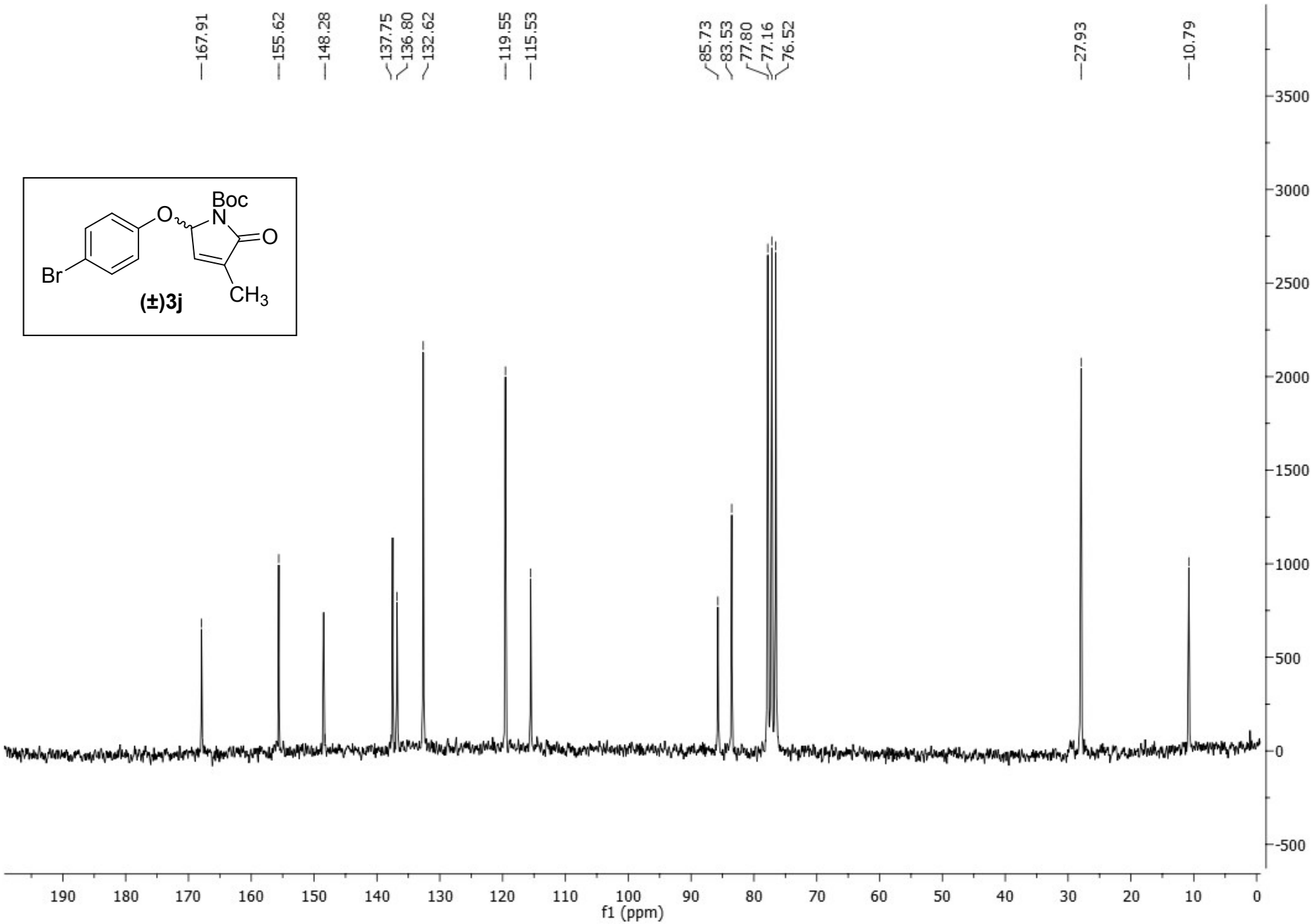


(±)3i

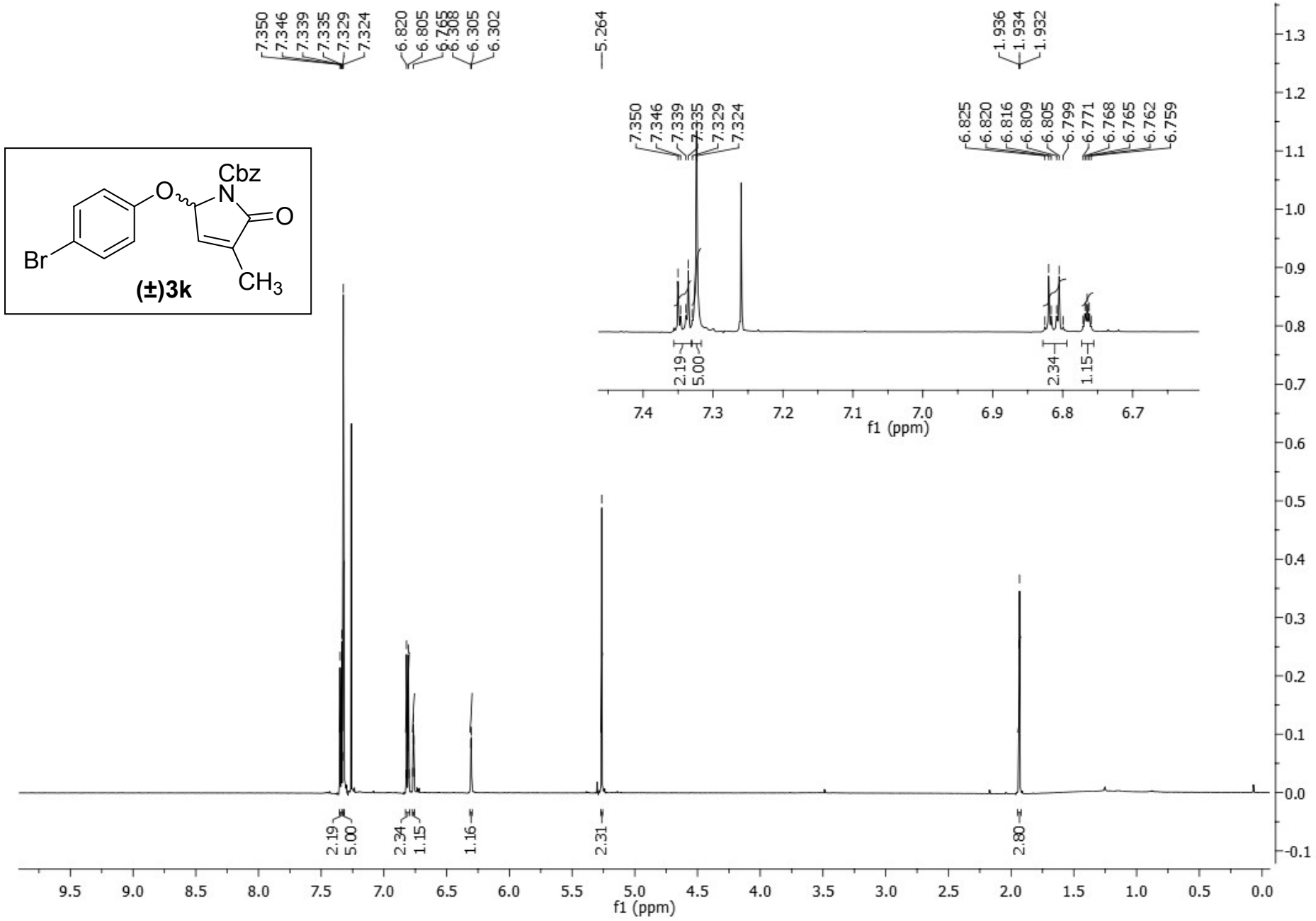
^{1}H NMR (200 MHz) spectrum of (±)3j in $CDCl_3$



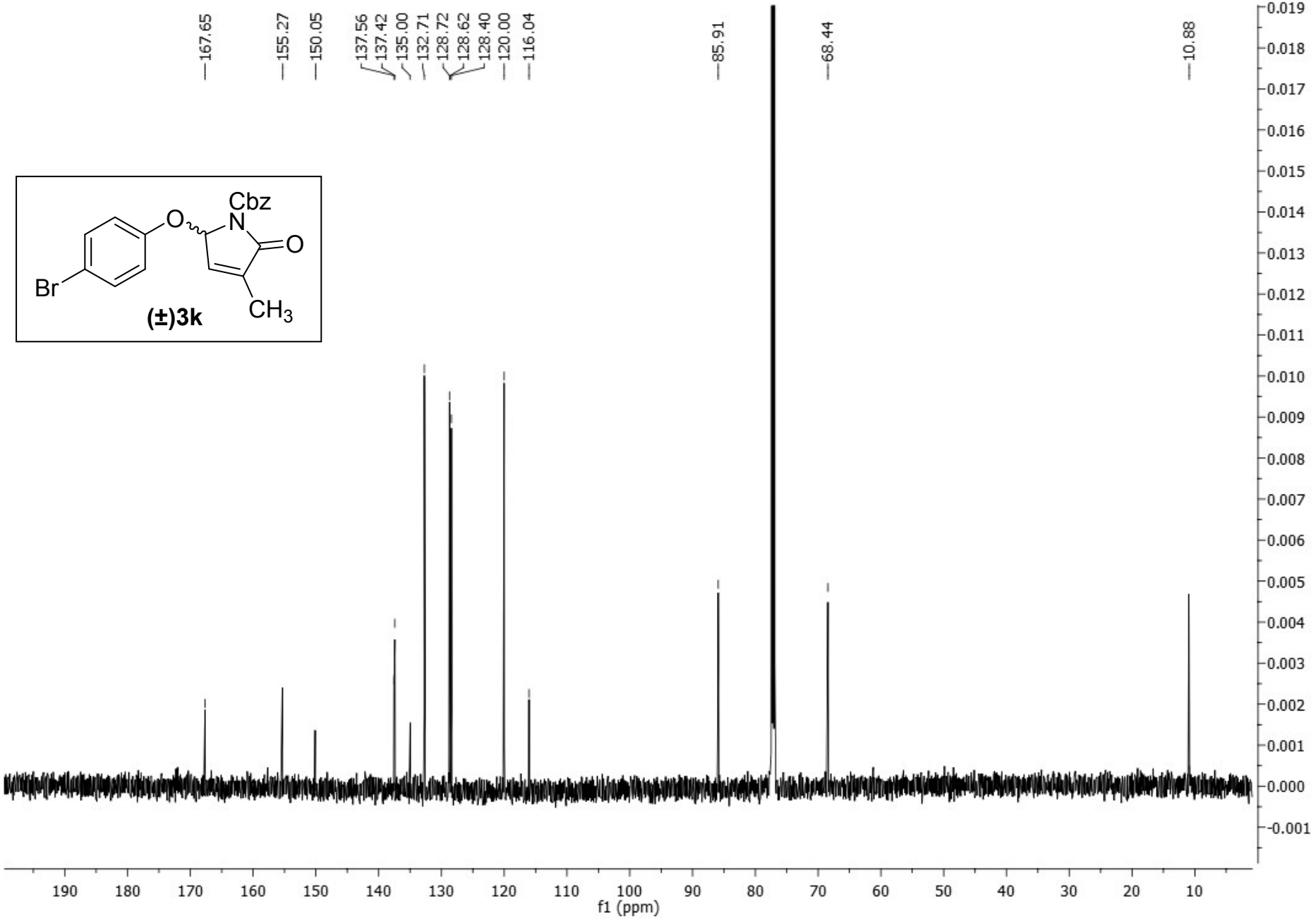
^{13}C NMR (50.2 MHz) spectrum of (±)3j in $CDCl_3$



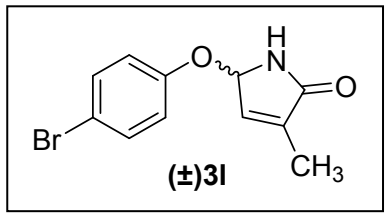
^{1}H NMR (600 MHz) spectrum of (±)3k in $CDCl_3$



^{13}C NMR (150 MHz) spectrum of (±)3k in $CDCl_3$

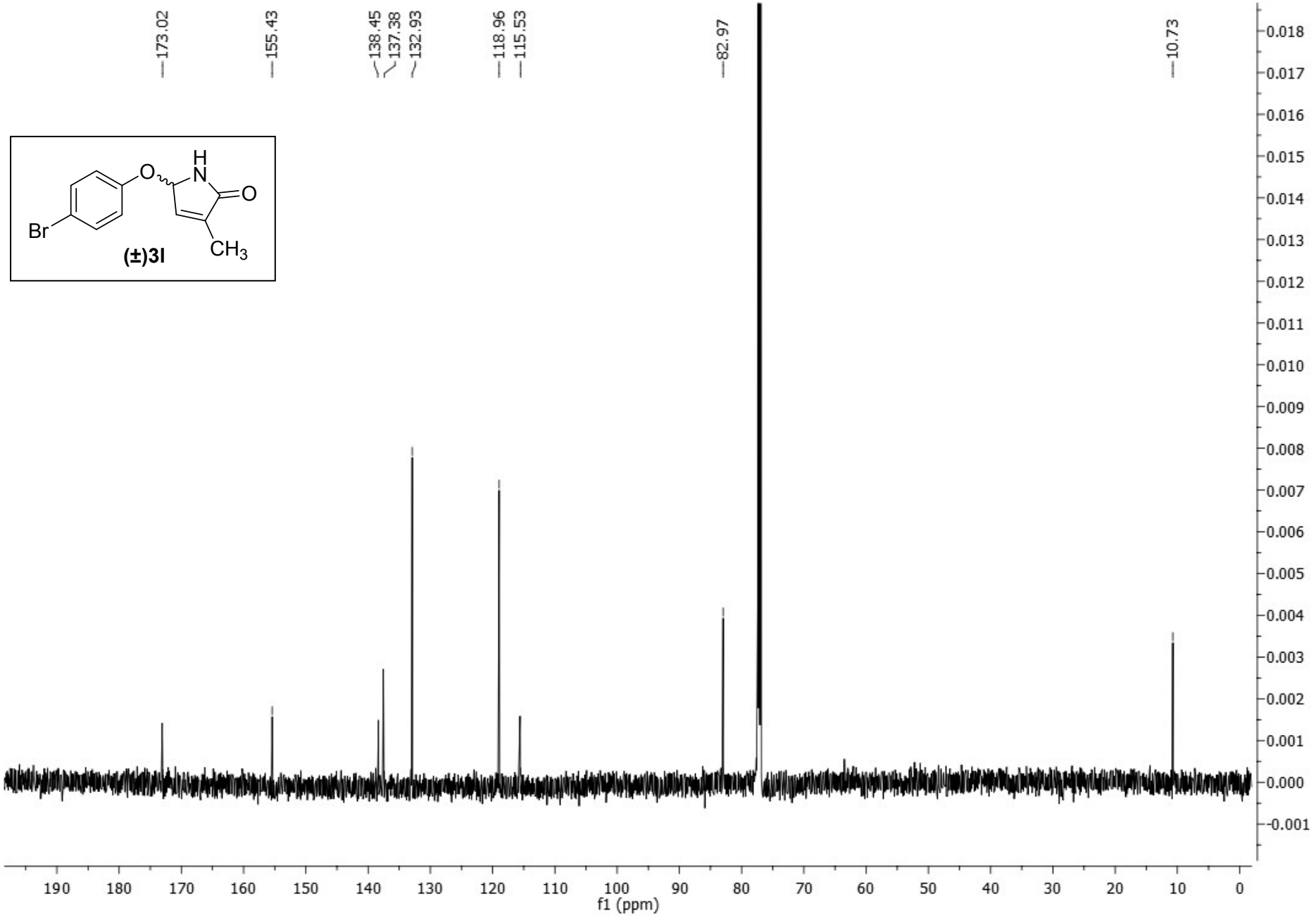


^{1}H NMR (600 MHz) spectrum of (±)3l in $CDCl_3$

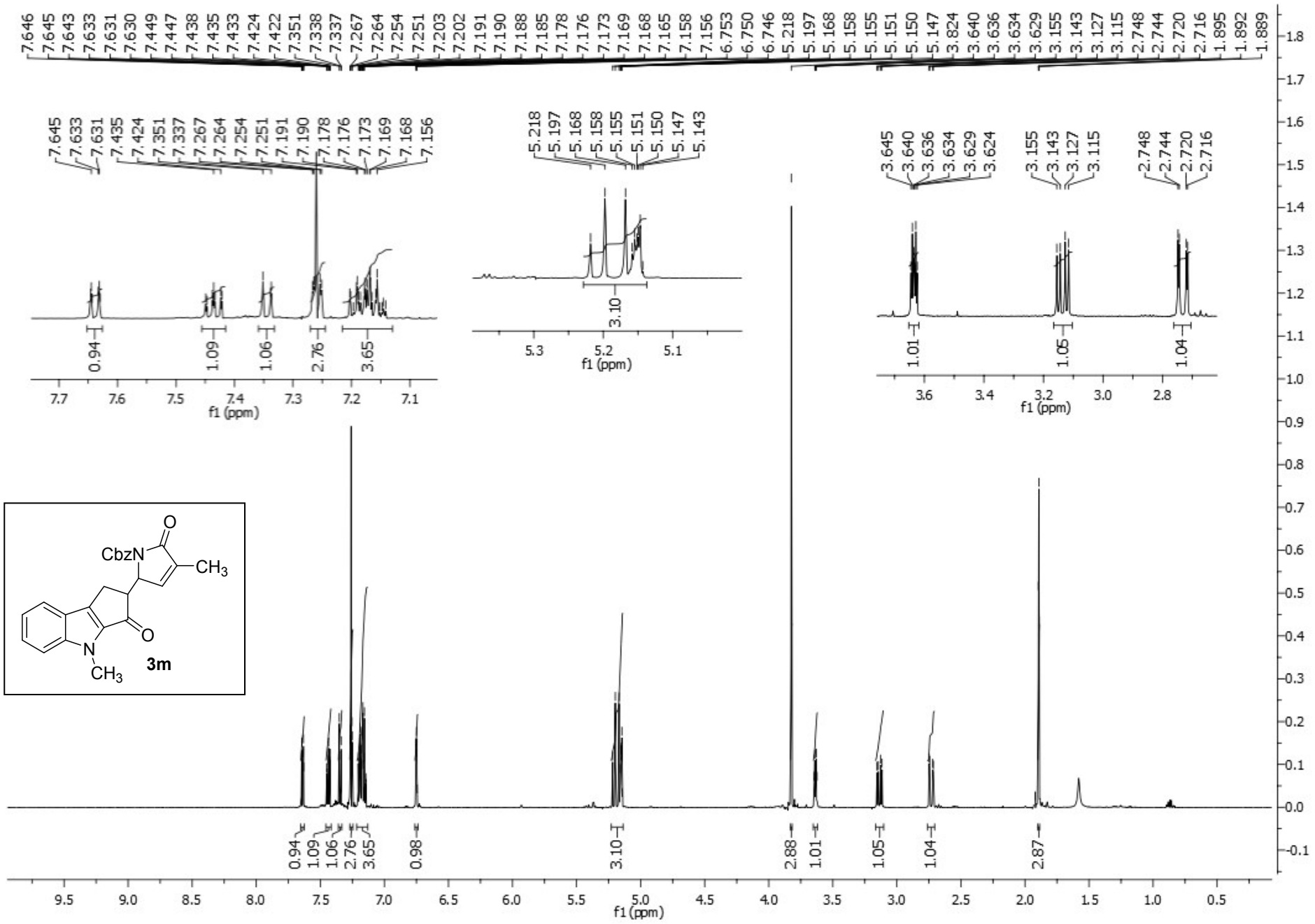


(±)3l

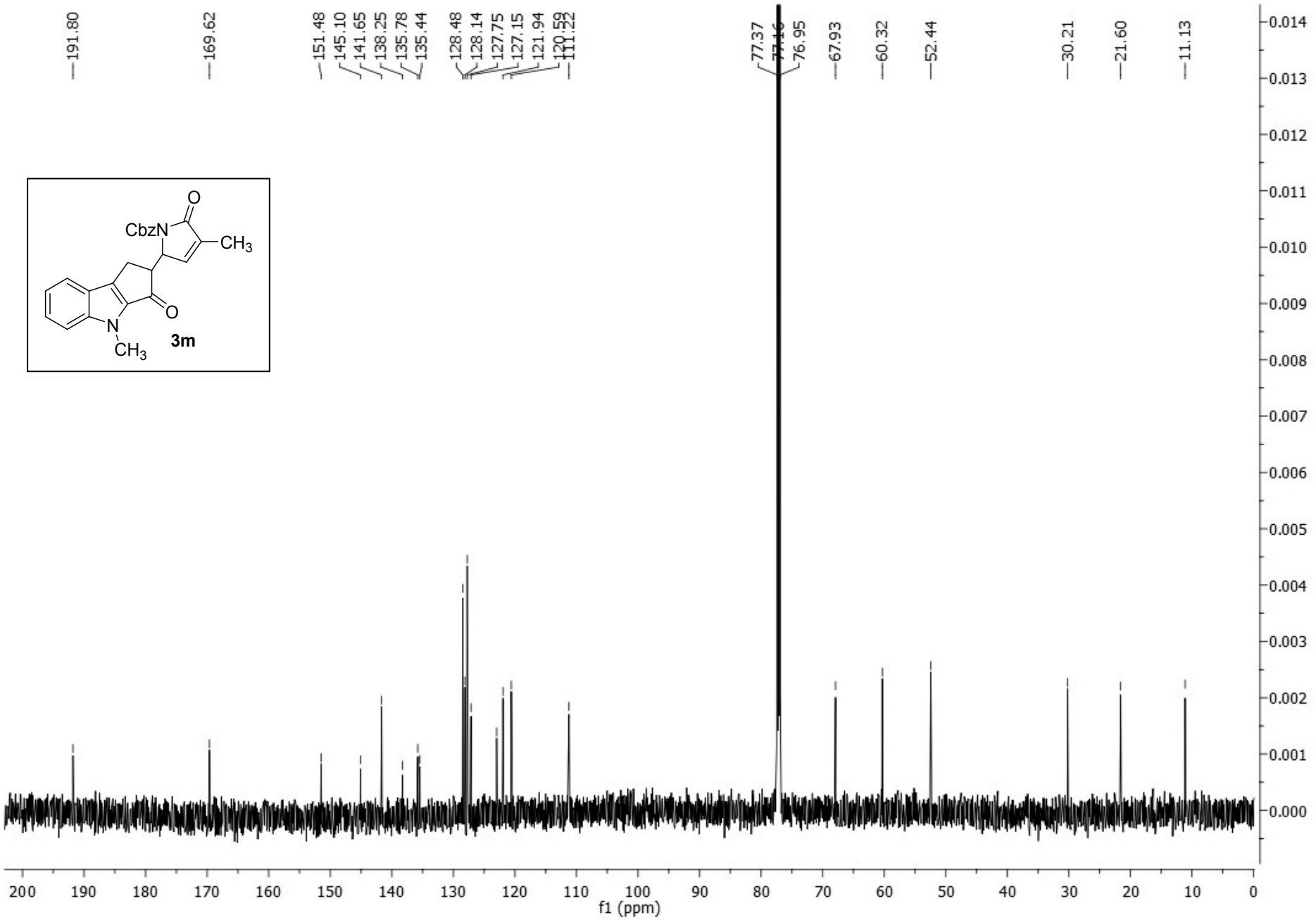
^{13}C NMR (150 MHz) spectrum of (±)3l in $CDCl_3$



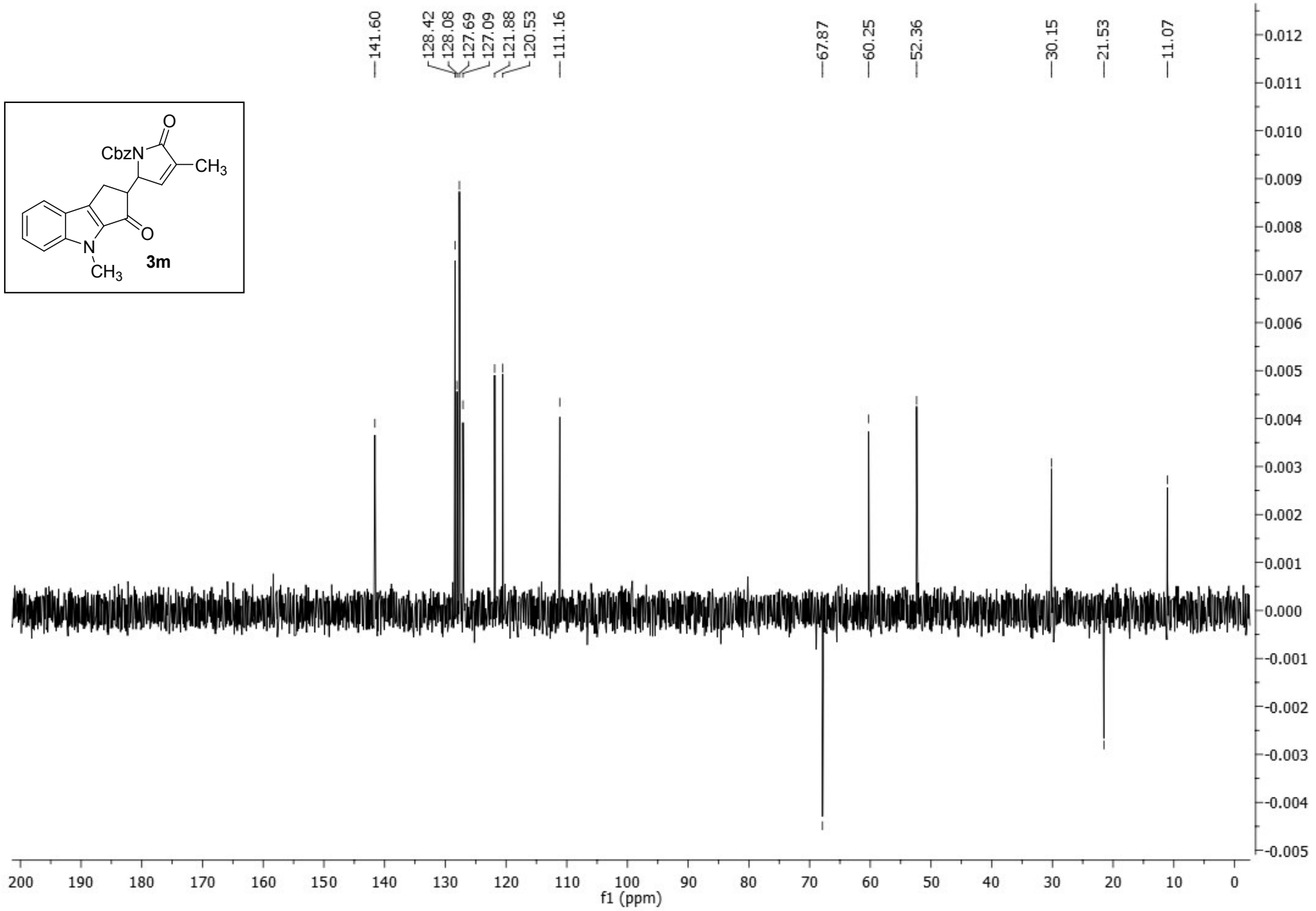
^{1}H NMR (600 MHz) spectrum of 3m in $CDCl_3$



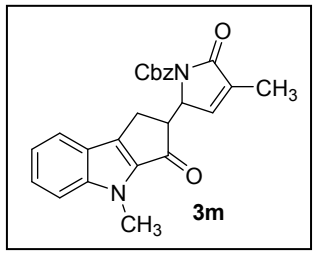
^{13}C NMR (150 MHz) spectrum of 3m in $CDCl_3$



DEPT-135 spectrum of 3m in $CDCl_3$

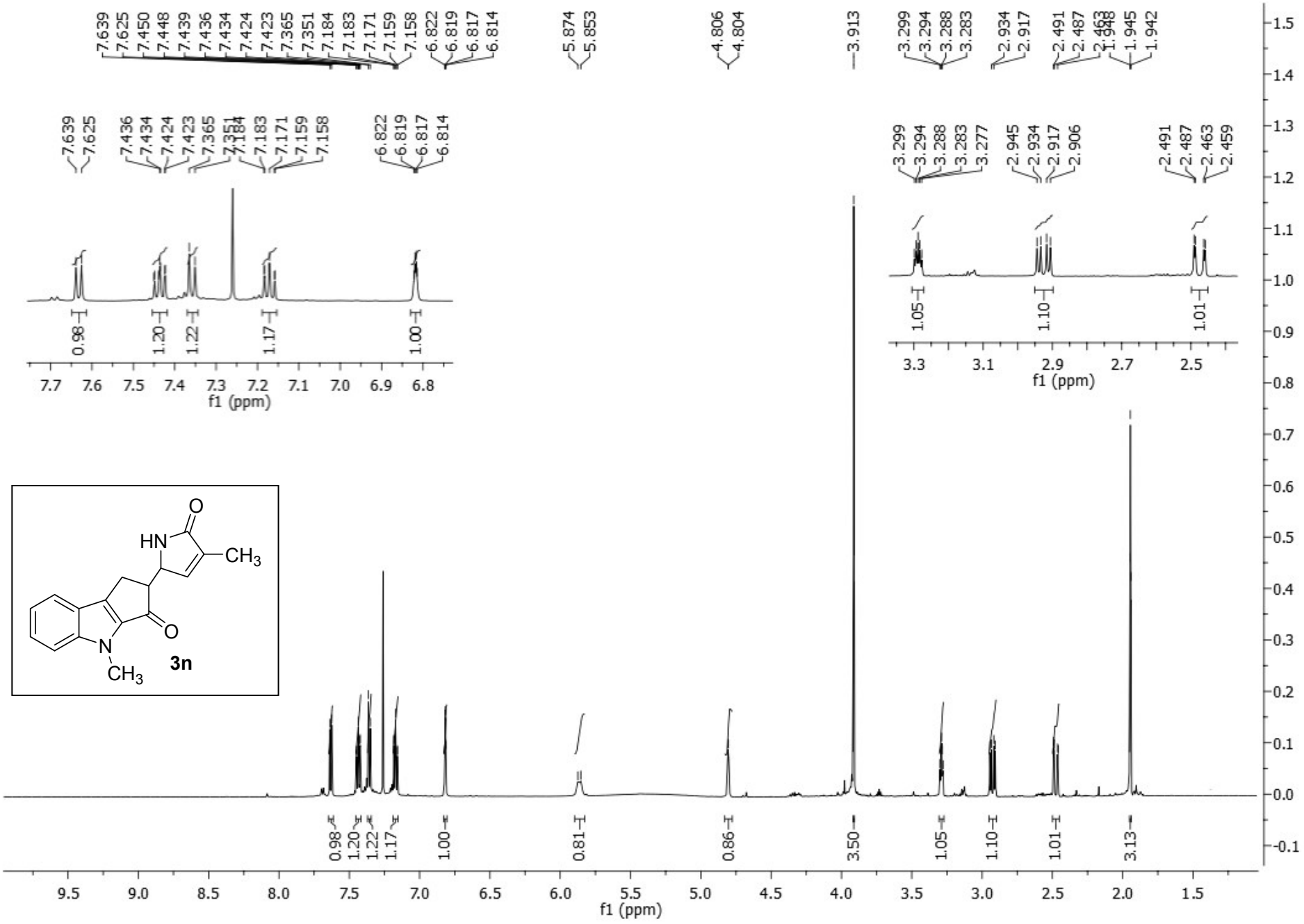


^{1}H-^{1}H COSY spectrum of 3m in $CDCl_3$

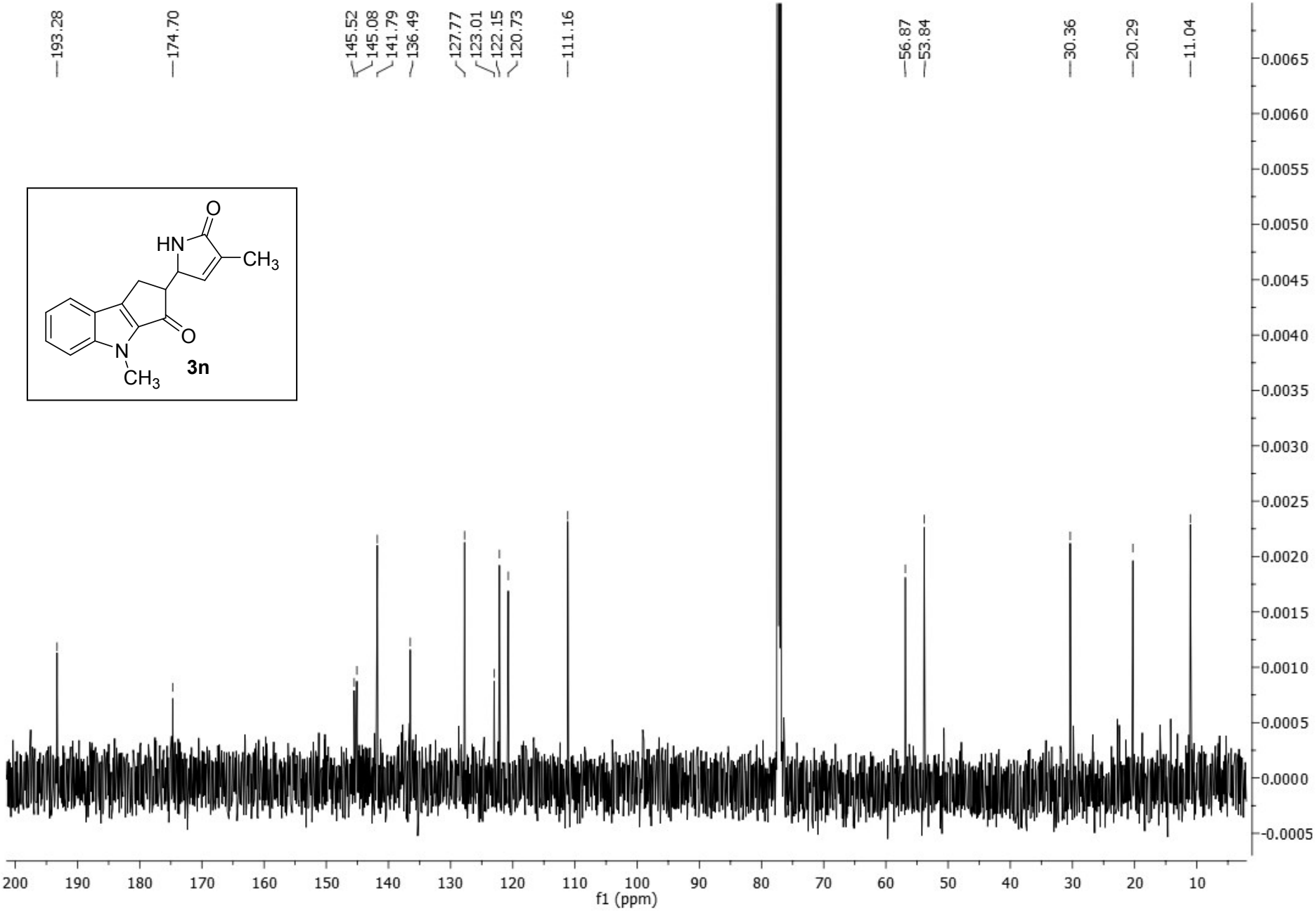


3m

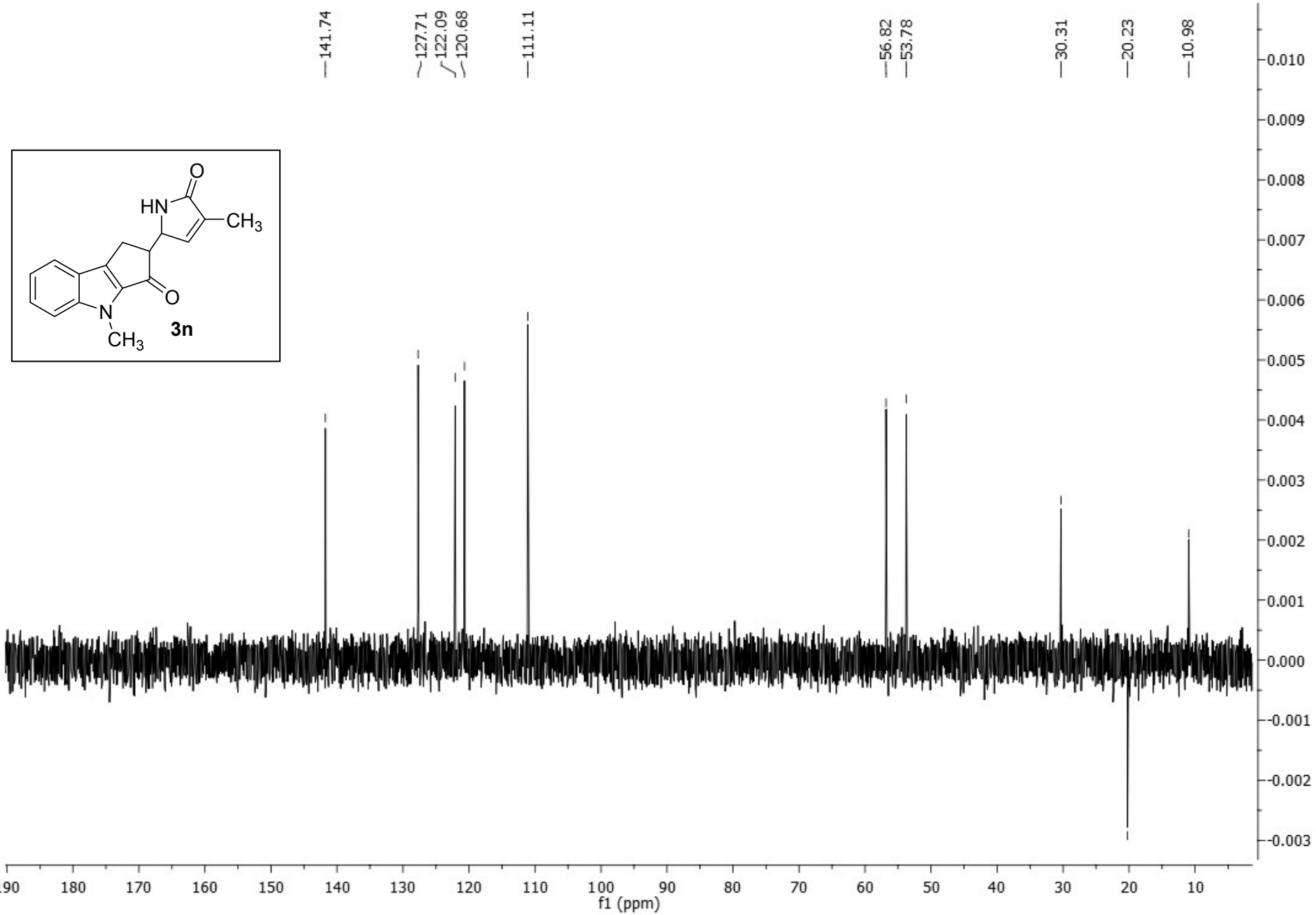
^{1}H NMR (600 MHz) spectrum of 3n in $CDCl_3$



^{13}C NMR (150 MHz) spectrum of 3n in $CDCl_3$



DEPT-135 spectrum of 3n in $CDCl_3$



Experimental X-ray diffraction analysis details

Table 1. Crystal data and structure refinement for Compound (+) 3a.

Empirical formula	$C_{22}\ H_{23}\ N\ O_6$
Formula weight	397.41
Crystal size (mm)	0.46 x 0.24 x 0.09
Crystal color, shape	Colourless, platelett
Crystal system, space group	Orthorhombic, $P2_12_12_1$
a, b, c (A)	9.0736(13), 10.7768(12), 21.461(3)
V (A3), Z	2098.5(5), 4
Temperature (K)	295
Wavelength	1.54184
Dcalc (g cm^{-3})	1.258
μ(cm^{-1})	0.760
Min/max transmission	0.91030/1.0000
Scan mode	ω
θ range (°)	1.90- 66.58
Index ranges	-9<=h<=10 -11<=k<=12 -25<=l<=20
Collected reflections	11813
Independent, Observed reflections (I≥2σ(I)	3745, 3702
Rint	0.0909
Parameters number	267
R1, wR2	0.0522, 0.0999
GooF	1.033

Largest peak and hole	0.122, -0.190
Flack parameter	0.01(8)
Completeness	99.9 %

Table 2. Bond lengths [A] and angles [deg] for Compound (+) 3a.

O(2)-C(1)	1.356(4)	C(1)-O(2)-C(12)	111.3(3)
O(2)-C(12)	1.466(4)	C(13)-O(3)-C(14)	117.8(3)
O(4)-C(15)	1.191(4)	C(2)-C(13)-O(3)	120.6(3)
N(1)-C(18)	1.394(4)	C(18)-N(1)-C(15)	125.3(3)
N(1)-C(18)	1.406(4)	C(18)-N(1)-C(14)	123.7(3)
C(13)-C(2)	1.316(5)	C(15)-N(1)-C(14)	110.9(3)
C(2)-C(1)	1.461(5)	C(13)-C(2)-C(1)	119.5(3)
C(2)-C(3)	1.485(5)	C(13)-C(2)-C(1)	119.5(3)

Figure 1: ORTEP plot of the asymmetric unit of compound with atom labeling. Thermal ellipsoids of non-hydrogen atoms are represented at 50% probability.