Supporting Information

EosinY and Copper- Catalyzed Oxidative [2+3] Annulation of Glycine Esters with Oxiranes and Thiiranes Under Light Free Conditions

Raghunath Chowdhury,*[a,b]

[a]Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085

[b]Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094

Fax: +91-22-25505151

E-mail: raghuc@barc.gov.in

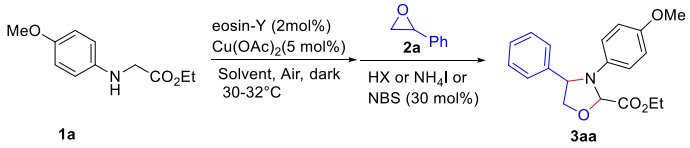
Table of contents

1. General experimental

General information Solvent removal was performed with a rotary evaporator that was connected to a dry ice condenser. TLC was carried out using Merck TLC plate. Column chromatography was performed on silica gel (230-400 mesh). The ^{1}H and ^{13}C NMR spectroscopic data were recorded with 500 MHz (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz), Varian spectrometer. The ^{1}H and ^{13}C chemical shifts are given in ppm (δ scale) from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26 for ^{1}H-NMR and δ 77.00 for ^{13} C-NMR) NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, sext = sextet, dd = double doublet, dt = doublet of triplets, td = triplet of doublet, m = multiplet), coupling constants (Hz) High resolution mass spectra were recorded under ESI-Q-TOF conditions. Melting points (mp) were measured in a Büchi B-540 apparatus and uncorrected. All the solvents were distilled out prior to use. Solvent were dried according to literature procedure. 1,2-dichloroethane and CH_3CN was distilled over CaH_2 and stored over 4Å molecular sieves. Eosin-Y (Dye content ~99%, Powder) was purchased from Sigma-Aldrich and used as received. Rhodamine 6G was purchased from sigma and used as received. $Cu(OAc)_2$ was purchased from Merck and used as received. HI (~57 wt. % in H_2O) was purchased from sigma and used as received.

2. Optimization study

Table S1. Optimization of the reaction conditions[a]

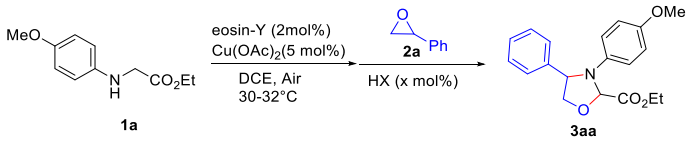


Entry	HX (30 mol%)	Solvent	dr[b]	**3aa**[c]
1	HBr	DCE	80:20	59
2	HCl	DCE	ND	<2
3	NH_4I	DCE	-	NR[d]

4	NBS	DCE	73:27	ND[e]
5[f]	HI	DMSO	50:50	ND[e]

Reaction conditions: 0.4 mmol of **1a,** eosin-Y (2 mol%), Cu(II) salt (5 mol%), solvent (2 mL) in the dark (without irradiation of light) under air for 12-16h at 30-32 °C, then **2a** (0.6 mmol), HI (30 mol%) were introduced in the reaction mixture and stirred for another 5 h. [b]determined from ^{1}H NMR of the crude reaction mixture. [c]Combined isolated yield of diastereomers after column chromatography. [d]NR = no reaction. ND[e] = yield not determined (small amount of product formation as judge from TLC). [f] the first step was 16h and 2nd step was 7h.

Table S2. Effect of HI loading in the diastereoselectivity of the reaction[a]



Entry	HI (X mol%)	dr[b]
1	30	84:16
2	100	50:50
3	150	25:75

[a]Reaction conditions: 0.4 mmol of **1a,** eosin-Y (2 mol%), $Cu(OAc)_2$ (5 mol%), solvent (2 mL) in the dark (without irradiation of light) under air at 30-32 °C, then **2a** (0.6 mmol), HI (xmol%) were introduced in the reaction mixture and stirred for another 5 h. [b]determined from ^{1}H NMR of the crude reaction mixture.

3. Experimental Setup

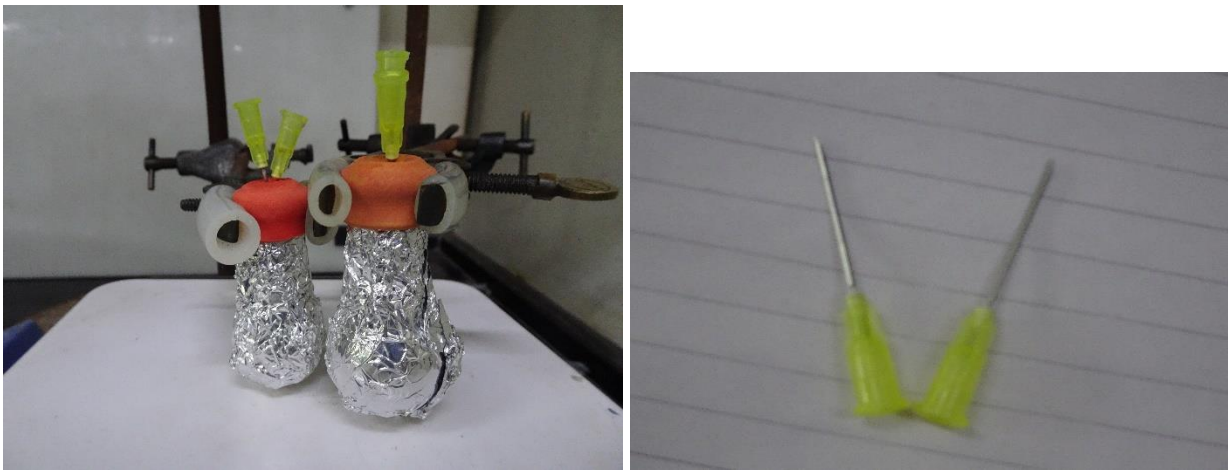


Figure S1: Left: Reaction set-up. Right: Needles used in this study. (Pictures custody: Raghunath Chowdhury)

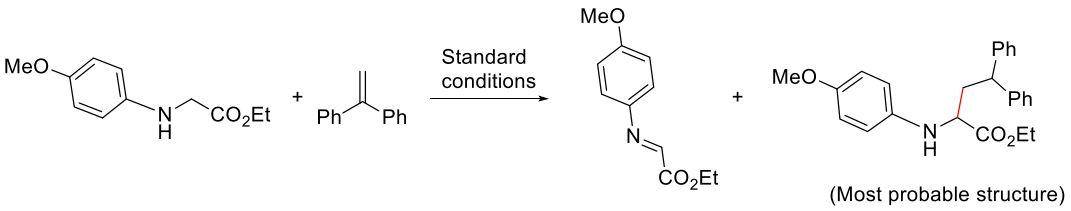
4. Preparation of Substrates 1, 2 and 4

Glycine derivatives **1** were prepared from literature procedure.[1] The data is close agreement with the reported literature.[2,3]

Oxirane **2a** was purchased from Sigma and used as received. Other Oxiranes were prepared according to literature procedure.[4] Thiiranes **4** were prepared following the reported literature.[5]

5. Radical trapping experiment

To an oven dried 5mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar, glycinate ester **1a** (0.4 mmol, 1 equiv), 1,1-diphenyl ethylene **14** (1.2 mmol, 3 equiv) and eosin-Y (5.2 mg, 0.008 mmol, 2 mol%) were dissolved in anhydrous DCE (2 mL). The $Cu(OAc)_2$ (3.66 mg, 0.02 mmol, 5 mol%) was added to the reaction mixture in one shot. The reaction mixture was stirred under air atmosphere at room temperature (30-32ºC) for 12h. A small amount of the reaction mixture was taken and subjected to HRMS analysis. The 1,1-diphenyl ethylene-**1a** trapped product **15** along with the imine **11** were detected in HRMS (**Figure S2 and S3**). This fact indicate that a radical process may be involved in this first step of this method.



1a **14** **11** (Most probable structure) **15**

Detected in HRMS
$C_{11}H_{14}NO_3$
[M + H]+:208.0968,
found: 208.0968

Detected in HRMS
$C_{25}H_{28}NO_3$
[M + H]+:390.2035,
found: 390.2035

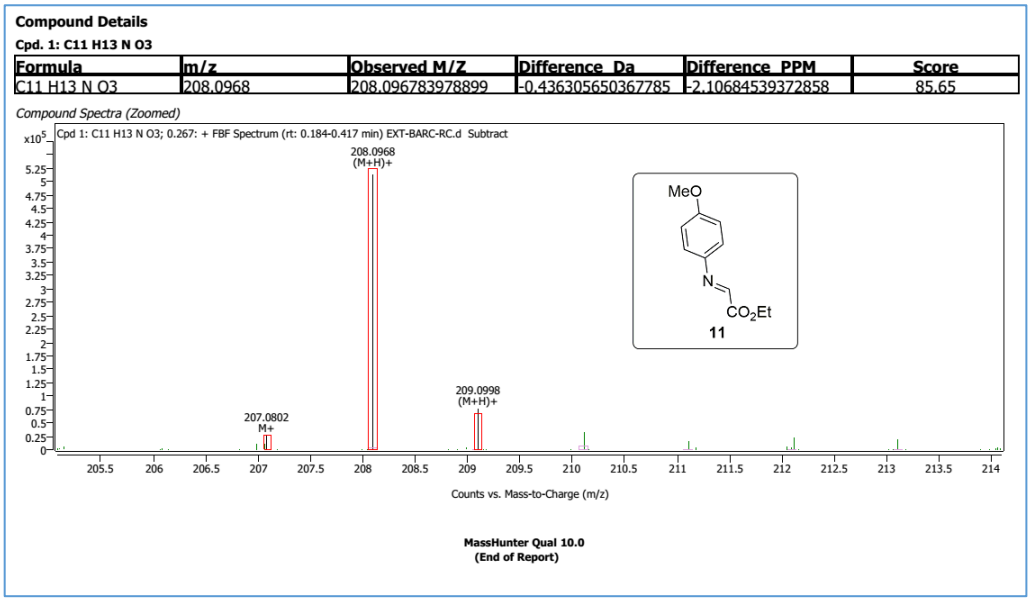


Figure S2. Detection of intermediate 11 in HRMS analysis

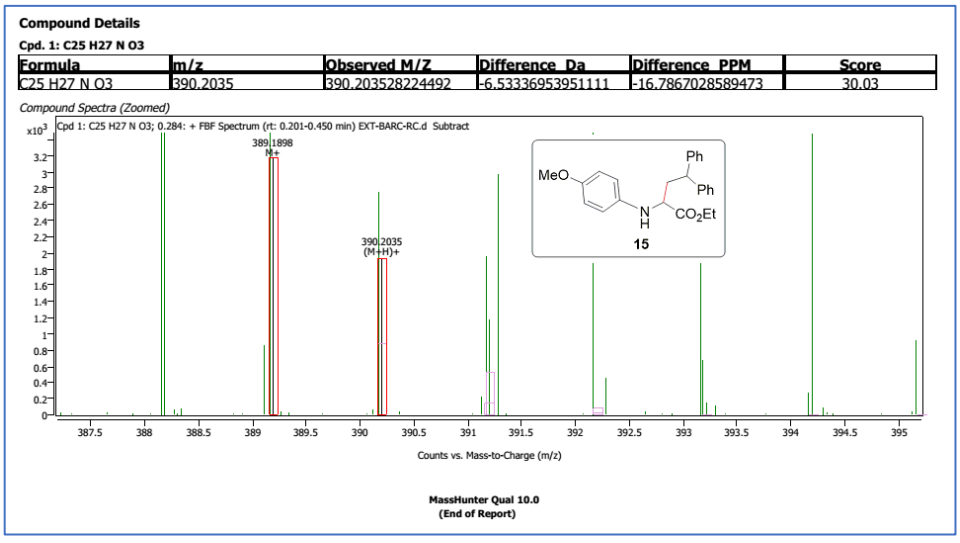
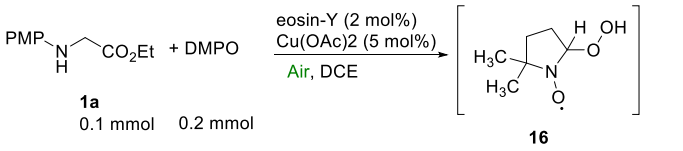


Figure S3. Detection of radical trapped product 15 in HRMS analysis

Detection of $O_2^{\bullet-}$ in the reaction mixture

To an oven dried 4mL glass vial (wrapped in aluminium foil) with a magnetic stirring bar, glycinate ester **1a** (0.1 mmol, 21 mg), and eosin-Y (1.3 mg, 2 mol%) were dissolved in anhydrous DCE (0.25 mL). The $Cu(OAc)_2$ (0.9-1.0 mg, 5 mol%) was added to the reaction mixture in one shot. The dimethyl-1-pyrroline N-oxide (DMPO) (0.2 mmol, 23 mg) was dissolved anhydrous DCE (0.25 mL) and added to the reaction mixture. The reaction mixture was stirred under air atmosphere at room temperature (28-30 ºC) for 3h. An aliquot was taken and subjected to HRMS analysis. The corresponding adduct DMPO-OOH was detected in HRMS analysis.

Note: The anhydrous DCE (10 mL) was purged with O_2 balloon for 3 minutes. This DCE was used in the reaction.



HRMS (Q-TOF) calcd for $C_6H_{13}NO_3$
[M + H]+: 147.0917, found: 147.0917

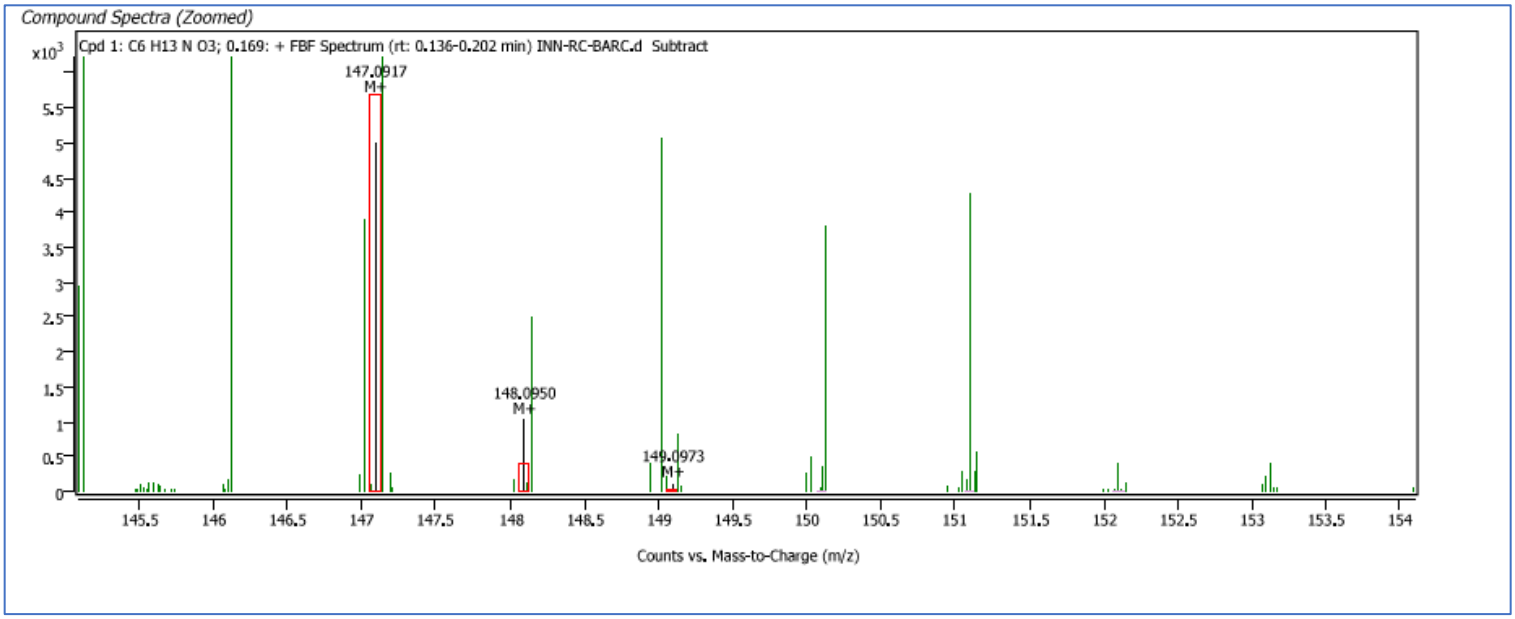


Figure S4. Detection of intermediate 16 in HRMS analysis

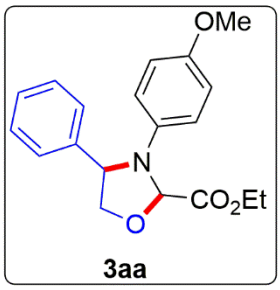
6. General procedure for the synthesis of product 3 and 5

To an oven dried 5mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar, glycinate ester **1** (0.4 mmol, 1 equiv) and eosin-Y (5.2 mg, 0.008 mmol, 2 mol%) were dissolved in anhydrous DCE or anhydrous CH_3CN. The $Cu(OAc)_2$ (~3.7mg, 0.02 mmol, 5 mol%) was added to the reaction mixture in one shot. The reaction mixture was stirred under air atmosphere* at room temperature (30-32ºC). After 12-18h**,** oxirane **2** (0.6 mmol or 0.8 mmol) dissolved in 0.4 mL of anhydrous DEC or thiirane **4** (0.6 mmol or 0.8 mmol) dissolved in 0.4 mL of anhydrous CH_3CN was added dropwise to the reaction mixture. HI (~ 57 wt.% in H_2O, 30 mol%, ~ 27 mg) dissolved in 0.1 mL of anhydrous DEC (for **3**) or 0.1 mL anhydrous CH_3CN (for **5**) was added dropwise. The resulting reaction mixture was further stirred for 3-6 h (for the synthesis of **3**) or 3-4 h (for the synthesis of **5**). After completion of the reaction, the reaction mixture was passed through a pad of Celite® and eluted with 50% EtOAc/petroleum ether. The solvent was concentrated under reduced pressure. The crude product was analysed by ^{1}H NMR spectroscopy to determine the diastereomeric ratio. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford product **3** or **5**.

*Two small needles were inserted through the rubber septum to maintain the oxygen (air) level inside the flask (More details, see Figure S1). Note:The glycinate ester (**1a** or **1b** or **1d**) was consumed in 8 h (monitored by TLC) but stirred for 12 h.

Note: the starting materials, eosin-Y, $Cu(OAc)_2$ and HI were weighed in ambient light and without out any protection of Argon or Nitrogen.

7. Characterization data of Products

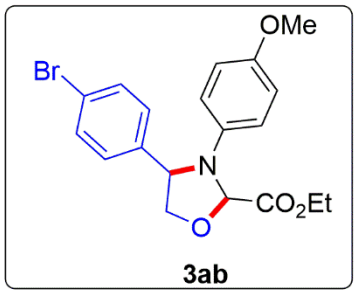


3aa

Ethyl-3-(4-methoxyphenyl)-4-phenyloxazolidine-2-carboxylate (3aa)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 64% (84 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.32-7.31 (m, 4 H), 7.27-7.25 (m, 1 H), 6.70 (d, J = 9.0 Hz, 2 H), 6.50 (d, J = 9.0 Hz, 2 H), 5.78 (s, 1 H), 4.98 (dd, J = 7.4, 3.7 Hz, 1 H), 4.79 (t, J = 7.8 Hz, 1

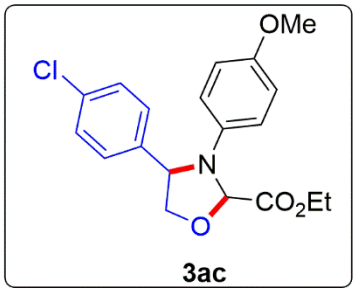
H), 4.21-4.13 (m, 2 H), 4.00 (dd, *J* = 7.8, 3.7 Hz, 1 H), 3.68 (s, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 170.0, 152.6, 141.1, 136.7, 128.8 (2 C), 127.5, 126.3 (3 C), 115.4, 114.7 (2 C), 89.2, 75.9, 61.2, 61.0, 55.4, 14.1. Spectroscopic data is well matched with the literature report.[6a]



3ab

Ethyl-4-(4-bromophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ab)

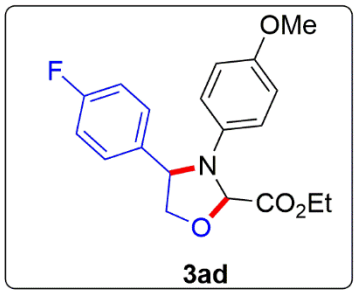
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 66% (108 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: *δ* 7.43 (d, *J* = 7.9 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 6.71 (d, *J* = 8.9 Hz, 2 H), 6.48 (d, *J* = 8.6 Hz, 2 H), 5.77 (s, 1 H), 4.94 (dd, *J* = 7.4, 3.7 Hz, 1 H), 4.78 (t, *J* = 7.7 Hz, 1 H), 4.19-4.12 (m, 2 H), 3.97 (dd, *J* = 7.6, 3.3 Hz, 1 H), 3.69 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 169.8, 152.8, 140.3, 136.4, 131.9 (2 C), 128.1 (2 C), 121.4, 115.6 (2 C), 114.7 (2 C), 89.1, 75.6, 61.3, 60.5, 55.5, 14.1. Spectroscopic data is well matched with the literature report.[6a]



3ac

Ethyl-4-(4-chlorophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ac)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 64% (93 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: *δ* 7.29-7.24 (m, 4 H), 6.71 (d, *J* = 8.9 Hz, 2 H), 6.48 (d, *J* = 9.0 Hz, 2 H), 5.76 (s, 1 H), 4.95 (dd, *J* = 7.4, 3.7 Hz, 1 H), 4.78 (t, *J* = 7.7 Hz, 1 H), 4.19-4.13 (m, 2 H), 3.97 (dd, *J* = 7.9, 3.7 Hz, 1 H), 3.69 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 169.8, 152.8, 139.7, 136.4, 133.3, 129.0 (2 C), 127.7 (2 C), 115.6 (2 C), 114.7 (2 C), 89.2, 75.7, 61.2, 60.4, 55.5, 14.1. Spectroscopic data is well matched with the literature report. [6a]

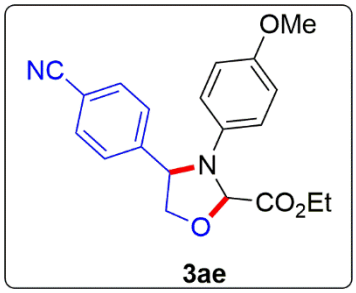


3ad

Ethyl-4-(4-fluorophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ad)

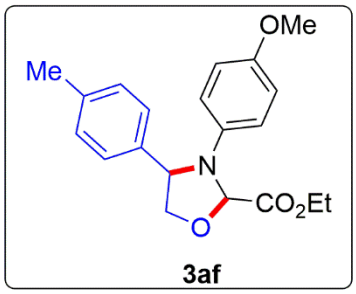
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 61% (84 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: *δ* 7.30-7.27 (m, 2 H), 7.00

(t, *J* = 8.7 Hz, 2 H), 6.73-6.71 (m, 2 H), 6.49 (d, *J* = 8.7 Hz, 2 H), 5.78 (s, 1 H), 4.97 (dd, *J* = 7.3, 3.7 Hz, 1 H), 4.78 (t, *J* = 7.7 Hz, 1 H), 4.21-4.12 (m, 2 H), 3.98 (dd, *J* = 7.9, 3.7 Hz, 1 H), 3.69 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: *δ* 169.9, 162.1 (J_{C-F} = 244.4 Hz), 152.7, 136.8 (J_{C-F} = 3.0 Hz), 136.5, 127.9 (*J* = 8.0 Hz, 2 C), 115.8 (J_{C-F} = 21.6 Hz, 2 C), 115.6 (2 C), 114.7 (2 C), 89.1, 75.8, 61.2, 60.3, 55.4, 14.1. Spectroscopic data is well matched with the literature report. [6a]



Ethyl-4-(4-cyanophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ae)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 60% (85 mg) yield. **Data of Major diastereomer**:**^{1}H NMR (500MHz, CDCl$_3$)**: *δ* 7.60 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.45 (d, *J* = 9.0 Hz, 2 H), 5.78 (s, 1 H), 5.00 (dd, *J* = 7.5, 3.6 Hz, 1 H), 4.82 (t, *J* = 7.9 Hz, 1 H), 4.19-4.12 (m, 2 H), 3.98 (dd, *J* = 8.0, 3.4 Hz, 1 H), 3.68 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: *δ* 169.6, 152.9, 146.9, 136.0, 132.7 (2 C), 127.0 (2 C), 118.6, 115.4 (2 C) , 114.8 (2 C), 111.5, 89.1, 75.2, 61.4, 60.6, 55.4, 14.0. Spectroscopic data is well matched with the literature report.[6a]



Ethyl-3-(4-methoxyphenyl)-4-(p-tolyl)oxazolidine-2-carboxylate (3af)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers 47% (64.5 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, CDCl$_3$)**: *δ* 7.20 (d, *J* = 7.9 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.52 (d, *J* = 9.0 Hz, 2 H), 5.78 (s,1 H), 4.96 (dd, *J* = 7.2, 3.7 Hz, 1 H), 4.78 (t, *J* = 7.7 Hz, 1 H), 4.20-4.13 (m, 2 H), 4.00 (dd, *J* = 7.8, 3.8 Hz, 1 H), 3.68 (s, 3 H), 2,31 (s, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: *δ* 170.1, 152.5, 138.1, 137.2, 136.8, 129.5 (2 C), 126.2 (3 C), 115.5, 114.6 (2 C), 89.1, 76.0, 61.2, 60.8, 55.5, 21.0, 14.1. **HRMS (ESI-TOF)** calcd for $C_{20}H_{24}NO_4$ $[M + H]^+$: 342.1700, found: 342.1704. ^{1}H NMR data is well matched with the literature report.[6a] (Note: 0.8 mmol of oxirane **2f** was used).

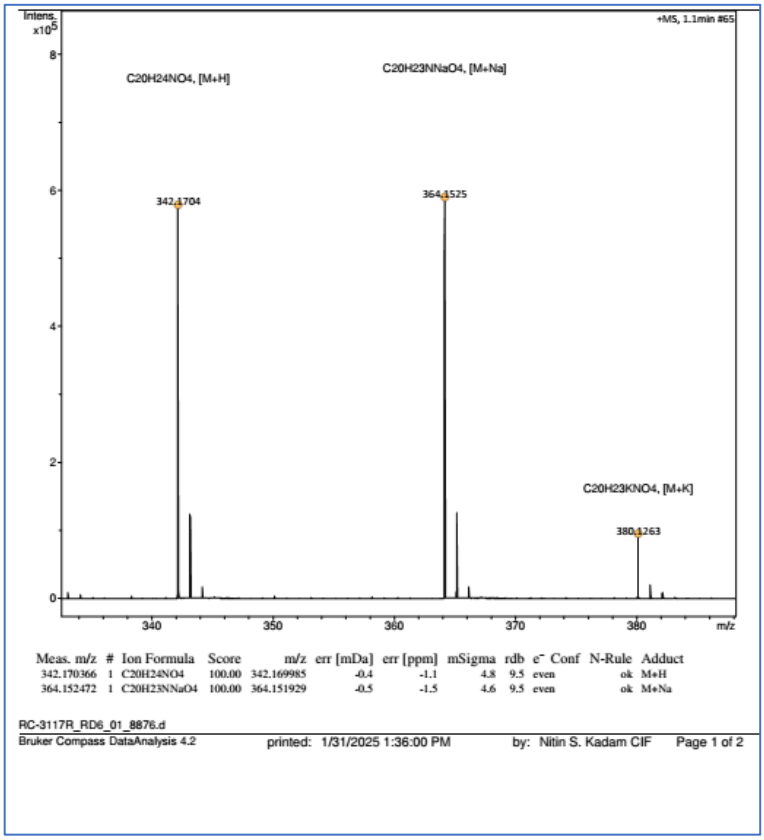
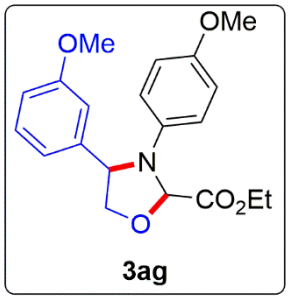
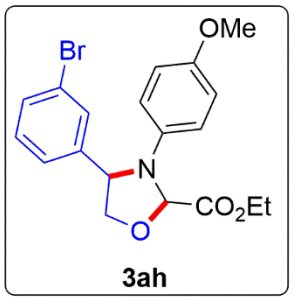


Figure S5. HRMS spectra of **3af**



Ethyl -4-(3-methoxyphenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ag)

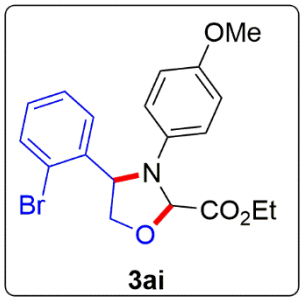
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 61% (87 mg) yield. **Data of Major diastereomer**:**^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.24 (t, J = 7.9 Hz, 1 H), 6.91 (d, J = 7.6 Hz, 1 H), 6.87 (bs, 1 H), 6.79 (dd, J = 8.1, 2.0 Hz, 1 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.52 (d, J = 9.0 Hz, 2 H), 5.78 (s, 1 H), 4.97 (dd, J = 7.4, 3.7 Hz, 1 H), 4.78 (t, J = 7.6 Hz, 1 H), 4.20-4.12 (m, 2 H), 4.00 (dd, J = 7.8, 3.7 Hz, 1 H), 3.77 (s, 3 H), 3.69 (s, 3 H), 1.21 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 170.0, 160.0, 152.6, 143.0, 136.8, 129.8, 118.6 (2 C), 115.4, 114.6 (2 C), 112.7, 111.9, 89.2, 75.8, 61.2, 61.0, 55.4, 55.1, 14.1. Spectroscopic data is well matched with the literature report.[6a] (Note: 0.8 mmol of oxirane **2g** was used).



3ah

Ethyl -4-(3-bromophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ah)

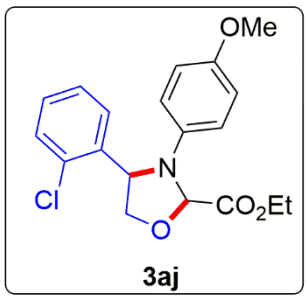
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 70% (114 mg) yield. Data of Major diastereomer: **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.48 (s, 1 H), 7.39-7.38 (m, 1 H), 7.25-7.24 (m, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 6.73 (d, *J* = 9.0 Hz, 2 H), 6.49 (d, *J* = 9.0 Hz, 2 H), 5.78 (s, 1 H), 4.97 (dd, *J* = 7.5, 3.5 Hz, 1 H), 4.78 (t, *J* = 7.8 Hz, 1 H), 4.20-4.11(m, 2 H), 4.00 (dd, *J* = 8.0, 3.5 Hz, 1 H), 3.69 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 169.8, 152.8, 143.8, 136.4, 130.8, 130.4, 129.3, 124.9 (2 C), 123.0, 115.4, 114.7 (2 C), 89.1, 75.6, 61.3, 60.5, 55.5, 14.1; **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}BrNO_4$ $[M + H]^+$: 408.0630, found: 408.0610.



3ai

Ethyl 4-(2-bromophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ai)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 59 % (96 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.58 (dd, *J* = 7.8, 0.7 Hz, 1 H), 7.23-7.18 (m, 2 H), 7.13-7.11 (m, 1 H), 6.74 (d, *J* = 9.0 Hz, 2 H), 6.41 (d, *J* = 9.0 Hz, 2 H), 5.80 (s, 1 H), 5.34 (dd, *J* = 7.4, 2.7 Hz, 1 H), 4.90 (t, *J* = 7.9 Hz, 1H), 4.24-4.10 (m, 2 H), 4.05 (dd, *J* = 8.1, 2.7 Hz, 1 H), 3.70 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 169.8, 152.6, 139.7, 136.4, 132.8, 129.0, 127.8, 127.7, 122.5, 114.9 (4 C), 89.0, 74.6, 61.4, 60.3, 55.5, 14.1; **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}BrNO_4$ $[M + H]^+$: 408.0630, found: 408.0617.

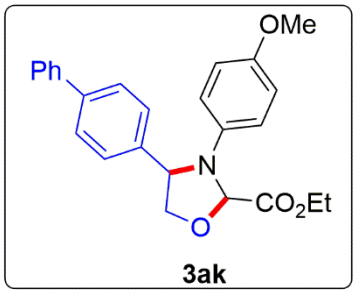


3aj

Ethyl-4-(2-chlorophenyl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3aj)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 60% (87 mg) yield. **Data of Major diastereomer**: **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.40 (dd, *J* = 8.7, 1.0 Hz, 1 H), 7.25-7.14 (m, 3 H, merged with solvent peak), 6.74 (d, *J* = 9.0 Hz, 2 H), 6.43 (d, *J* = 9.0 Hz, 2 H), 5.79 (s, 1 H),

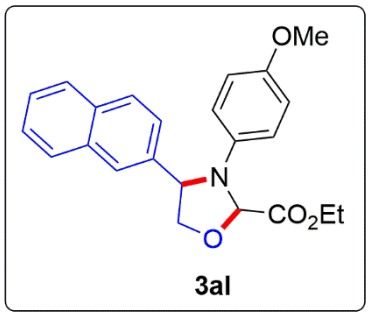
5.39 (dd, *J* = 7.4, 2.7 Hz, 1 H), 4.90 (t, *J* = 7.8 Hz, 1 H), 4.24-4.13 (m, 2 H), 4.06 (dd, *J* = 8.1, 2.8 Hz, 1 H), 3.70 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 169.8, 152.6, 138.2, 136.4, 132.5, 129.5, 128.6, 127.5, 127.2, 114.90 (2 C), 114.85 (2 C), 89.0, 74.6, 61.3, 57.9, 55.5, 14.1.(Note: 0.88 mmol of oxirane **2j** was used). Spectroscopic data is well matched with the literature report.[6a]



3ak

Ethyl-4-([1,1'-biphenyl]-4-yl)-3-(4-methoxyphenyl)oxazolidine-2-carboxylate (3ak)

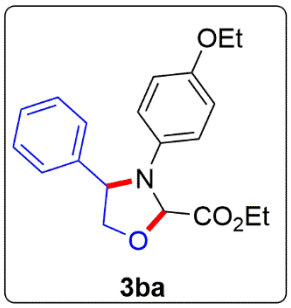
Purified by column chromatography on silica gel (10%- 15% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 66% (107 mg) yield. **Data of Major diastereomer**: **^1H NMR (500MHz, $CDCl_3$)**: *δ* 7.56 (t, *J* = 7.2 Hz, 4 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 6.74 (d, *J* = 9.0 Hz, 2 H), 6.56 (d, *J* = 9.0 Hz, 2 H), 5.83 (s, 1 H), 5.04 (dd, *J* = 7.3, 3.7 Hz, 1 H), 4.83 (t, *J* = 7.6 Hz, 1 H), 4.22-4.15 (m, 2 H), 4.07 (dd, *J* = 7.8, 3.7 Hz, 1 H), 3.69 (s, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 170.0, 152.6, 140.6, 140.5, 140.2, 136.7, 128.7 (2 C), 127.5 (2 C), 127.2, 127.0 (2 C), 126.7 (2 C), 115.5 (2 C), 114.7 (2 C), 89.2, 75.9, 61.2, 60.8, 55.5, 14.1; **HRMS (ESI)** calcd for $C_{25}H_{25}NO_4K$ $[M + K]^+$: 442.1420, found: 442.1422.



3al

Ethyl-3-(4-methoxyphenyl)-4-(naphthalen-2-yl)oxazolidine-2-carboxylate (3al)

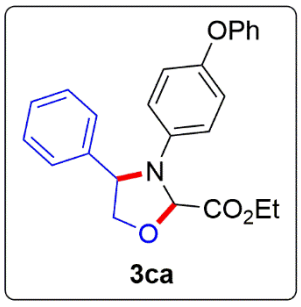
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 59% (89 mg) yield. **Data of Major diastereomer**: **^1H NMR (500MHz, $CDCl_3$)**: *δ* 7.84-7.80 (m, 4 H), 7.49-7.45 (m, 3 H), 6.70 (d, *J* = 9.1 Hz, 2 H), 6.58 (d, *J* = 9.1 Hz, 2 H), 5.88 (s, 1 H), 5.16 (dd, *J* = 7.5, 3.8 Hz, 1 H), 4.87 (t, *J* = 7.8 Hz, 1 H), 4.23-4.18 (m, 2 H), 4.10 (dd, *J* = 7.9, 3.8 Hz, 1 H), 3.66 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 170.0, 152.7, 138.7, 136.8, 133.4, 133.0, 128.9, 127.8, 127.7, 126.2, 125.8, 125.3 (2 C), 124.1, 115.5, 114.7 (2 C), 89.3, 75.8, 61.3, 61.2, 55.5, 14.1. Spectroscopic data is well matched with the literature report. [6a] [Note: the 2nd step of the reaction was incomplete even stirring for 5h]



3ba

Ethyl-3-(4-ethoxyphenyl)-4-phenyloxazolidine-2-carboxylate (3ba)

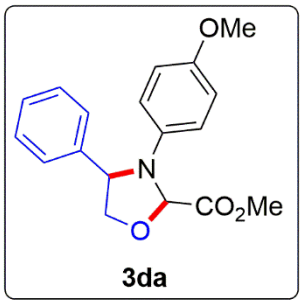
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 60% yield (82 mg). **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.32-7.31 (m, 4 H), 7.27-7.24 (m, 1 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 5.79 (s, 1 H), 4.98 (dd, *J* = 7.3, 3.7 Hz, 1 H), 4.79 (t, *J* = 7.7 Hz, 1 H), 4.20-4.11 (m, 2 H), 4.02 (dd, *J* = 7.8, 3.7 Hz, 1 H), 3.89 (q, *J* = 7.0 Hz, 2 H), 1.33 (t, *J* = 7.0 Hz, 3 H), 1.21 (t, *J* = 7.0 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 170.1, 152.0, 141.2, 136.7, 128.8 (2 C), 127.5, 126.3 (2 C), 115.5 (2 C), 115.4 (2 C), 89.3, 75.9, 63.7, 61.2, 61.1, 14.9, 14.1. Spectroscopic data is well matched with the literature report.[6a]



3ca

Ethyl-3-(4-phenoxyphenyl)-4-phenyloxazolidine-2-carboxylate (3ca)

Purified by column chromatography on silica gel (5%-8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 69% yield (108 mg). **Data of Major diastereomer**:**^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.38-7.31 (m, 5 H), 7.29-7.24 (m, 2 H, solvent peak merged), 7.00 (t, *J* = 7.3 Hz, 1 H), 6.88 (d, *J* = 8.1 Hz, 2 H), 6.83 (d, *J* = 8.9 Hz, 2 H), 6.51 (d, *J* = 8.9 Hz, 2 H), 5.81 (s, 1 H), 5.00 (dd, *J* = 7.3, 2.9 Hz, 1 H), 4.82 (t, *J* = 7.7 Hz, 1 H), 4.27-4.17 (m, 2 H), 4.05 (dd, *J* = 7.9, 2.9 Hz, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)**: δ 169.8, 158.4, 148.6, 141.1, 139.1, 129.5 (2 C), 128.9 (2 C), 127.7, 126.2 (2 C), 122.2, 120.6 (2 C), 117.5 (2 C), 114.9 (2 C), 88.8, 75.8, 61.4, 61.1, 14.1.(Note: the reaction time of first step was 18 h). Spectroscopic data is well matched with the literature report. [6a]

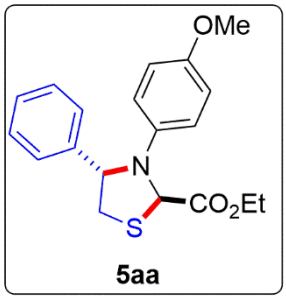


3da

Methyl-3-(4-ethoxyphenyl)-4-phenyloxazolidine-2-carboxylate (3da)

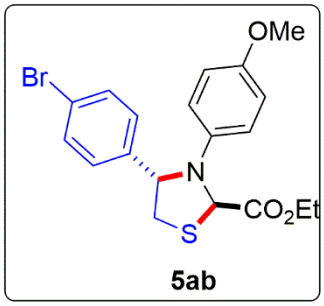
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a mixture of diastereomers in 65% yield (81.5 mg). **Data of Major diastereomer**: **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.32-7.31 (m, 4 H), 7.27-7.24 (m, 1 H), 6.72-6.71 (m, 2 H), 6.51-6.49 (m, 2 H), 5.82 (s, 1 H), 4.99 (dd, *J* = 7.3, 3.5 Hz, 1 H), 4.79 (t, *J* = 7.7 Hz, 1

H), 4.03 (dd, J = 7.9, 3.5 Hz, 1 H), 3.72 (s, 3 H), 3.68 (s, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: δ 170.5, 152.5, 141.1, 136.6, 128.8 (2 C), 127.6, 126.3 (2 C), 115.3 (2 C), 114.7 (2 C), 88.9, 75.8, 61.0, 55.4, 52.1. Spectroscopic data is well matched with the literature report. [6a]



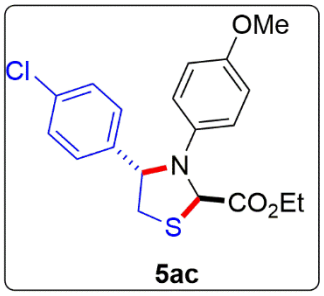
Ethyl-3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (5aa)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 73% yield (101 mg). **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.34-7.31 (m, 4 H), 7.27-7.26 (m, 1 H), 6.72 (d, J = 8.7 Hz, 2 H), 6.48 (d, J = 9.0 Hz, 2 H), 5.40 (s, 1 H), 5.28 (d, J = 7.0 Hz, 1 H), 4.27-4.20 (m, 2 H), 3.99 (dd, J = 11.0, 7.2 Hz, 1 H), 3.69 (s, 3 H), 2.90 (d, J = 11.2 Hz, 1 H), 1.29 (t, J = 7.1 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: δ 171.6, 152.1, 142.3, 138.5, 128.5 (2 C), 127.4, 126.3 (2 C), 114.74 (2 C), 114.69 (2 C), 65.8, 63.9, 61.4, 55.4, 39.1, 14.0. Spectroscopic data is well matched with the literature report.



Ethyl-4-(4-bromoophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5ab)

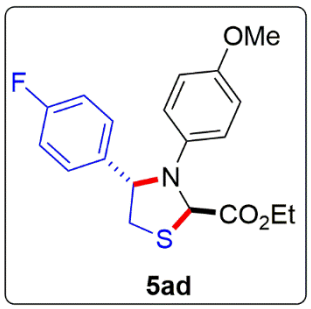
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 68% yield (115 mg). **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.43 (d, J = 8.3 Hz, 2 H), 7.21 (d, J = 8.3 Hz, 2 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.43 (d, J = 9.0 Hz, 2 H), 5.37 (s, 1 H), 5.21 (d, J = 7.1Hz, 1 H), 4.26-4.18 (m, 2 H), 3.96 (dd, J = 11.3, 7.3 Hz, 1 H), 3.68 (s, 3 H), 2.84 (d, J = 11.3 Hz, 1 H), 1.27 (t, J = 7.1 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: δ 171.4, 152.2, 141.4, 138.2, 131.6 (2 C), 128.0 (2 C), 121.2, 114.73 (2 C), 117.72 (2 C), 65.1, 63.7, 61.5, 55.4, 38.8, 14.0. **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}BrNO_3S$ $[M + H]^+$: 424.0400, found: 424.0377.



Ethyl-4-(4-chlorophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5ac)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 55% yield (83.5 mg). **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.29-7.25 (m, 4 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.43 (d, J = 9.1

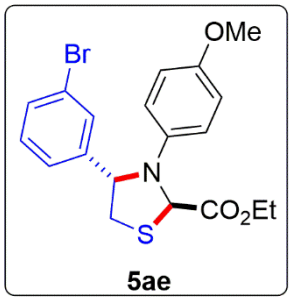
Hz, 2 H), 5.36 (s, 1 H), 5.23 (d, *J* = 7.1 Hz, 1 H), 4.27-4.17 (m, 2 H), 3.96 (dd, *J* = 11.3, 7.3 Hz, 1 H), 3.69 (s, 3 H), 2.85 (d, *J* = 11.3 Hz, 1 H), 1.27 (t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: δ 171.5, 152.3, 141.0, 138.3, 133.1, 128.7 (2 C), 127.7 (2 C), 114.8 (2 C), 114.78 (2 C), 65.2, 63.8, 61.6, 55.5, 39.0, 14.1. **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}ClNO_3S$ $[M + H]^+$: 378.0925, found: 378.0905.



5ad

Ethyl-4-(4-fluorophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5ad)

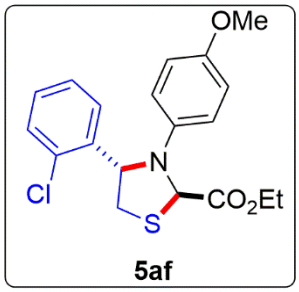
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 77.5% yield (112 mg). **^{1}H NMR (500MHz, $CDCl_3$)**: δ (dd, *J* = 8.3, 5.5 Hz, 2 H), 7.0 (t, *J* = 8.5 Hz, 2 H), 6.72 (d, *J* = 9.1 Hz, 2 H), 6.44 (d, *J* = 9.1 Hz, 2 H), 5.37 (s, 1 H), 5.24 (d, *J* = 7.0 Hz, 1 H), 4.26-4.18 (m, 2 H), 3.96 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.68 (s, 3 H), 2.84 (d, *J* = 11.2 Hz, 1 H), 1.27 (t, *J* = 7.1 Hz, 3 H); **$^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$)**: δ 171.6, 162.1 ($J_{C\text{-}F}$ = 244.2 Hz), 152.2, 138.4, 138.1 ($J_{C\text{-}F}$ = 3.0 Hz), 127.9 ($J_{C\text{-}F}$ = 32.1 Hz, 2 C), 115.4 ($J_{C\text{-}F}$ = 21.4 Hz, 2 C), 114.9 (2 C), 114.8 (2 C), 65.2, 63.8, 61.6, 55.5, 39.1, 14.1; **^{19}F NMR (470 MHz, $CDCl_3$)**: δ -115.2 (tt, *J* = 8.5, 5.2 Hz); **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}FNO_3S$ $[M + H]^+$: 362.1226, found: 362.1232. (Note: 0.8 mmol of thiirane **4d** was used).



5ae

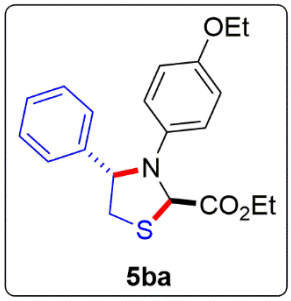
Ethyl-4-(3-bromophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5ae)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 85% yield (144 mg). **^{1}H NMR (500MHz, $CDCl_3$)**: δ 7.49 (s, 1 H), 7.39 (d, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 6.5 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 6.72 (d, *J* = 9.1 Hz, 2 H), 6.43 (d, *J* = 9.0 Hz, 2 H), 5.37 (s, 1 H), 5.20 (d, *J* = 7.2 Hz, 1 H), 4.25-4.18 (m, 2 H), 3.96 (dd, *J* = 11.3, 7.4 Hz, 1 H), 3.69 (s, 3 H), 2.86 (d, *J* = 11.3 Hz, 1 H), 1.27 (t, *J* = 7.1 Hz, 3 H); **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)**: δ 171.5, 152.3, 145.1, 138.2, 136.6, 130.1, 129.3, 125.0, 122.7, 114.8 (2 C), 114.7 (2 C), 65.3, 63.9, 61.6, 55.5, 38.9, 14.1; **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}BrNO_3S$ $[M + H]^+$: **HRMS (ESI)** calcd for $C_{19}H_{21}BrNO_3S$ $[M + H]^+$: 424.0400, found: 424.0379.



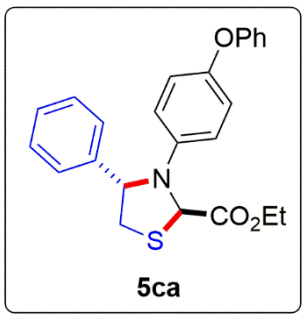
Ethyl-4-(2-chlorophenyl)-3-(4-methoxyphenyl)thiazolidine-2-carboxylate (5af)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 69% yield (104 mg). **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.41 (d, J = 7.9 Hz, 1 H), 7.24 (td, J = 7.6, 1.5 Hz, 1 H), 7.21 (dd, J = 7.8, 1.5 Hz, 1 H), 7.17-7.14 (m, 1 H), 6.73 (d, J = 9.1 Hz, 2 H), 6.38 (d, J = 9.0 Hz, 2 H), 5.63 (d, J = 7.2 Hz, 1 H), 5.40 (s, 1 H), 4.28-4.19 (m, 2 H), 4.03 (dd, J = 11.6, 7.3 Hz, 1 H), 3.68 (s, 3 H), 2.95 (d, J = 12.0 Hz, 1 H), 1.28 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 171.5, 152.1, 138.8, 138.1, 131.8, 129.6, 128.7, 128.5, 126.7, 114.9 (2 C), 114.2 (2 C), 63.8, 63.0, 61.6, 55.5, 37.4, 14.1. **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}ClNO_3S$ [M + H]$^+$: 378.0925, found: 378.0906.



Ethyl-3-(4-ethoxyphenyl)-4-phenylthiazolidine-2-carboxylate (5ba)

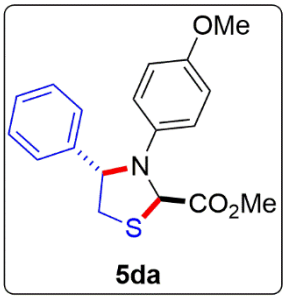
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in ~70% yield (100 mg). Physical state : White solid (M.p: 88-90 °C); **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.33-7.31 (m, 4 H), 7.27-7.26 (m, 1 H), 6.71 (d, J = 9.0 Hz, 2 H), 6.46 (d, J = 9.1 Hz, 2 H), 5.39 (s, 1 H), 5.27 (d, J = 6.8 Hz, 1 H), 4.27-4.19 (m, 2 H), 3.99 (dd, J = 11.2, 7.3 Hz, 1 H), 3.90 (q, J = 7.0 Hz, 2 H), 2.90 (dd, J = 11.2, 0.8 Hz, 1 H), 1.34 (t, J = 7.0 Hz, 3 H), 1.28 (t, J = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 171.7, 151.4, 142.4, 138.5, 128.5 (2 C), 127.4, 126.3 (2 C), 115.5 (2 C), 114.7 (2 C), 65.8, 63.9, 63.7, 61.5, 39.1, 14.9, 14.1; **HRMS (ESI-TOF)** calcd for $C_{20}H_{24}NO_3S$ [M + H]$^+$: 358.1471, found: 358.1451.



Ethyl-3-(4-phenoxyphenyl)-4-phenylthiazolidine-2-carboxylate (5ca)

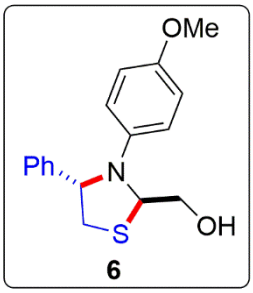
Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 57% yield (93 mg). Physical state : White solid (M.p: 90-92°C); **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.36-7.35 (m, 4 H), 7.31-7.29 (m, 1 H), 7.27 (t, J = 7.8 Hz, 2 H), 7.02 (t, J = 7.4 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 2 H),

6.85 (d, *J* = 9.0 Hz, 2 H), 6.48 (d, *J* = 9.0 Hz, 2 H), 5.40 (s, 1 H), 4.32-4.22 (m, 2 H), 5.31 (d, *J* = 7.0 Hz, 1 H), 4.03 (dd, *J* = 11.3, 7.2 Hz, 1 H), 2.91 (d, *J* = 11.3 Hz, 1 H), 1.31(t, *J* = 7.2 Hz, 3 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 171.5, 158.4, 148.2, 142.1, 140.7, 129.5 (2 C), 128.5 (2 C), 127.5, 126.2 (2 C), 122.2, 120.7 (2 C), 117.5 (2 C), 114.4 (2 C), 65.9, 63.6, 61.6, 39.1, 14.1; **HRMS (ESI-TOF)** calcd for $C_{24}H_{24}NO_3S$ $[M + H]^+$: 406.1471, found: 406.1450.



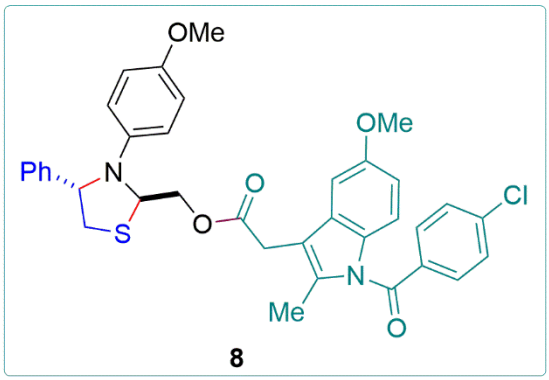
Methyl-3-(4-methoxyphenyl)-4-phenylthiazolidine-2-carboxylate (5da)

Purified by column chromatography on silica gel (5%- 8% EtOAc/petroleum ether). The above titled compound was isolated as a single diastereomer in 74% yield (98 mg). **^1H NMR (500MHz, $CDCl_3$)**: *δ* 7.33-7.32 (m, 4 H), 7.28-7.25 (m, 1 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.46 (d, *J* = 9.0 Hz, 2 H), 5.41 (s, 1 H), 5.28 (d, *J* = 7.0 Hz, 1 H), 3.97 (dd, *J* = 11.1, 7.3 Hz, 1 H), 3.78 (s, 3 H), 3.68 (s, 3 H), 2.90 (d, *J* = 11.2 Hz, 1 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 172.2, 152.1, 142.2, 138.4, 128.5 (2 C), 127.4, 126.3 (2 C), 114.76 (2 C), 114.72 (2 C), 65.7, 63.6, 55.5, 52.6, 39.1; **HRMS (ESI-TOF)** calcd for $C_{18}H_{20}NO_3S$ $[M + H]^+$: 330.1158, found: 330.1144.



3-(4-methoxyphenyl)-4-phenylthiazolidin-2-yl)methanol (6)

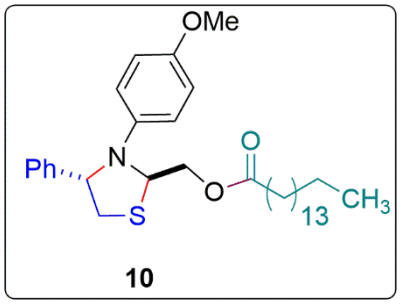
A solution of product **3aa** (600 mg, 1.74 mmol) in Et_2O (15 ml) was added slowly to a suspension of $LiAlH_4$ (50 mg, 2 mmol) in Et_2O (15 mL) at 0 °C under N_2 atmosphere. The resulting reaction mixture was stirred at 0-2 °C for 4 h. The reaction was quenched with ice flakes (carefully). The resulting solution was pass through a pad of celite and then extracted with EtOAc. The organic layers were combined and evaporated under reduced pressure to afford the product **6** in 79% (416 mg) yield as creamy solid which was pure enough and used in the next step. **^1H NMR (500MHz, $CDCl_3$)**: *δ* 7.26-7.23 (m, 2 H), 7.22-7.17 (m, 3 H), 6.70-6.68 (m, 2 H), 6.63-6.61 (m, 2 H), 5.25 (dd, *J* = 7.1, 4.1 Hz, 1 H), 5.11(dd, *J* = 6.0, 3.5 Hz, 1 H), 3.90 (dd, *J* = 11.5, 3.5 Hz, 1 H), 3.69 (s, 3 H), 3.63 (dd, *J* = 11.2, 6.3 Hz, 1 H), 3.56 (dd, *J* = 11.5, 7.3 Hz, 1 H), 2.94 (dd, *J* = 11.2, 3.2 Hz, 1 H), 2.16 (bs, 1 H); **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)**: *δ* 152.4, 140.9, 138.2, 128.2 (2 C), 127.3, 127.1 (2 C), 117.8 (2 C), 114.5 (2 C), 69.0, 65.7, 63.0, 55.4, 37.5; **HRMS (ESI-TOF)** calcd for $C_{17}H_{20}NO_2S$ $[M + H]^+$: 302.1209, found: 302.1190.



8

3-(4-methoxyphenyl)-4-phenylthiazolidin-2-yl)methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (8)

To an oven dried 10 mL round bottom flask fitted a magnetic stirring bar, Indomethacin **7** (175 mg, 0.49 mmol, 2 equiv) and DMAP (6 mg, 20 mol%) were dissolved in 1 mL anhydrous DCM under N_2 atmosphere. The resulting solution was cooled to 0 °C. A solution of N,N′-Diisopropylcarbodiimide (75 µl, 0.49 mmol, 2 equiv) in DCM (0.5 mL) was added to the reaction mixture dropwise. The reaction mixture was stirred at 0 °C for 45 minutes. After that, a solution of **6** (0.245 mmol, 74 mg) in 1 mL DCM was added to the reaction mixture slowly. The reaction mixture was slowly warmed to room temperature. After completion, the reaction solvent was evaporated under reduce pressure and the residue was directly loaded into column and purified on silica gel (petroleum ether/EtOAc as the eluent) to afford product **8** as slightly yellow floppy solid in 81% (127 mg) yield. **^{1}H NMR (500MHz, CDCl$_3$)**: *δ* 7.65 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.22-7.16 (m, 3 H), 7.08 (d, *J* = 6.8 Hz, 2 H), 6.96 (d, *J* = 2.2 Hz, 1 H), 6.92 (d, *J* = 9.0 Hz, 1 H), 6.71 (dd, *J* = 9.0, 2.3 Hz, 1 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 9.0 Hz, 2 H), 5.31(dd, *J* = 6.8, 4.1 Hz, 1 H), 4.87 (dd, *J* = 6.2, 3.4 Hz, 1 H), 4.54 (dd, *J* = 11.4, 4.0 Hz, 1 H), 4.13-4.09 (m, 1 H), 3.82 (s, 3 H), 3.69-3.64 (m, 2 H), 3.66 (s, 3 H), 3.48 (dd, *J* = 11.1, 6.5 Hz, 1 H), 2.85 (dd, *J* = 11.2, 3.4 Hz, 1 H), 2.39 (s, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: *δ* 170.6, 168.2, 156.0, 152.6, 140.9, 139.2, 137.9, 135.9, 133.7, 131.1 (2 C), 130.7, 130.6, 129.1 (2 C), 128.2 (2 C), 127.2, 127.0 (2 C), 118.0, 114.9 (2 C), 114.4 (2 C), 112.3, 111.8, 101.1, 65.4, 65.2, 64.8, 55.6, 55.3, 37.7, 30.2, 13.4; **HRMS (ESI-TOF)** calcd for $C_{36}H_{34}ClN_2O_5S$ $[M + H]^+$: 641.1871, found: 641.1842.



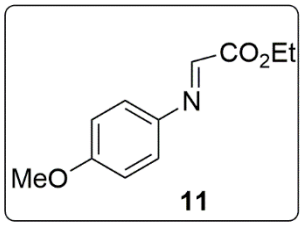
10

3-(4-methoxyphenyl)-4-phenylthiazolidin-2-yl)methyl palmitate (10)

To an oven dried 10 mL round bottom flask fitted a magnetic stirring bar, palmitic acid **9** (200 mg, 0.78 mmol, 2 equiv) and DMAP (10 mg, 20 mol%) were dissolved in 1 mL anhydrous DCM under N_2 atmosphere. The resulting solution was cooled to 0 °C. A solution of *N*,*N*′-diisopropylcarbodiimide (121 µl, 0.78 mmol, 2 equiv) in DCM (1.0 mL) was added to the reaction mixture dropwise. The reaction mixture was stirred at 0 °C for 45 minutes. After that, a solution of **6** (0.39

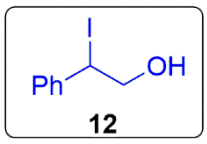
mmol, 118 mg) in 2 mL DCM was added to the reaction mixture slowly. The reaction mixture was slowly warmed to room temperature. After completion, the reaction solvent was evaporated under reduce pressure and the residue was directly loaded into column and purified on silica gel (petroleum ether/EtOAc as the eluent) to afford product **10** as colourless liquid in 58% (122 mg) yield. **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.26-7.23 (m, 2 H), 7.21-7.17 (m, 3 H), 6.71-6.65 (m, 4 H), 5.35 (dd, *J* = 7.9, 4.3 Hz, 1 H), 5.12 (dd, *J* = 6.3, 2.7 Hz, 1 H), 4.59 (dd, *J* = 11.3, 4.3 Hz, 1 H), 3.69-3.66 (m, 1 H), 3.68 (s, 3 H), 2.93 (dd, *J* = 11.3, 2.9 Hz, 1 H), 2.30 (td, *J* = 7.5, 2.3 Hz, 2 H), 1.62 (quint, *J* = 7.2 Hz, 2 H), 1.30-1.26 (m, 25 H), 0.89 (t, *J* = 6.8 Hz, 3 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 173.7, 152.4, 141.0, 138.2, 128.2 (2 C), 127.3, 127.0 (2 C), 117.6 (2 C), 114.5 (2 C), 65.4, 64.7, 64.5, 55.4, 37.8, 34.2, 31.9, 29.7 (2 C), 29.65 (2 C), 29.62 (2 C), 29.6, 29.3, 29.2, 29.1, 24.9, 22.7, 14.1; **HRMS (ESI-TOF)** calcd for $C_{33}H_{50}NO_3S$ $[M + H]^+$: 540.3506, found: 540.3475.

8. Characterization data of Intermediates



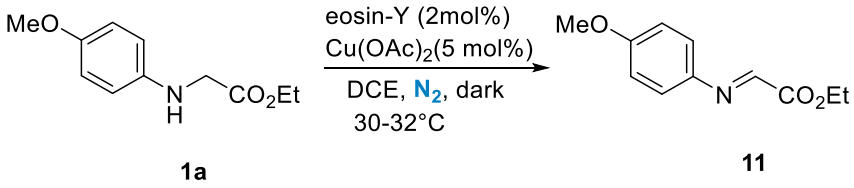
Ethyl (*E*)-2-((4-methoxyphenyl)imino)acetate (11)

^{1}H NMR (500MHz, CDCl$_3$): δ 7.93 (s, 1 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 6.94 (d, *J* = 8.9 Hz, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 3.82 (s, 3 H), 1.39 (t, *J* = 7.1 Hz, 3 H); **^{13}C{^{1}H} NMR (201.2 MHz, CDCl$_3$)**: δ 163.5, 160.4, 147.9, 141.2, 123.6 (2 C) , 114.4 (2 C), 61.8, 55.4, 14.1. Spectroscopic data is well matched with the literature report.[3,7]



2-iodo-2-phenylethan-1-ol (12)

The title compound was prepared according to previous literature report.[8] Spectroscopic data is well matched with the literature report.[6a] **^{1}H NMR (500MHz, CDCl$_3$)**: δ 7.43-7.42 (m, 2 H), 7.34-7.32 (m, 2 H), 7.29-7.27 (m, 1 H), 5.19 (t, *J* = 7.0 Hz, 1 H), 4.08 (dd, *J* = 12.2, 7.3 Hz, 1 H), 3.88 (dd, *J* = 12.2, 7.1 Hz, 1 H), 2.06 (s, 1 H); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)**: δ 139.9, 128.9 (2 C), 128.6, 127.9 (2 C), 68.6, 36.7.



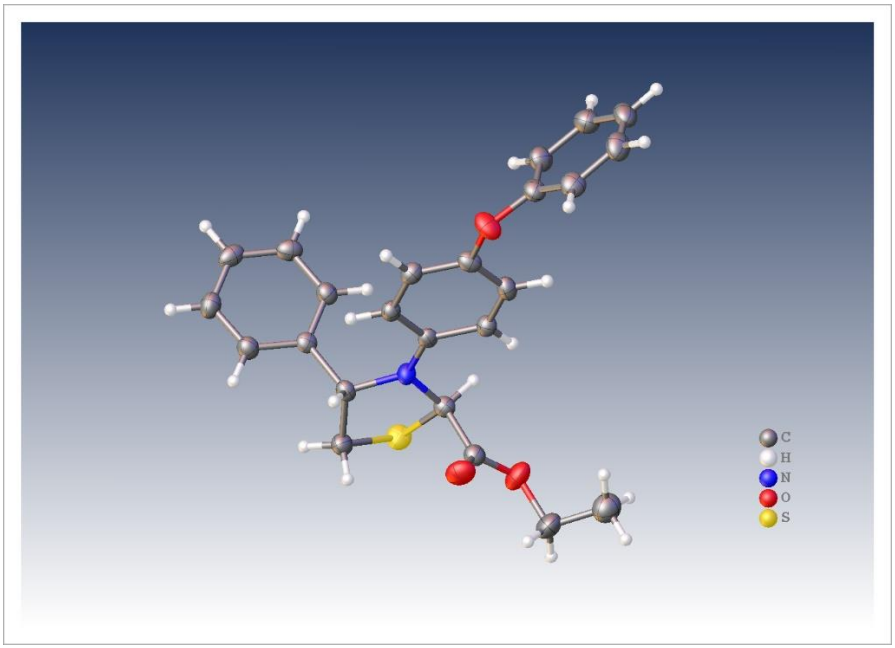
1a **11**

An oven dried 4-mL clear glass vials equipped with a PTFE/Silicone septa and magnetic stirring bar, was charged with glycinate ester **1a** (0.4 mmol, ~84 mg), eosin- Y (2 mol%) and $Cu(OAc)_2$ (5 mol%). The vial was wrapped in aluminium foil. The air inside the vial was evacuated for 30 min and backfield with nitrogen. Then 2.0 mL dry degassed [three cycles of freeze−pump−thaw (3 × 15 min under vacuum)] DCE was added via syringe. Finally, the reaction mixture was degassed by three cycles of freeze−pump−thaw (3 × 10 min under vacuum) and the reaction mixture was stirred for 8 h at room temperature under dark. An aliquot (aaprox.30 μL) of the reaction mixture was taken and diluted with 700 μL of $CDCl_3$, and analysed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra revealed 32% conversion of **1a**.

9. References:

1. Z. -H. Wang, P.-S. Gao, X. Wang, J. -Q. Gao, X.-T. Xu, Z. He, C. Ma and T. -S. Mei, *J. Am. Chem. Soc.* 2021, **143**, 15599-15605.
2. R. Rohlmann, T. Stopka, H. Richter and O. G. Mancheño, *J. Org. Chem.* 2013, **78**, 6050-6064.
3. R. Chowdhury, *Org. Biomol. Chem.*, 2022, **20**, 5387-5392.
4. J. Qu, Z. Yan, X. Wang, J. Deng, F. Liu and Z. -Q. Rong, *Chem. Commun.*, 2022, **58**, 9214-9217.
5. J. S. Yadav, B. V. S. Reddy, G. Baishya, *Synlett.*, 2003, 396-398.
6. (a) X. Yang, Y. Zhu, Z. Xie, Y. Li and Y. Zhang, *Org. Lett.* 2020, **22**, 1638–1643; (b) S. Wang, Y. Gao, Y. Hu, J. Zhou, Z. Chen, Z. Liu and Y. Zhang, *Chem. Commun.*, 2023, **59**, 12783-12786.
7. C. Retich, S. Bräse, *Eur. J. Org. Chem.* 2018, 66-70.
8. M. Yoshimine and M. J. Hatch, *J. Am. Chem. Soc.* 1967, **89**, 5831.

10. Crystal data and structure refinement for compound 5ca



CCDC 2414258

Table 1 Crystal data and structure refinement for BARC_RC_3196_0m. (5ca)

Identification code	BARC_RC_3196_0m
Empirical formula	$C_{48}H_{46}N_2O_6S_2$
Formula weight	810.99
Temperature/K	168.00
Crystal system	triclinic
Space group	P-1
a/Å	9.7838(10)
b/Å	11.8694(13)
c/Å	18.5982(19)
α/°	79.676(3)
β/°	86.767(3)
γ/°	77.991(3)

Volume/Å^3	2077.9(4)
Z	2
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.181
F(000)	856.0
Crystal size/mm^3	0.45 × 0.297 × 0.21
Radiation	MoKα (λ = 0.71073) 2Θ range for data collection/° 3.56 to 50.24
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-22 \le l \le 22$
Reflections collected	40745
Independent reflections	7393 [R_{int} = 0.0644, R_{sigma} = 0.0441] Data/restraints/parameters 7393/0/525
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0876 Final R indexes [all data] R_1 = 0.0551, wR_2 = 0.0956 Largest diff. peak/hole / e Å^{-3} 0.19/-0.25

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BARC_RC_3196_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S(1)	8327.9(5)	3126.0(4)	1059.3(3)	34.21(13)
S(2)	5090.5(5)	1174.8(4)	4198.9(3)	31.42(13)
O(5)	7368.4(15)	2978.5(13)	2923.1(8)	41.7(4)
O(2)	2297.6(14)	6315.2(11)	815.8(7)	32.8(3)
O(6)	3714.5(13)	3777.0(11)	4643.2(7)	29.5(3)
O(4)	2012.1(14)	3206.6(12)	4116.9(7)	35.4(3)
O(1)	9265.0(15)	1692.9(12)	2633.7(8)	43.6(4)
N(2)	8115.9(15)	4742.8(13)	1853.3(8)	25.3(3)
O(3)	9258.3(14)	7499.8(13)	3793.6(7)	38.0(3)
N(4)	3943.0(15)	2488.6(13)	3030.9(8)	24.4(3)
C(1)	9947(3)	569(2)	3809.2(13)	52.2(6)
C(2)	8929(2)	778(2)	3222.4(13)	47.9(6)
C(3)	8381(2)	2728.0(17)	2545.9(10)	28.6(4)
C(4)	8822.2(19)	3542.9(16)	1883.3(10)	26.0(4)

C(5)	8405.1(18)	5404.6(16)	2349.8(9)	22.9(4)
C(6)	9522.2(18)	4995.0(16)	2831.0(10)	25.9(4)
C(7)	9832.5(19)	5678.1(17)	3304.0(10)	28.6(4)
C(8)	9052.3(19)	6787.3(17)	3304.1(10)	28.0(4)
C(9)	10613(2)	7465.1(17)	3992.2(11)	31.4(4)
C(10)	10817(2)	7495.6(18)	4718.0(11)	36.8(5)
C(11)	12121(2)	7554.7(19)	4933.0(12)	43.0(5)
C(12)	13223(2)	7565.1(18)	4435.7(12)	42.0(5)
C(13)	7613.7(18)	6528.4(16)	2371.5(9)	24.6(4)
C(14)	7932.6(19)	7209.7(16)	2843.3(10)	27.1(4)
C(15)	13012(2)	7521.6(18)	3713.4(12)	39.9(5)
C(16)	11702(2)	7482.2(18)	3487.3(11)	36.5(5)
C(17)	6872.7(18)	5125.7(16)	1397.5(10)	25.2(4)
C(18)	6617(2)	4042.6(17)	1129.6(11)	31.9(5)
C(19)	7007.1(18)	6129.1(16)	777.8(9)	23.7(4)
C(20)	5806(2)	6752.8(17)	416.8(10)	30.5(4)
C(21)	5868(2)	7675.1(18)	-147.2(11)	34.9(5)
C(22)	7129(2)	8004.2(17)	-348.2(10)	33.4(5)
C(23)	8331(2)	7392.3(17)	7.7(10)	32.8(5)
C(24)	8271.3(19)	6450.2(17)	567.1(10)	28.0(4)
C(25)	488(2)	9687.1(18)	1099.1(12)	40.6(5)
C(26)	1402(2)	9475.7(17)	520.1(11)	36.3(5)
C(27)	2004.8(19)	8347.6(16)	443.2(10)	28.7(4)
C(28)	1687.7(18)	7422.3(16)	944.0(10)	24.8(4)
C(29)	2625.2(18)	5407.8(16)	1409.2(9)	25.0(4)
C(30)	2430.5(18)	4322.7(16)	1323.7(10)	25.6(4)
C(31)	2851.8(18)	3361.1(16)	1863.3(9)	24.3(4)
C(32)	3467.9(18)	3470.1(15)	2503.0(9)	22.6(4)
C(33)	3541.7(19)	1368.5(16)	3020.8(10)	26.2(4)
C(34)	4375.9(19)	708.0(16)	2456.9(10)	26.8(4)
C(35)	3839(2)	-137.6(17)	2199.1(11)	35.9(5)
C(36)	4581(3)	-767.8(18)	1691.9(12)	44.2(6)
C(37)	5872(2)	-553.8(19)	1434.2(12)	43.4(6)
C(38)	3462(2)	4659.8(19)	5717.3(11)	37.7(5)
C(39)	2682(2)	4361(2)	5127.2(11)	37.6(5)
C(40)	3225.3(19)	3234.3(16)	4175.5(9)	25.5(4)
C(41)	4414.7(19)	2641.6(16)	3722.8(9)	25.0(4)
C(42)	3721(2)	679.4(17)	3805.3(10)	32.8(5)
C(43)	5671(2)	917.9(17)	2191.1(10)	31.6(4)
C(44)	6411(2)	288.3(18)	1680.4(11)	38.7(5)
C(45)	3226.8(18)	5540.4(16)	2035.0(10)	25.3(4)
C(46)	3640.1(18)	4584.8(16)	2578.4(10)	24.7(4)
C(47)	160(2)	8758.9(18)	1588.0(11)	36.6(5)
C(48)	746.4(19)	7620.5(16)	1513.0(10)	28.7(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for BARC_RC_3196_0m.
The Anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	41.9(3)	34.0(3)	29.1(3)	-12.8(2)	-0.3(2)	-6.6(2)
S(2)	38.2(3)	27.6(3)	26.8(3)	-1.4(2)	-6.9(2)	-4.0(2)
O(5)	40.0(8)	41.1(9)	42.8(9)	-4.1(7)	13.3(7)	-12.0(7)
O(2)	50.4(8)	23.4(7)	21.7(7)	-1.4(6)	-0.6(6)	-2.9(6)
O(6)	31.0(7)	35.2(8)	25.2(7)	-11.2(6)	3.5(5)	-9.1(6)
O(4)	28.7(8)	47.5(9)	32.3(8)	-11.2(7)	1.0(6)	-9.5(6)
O(1)	48.2(9)	30.9(8)	43.6(9)	5.0(7)	0.1(7)	0.5(7)
N(2)	27.9(8)	23.5(8)	23.9(8)	-4.8(7)	-5.8(6)	-2.4(7)
O(3)	33.5(8)	48.2(9)	39.2(8)	-25.2(7)	-2.7(6)	-7.8(7)
N(4)	32.2(8)	21.3(8)	19.9(8)	-2.4(6)	-2.7(6)	-5.8(7)
C(1)	62.8(16)	47.7(14)	45.9(14)	-5.7(12)	-6.5(12)	-11.7(12)
C(2)	54.4(14)	34.1(12)	51.1(14)	7.4(11)	-9.5(11)	-10.4(11)
C(3)	30.1(10)	29.0(11)	28.1(10)	-6.6(8)	-3.2(9)	-7.1(8)
C(4)	25.9(9)	27.7(10)	25.5(10)	-7.6(8)	0.7(8)	-5.5(8)
C(5)	23.2(9)	27.3(10)	17.8(9)	-1.6(8)	1.7(7)	-7.0(8)
C(6)	25.2(9)	26.4(10)	25.3(10)	-4.2(8)	0.0(8)	-3.6(8)
C(7)	24.7(10)	37.7(11)	23.4(10)	-4.9(9)	-3.4(8)	-5.5(8)
C(8)	30.5(10)	34.7(11)	22.9(10)	-10.2(8)	2.4(8)	-12.0(9)
C(9)	35.7(11)	29.4(11)	31.9(11)	-8.9(9)	-5.6(9)	-8.5(9)
C(10)	46.1(13)	35.8(12)	31.5(11)	-12.3(9)	-3.6(9)	-8.7(10)
C(11)	54.3(14)	41.5(13)	35.4(12)	-12.4(10)	-14.8(11)	-6.2(11)
C(12)	43.6(13)	35.6(12)	50.6(14)	-10.2(11)	-17.3(11)	-10.1(10)
C(13)	24.7(9)	27.6(10)	21.0(9)	-2.4(8)	-1.1(7)	-5.5(8)
C(14)	29.9(10)	25.5(10)	24.8(10)	-4.2(8)	2.0(8)	-3.8(8)
C(15)	38.6(12)	39.2(12)	43.1(13)	-5.4(10)	-2.3(10)	-12.0(10)
C(16)	41.4(12)	41.4(12)	29.1(11)	-6.6(9)	-6.7(9)	-12.0(10)
C(17)	21.7(9)	31.2(10)	23.3(9)	-5.2(8)	-0.7(7)	-6.3(8)
C(18)	35.3(11)	32.8(11)	29.0(10)	-2.5(9)	-6.9(9)	-10.7(9)
C(19)	27.6(10)	27.1(10)	18.1(9)	-8.1(8)	-0.1(7)	-5.9(8)
C(20)	29.6(10)	35.3(11)	27.2(10)	-4.9(9)	-1.2(8)	-7.9(9)
C(21)	39.7(12)	33.6(11)	28.8(11)	-3.0(9)	-7.0(9)	-1.8(9)
C(22)	52.6(13)	27.4(11)	21.7(10)	-4.3(8)	0.9(9)	-11.6(9)
C(23)	39.0(11)	36.0(12)	27.4(10)	-8.1(9)	5.0(9)	-15.6(9)
C(24)	27.5(10)	33.0(11)	24.9(10)	-7.2(8)	-2.1(8)	-7.3(8)
C(25)	45.4(13)	25.9(11)	47.5(13)	-5.9(10)	-8.9(11)	1.4(9)
C(26)	41.4(12)	26.7(11)	40.5(12)	4.6(9)	-8.7(10)	-12.6(9)
C(27)	28.3(10)	30.7(11)	27.4(10)	-0.1(8)	-3.7(8)	-10.2(8)
C(28)	28.0(10)	24.0(10)	22.5(9)	-2.8(8)	-6.6(8)	-5.1(8)
C(29)	28.2(10)	23.9(10)	20.1(9)	-1.4(8)	3.7(8)	-2.4(8)
C(30)	28.3(10)	28.3(10)	20.1(9)	-5.6(8)	-0.9(8)	-4.2(8)
C(31)	28.1(10)	22.3(9)	23.3(9)	-6.2(8)	1.5(8)	-5.7(8)
C(32)	21.9(9)	24.7(10)	20.1(9)	-3.4(8)	3.1(7)	-3.2(7)
C(33)	29.6(10)	24.0(10)	25.5(10)	-2.2(8)	-2.7(8)	-7.5(8)
C(34)	34.2(11)	20.2(9)	24.4(10)	-0.3(8)	-8.6(8)	-2.4(8)
C(35)	45.5(12)	28.8(11)	34.8(11)	-4.3(9)	-10.3(9)	-9.1(9)
C(36)	68.4(16)	26.1(11)	39.8(13)	-10.9(10)	-18.8(12)	-4.2(11)
C(37)	59.7(15)	32.6(12)	31.2(12)	-10.1(10)	-6.5(10)	10.8(11)
C(38)	44.4(12)	43.7(13)	29.2(11)	-15.2(10)	9.2(9)	-13.3(10)
C(39)	37.1(12)	45.9(13)	32.5(11)	-17.0(10)	8.5(9)	-8.5(10)
C(40)	30.2(11)	26.4(10)	18.8(9)	-0.3(8)	-1.8(8)	-6.4(8)
C(41)	27.4(10)	27.0(10)	20.7(9)	-3.1(8)	-1.7(7)	-6.1(8)
C(42)	42.3(12)	29.4(11)	27.5(10)	0.3(9)	-3.4(9)	-13.1(9)
C(43)	34.2(11)	28.0(10)	31.4(11)	-3.9(9)	-7.3(9)	-3.0(9)
C(44)	39.4(12)	34.9(12)	34.5(12)	-2.9(10)	-2.4(9)	6.7(9)
C(45)	29.5(10)	21.9(9)	25.4(10)	-7.2(8)	2.0(8)	-5.1(8)
C(46)	26.2(9)	27.3(10)	21.7(9)	-6.3(8)	-0.1(7)	-5.9(8)
C(47)	34.9(11)	35.4(12)	35.4(12)	-6.4(10)	1.0(9)	1.7(9)
C(48)	30.3(10)	25.9(10)	28.2(10)	1.3(8)	-2.6(8)	-6.1(8)

Table 4 Bond Lengths for BARC_RC_3196_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	C(4)	1.8118(19)	C(13)	C(14)	1.383(3)
S(1)	C(18)	1.808(2)	C(15)	C(16)	1.384(3)
S(2)	C(41)	1.8129(18)	C(17)	C(18)	1.530(3)
S(2)	C(42)	1.808(2)	C(17)	C(19)	1.523(2)
O(5)	C(3)	1.199(2)	C(19)	C(20)	1.388(3)
O(2)	C(28)	1.382(2)	C(19)	C(24)	1.384(3)
O(2)	C(29)	1.397(2)	C(20)	C(21)	1.383(3)
O(6)	C(39)	1.463(2)	C(21)	C(22)	1.382(3)
O(6)	C(40)	1.333(2)	C(22)	C(23)	1.381(3)
O(4)	C(40)	1.206(2)	C(23)	C(24)	1.393(3)
O(1)	C(2)	1.473(2)	C(25)	C(26)	1.385(3)
O(1)	C(3)	1.336(2)	C(25)	C(47)	1.378(3)
N(2)	C(4)	1.441(2)	C(26)	C(27)	1.375(3)
N(2)	C(5)	1.390(2)	C(27)	C(28)	1.383(3)
N(2)	C(17)	1.467(2)	C(28)	C(48)	1.383(3)
O(3)	C(8)	1.397(2)	C(29)	C(30)	1.378(3)
O(3)	C(9)	1.386(2)	C(29)	C(45)	1.381(3)
N(4)	C(32)	1.398(2)	C(30)	C(31)	1.386(3)
N(4)	C(33)	1.466(2)	C(31)	C(32)	1.402(2)
N(4)	C(41)	1.445(2)	C(32)	C(46)	1.400(3)
C(1)	C(2)	1.472(3)	C(33)	C(34)	1.521(3)
C(3)	C(4)	1.525(3)	C(33)	C(42)	1.539(3)
C(5)	C(6)	1.402(2)	C(34)	C(35)	1.391(3)
C(5)	C(13)	1.402(3)	C(34)	C(43)	1.389(3)
C(6)	C(7)	1.382(3)	C(35)	C(36)	1.388(3)
C(7)	C(8)	1.378(3)	C(36)	C(37)	1.382(3)
C(8)	C(14)	1.382(3)	C(37)	C(44)	1.377(3)
C(9)	C(10)	1.383(3)	C(38)	C(39)	1.503(3)
C(9)	C(16)	1.381(3)	C(40)	C(41)	1.523(3)
C(10)	C(11)	1.378(3)	C(43)	C(44)	1.392(3)
C(11)	C(12)	1.381(3)	C(45)	C(46)	1.384(3)
C(12)	C(15)	1.382(3)	C(47)	C(48)	1.382(3)

Table 5 Bond Angles for BARC_RC_3196_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(18)	S(1)	C(4)	89.38(9)	C(24)	C(19)	C(20)	118.90(17)
C(42)	S(2)	C(41)	88.87(9)	C(21)	C(20)	C(19)	120.75(18)
C(28)	O(2)	C(29)	119.18(14)	C(22)	C(21)	C(20)	120.14(18)
C(40)	O(6)	C(39)	116.38(14)	C(23)	C(22)	C(21)	119.65(18)
C(3)	O(1)	C(2)	117.06(16)	C(22)	C(23)	C(24)	120.16(18)
C(4)	N(2)	C(17)	115.97(15)	C(19)	C(24)	C(23)	120.37(18)
C(5)	N(2)	C(4)	121.07(14)	C(47)	C(25)	C(26)	119.54(19)
C(5)	N(2)	C(17)	121.42(14)	C(27)	C(26)	C(25)	120.25(19)
C(9)	O(3)	C(8)	118.42(15)	C(26)	C(27)	C(28)	119.76(18)
C(32)	N(4)	C(33)	121.23(15)	O(2)	C(28)	C(27)	116.33(16)
C(32)	N(4)	C(41)	119.51(15)	O(2)	C(28)	C(48)	123.01(16)
C(41)	N(4)	C(33)	115.91(14)	C(48)	C(28)	C(27)	120.56(17)
C(1)	C(2)	O(1)	109.08(19)	C(30)	C(29)	O(2)	116.82(16)
O(5)	C(3)	O(1)	125.13(18)	C(30)	C(29)	C(45)	120.11(17)
O(5)	C(3)	C(4)	124.49(17)	C(45)	C(29)	O(2)	122.85(16)
O(1)	C(3)	C(4)	110.37(16)	C(29)	C(30)	C(31)	119.94(17)
N(2)	C(4)	S(1)	105.15(12)	C(30)	C(31)	C(32)	121.14(17)
N(2)	C(4)	C(3)	113.03(15)	N(4)	C(32)	C(31)	120.79(16)
C(3)	C(4)	S(1)	108.99(13)	N(4)	C(32)	C(46)	121.47(16)
N(2)	C(5)	C(6)	121.59(16)	C(46)	C(32)	C(31)	117.68(16)
N(2)	C(5)	C(13)	121.03(16)	N(4)	C(33)	C(34)	112.54(15)
C(6)	C(5)	C(13)	117.35(17)	N(4)	C(33)	C(42)	106.25(15)
C(7)	C(6)	C(5)	121.11(17)	C(34)	C(33)	C(42)	112.81(15)
C(8)	C(7)	C(6)	120.27(17)	C(35)	C(34)	C(33)	119.49(17)
C(7)	C(8)	O(3)	123.29(17)	C(43)	C(34)	C(33)	121.96(17)
C(7)	C(8)	C(14)	119.97(17)	C(43)	C(34)	C(35)	118.55(18)
C(14)	C(8)	O(3)	116.54(17)	C(36)	C(35)	C(34)	121.0(2)
C(10)	C(9)	O(3)	116.91(18)	C(37)	C(36)	C(35)	119.9(2)
C(16)	C(9)	O(3)	122.23(17)	C(44)	C(37)	C(36)	119.7(2)
C(16)	C(9)	C(10)	120.71(19)	O(6)	C(39)	C(38)	107.72(16)
C(11)	C(10)	C(9)	119.2(2)	O(6)	C(40)	C(41)	110.63(15)
C(10)	C(11)	C(12)	120.7(2)	O(4)	C(40)	O(6)	125.15(17)
C(11)	C(12)	C(15)	119.6(2)	O(4)	C(40)	C(41)	124.22(17)
C(14)	C(13)	C(5)	121.29(17)	N(4)	C(41)	S(2)	105.15(12)
C(8)	C(14)	C(13)	119.98(17)	N(4)	C(41)	C(40)	112.01(14)
C(12)	C(15)	C(16)	120.3(2)	C(40)	C(41)	S(2)	109.20(12)
C(9)	C(16)	C(15)	119.42(19)	C(33)	C(42)	S(2)	106.28(13)
N(2)	C(17)	C(18)	106.69(15)	C(34)	C(43)	C(44)	120.37(19)
N(2)	C(17)	C(19)	112.83(14)	C(37)	C(44)	C(43)	120.5(2)
C(19)	C(17)	C(18)	113.12(15)	C(29)	C(45)	C(46)	120.22(17)
C(17)	C(18)	S(1)	105.44(13)	C(45)	C(46)	C(32)	120.91(17)
C(20)	C(19)	C(17)	118.38(16)	C(25)	C(47)	C(48)	120.84(19)
C(24)	C(19)	C(17)	122.71(16)	C(47)	C(48)	C(28)	119.01(18)

Table 6 Torsion Angles for BARC_RC_3196_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O(5)	C(3)	C(4)	S(1)	-101.9(2)	C(18)	S(1)	C(4)	N(2)	-34.92(13)
O(5)	C(3)	C(4)	N(2)	14.6(3)	C(18)	S(1)	C(4)	C(3)	86.53(13)
O(2)	C(28)	C(48)	C(47)	-178.30(17)	C(18)	C(17)	C(19)	C(20)	73.8(2)
O(2)	C(29)	C(30)	C(31)	174.16(15)	C(18)	C(17)	C(19)	C(24)	-106.9(2)
O(2)	C(29)	C(45)	C(46)	-174.33(16)	C(19)	C(17)	C(18)	S(1)	93.88(15)
O(6)	C(40)	C(41)	S(2)	88.72(16)	C(19)	C(20)	C(21)	C(22)	-1.4(3)
O(6)	C(40)	C(41)	N(4)	-155.22(14)	C(20)	C(19)	C(24)	C(23)	0.7(3)
O(4)	C(40)	C(41)	S(2)	-90.96(19)	C(20)	C(21)	C(22)	C(23)	1.3(3)
O(4)	C(40)	C(41)	N(4)	25.1(3)	C(21)	C(22)	C(23)	C(24)	-0.1(3)
O(1)	C(3)	C(4)	S(1)	76.74(17)	C(22)	C(23)	C(24)	C(19)	-0.9(3)
O(1)	C(3)	C(4)	N(2)	-166.74(15)	C(24)	C(19)	C(20)	C(21)	0.4(3)
N(2)	C(5)	C(6)	C(7)	177.57(17)	C(25)	C(26)	C(27)	C(28)	0.5(3)
N(2)	C(5)	C(13)	C(14)	-177.29(16)	C(25)	C(47)	C(48)	C(28)	0.9(3)
N(2)	C(17)	C(18)	S(1)	-30.76(16)	C(26)	C(25)	C(47)	C(48)	0.9(3)
N(2)	C(17)	C(19)	C(20)	-164.97(16)	C(26)	C(27)	C(28)	O(2)	177.86(16)
N(2)	C(17)	C(19)	C(24)	14.3(2)	C(26)	C(27)	C(28)	C(48)	1.4(3)
O(3)	C(8)	C(14)	C(13)	-176.43(16)	C(27)	C(28)	C(48)	C(47)	-2.1(3)
O(3)	C(9)	C(10)	C(11)	-175.01(18)	C(28)	O(2)	C(29)	C(30)	142.65(17)
O(3)	C(9)	C(16)	C(15)	175.87(18)	C(28)	O(2)	C(29)	C(45)	-42.7(2)
N(4)	C(32)	C(46)	C(45)	176.80(16)	C(29)	O(2)	C(28)	C(27)	148.62(16)
N(4)	C(33)	C(34)	C(35)	-158.14(16)	C(29)	O(2)	C(28)	C(48)	-35.0(2)
N(4)	C(33)	C(34)	C(43)	22.2(2)	C(29)	C(30)	C(31)	C(32)	0.5(3)
N(4)	C(33)	C(42)	S(2)	-28.72(17)	C(29)	C(45)	C(46)	C(32)	0.5(3)
C(2)	O(1)	C(3)	O(5)	2.6(3)	C(30)	C(29)	C(45)	C(46)	0.1(3)
C(2)	O(1)	C(3)	C(4)	-175.96(16)	C(30)	C(31)	C(32)	N(4)	-177.31(16)
C(3)	O(1)	C(2)	C(1)	-110.0(2)	C(30)	C(31)	C(32)	C(46)	0.1(3)
C(4)	S(1)	C(18)	C(17)	38.17(13)	C(31)	C(32)	C(46)	C(45)	-0.6(3)
C(4)	N(2)	C(5)	C(6)	9.1(3)	C(32)	N(4)	C(33)	C(34)	78.5(2)
C(4)	N(2)	C(5)	C(13)	-173.02(16)	C(32)	N(4)	C(33)	C(42)	-157.55(16)
C(4)	N(2)	C(17)	C(18)	5.0(2)	C(32)	N(4)	C(41)	S(2)	-174.52(13)
C(4)	N(2)	C(17)	C(19)	-119.78(17)	C(32)	N(4)	C(41)	C(40)	67.0(2)
C(5)	N(2)	C(4)	S(1)	-171.06(13)	C(33)	N(4)	C(32)	C(31)	-13.9(2)
C(5)	N(2)	C(4)	C(3)	70.2(2)	C(33)	N(4)	C(32)	C(46)	168.71(16)
C(5)	N(2)	C(17)	C(18)	-160.92(15)	C(33)	N(4)	C(41)	S(2)	25.89(17)
C(5)	N(2)	C(17)	C(19)	74.3(2)	C(33)	N(4)	C(41)	C(40)	-92.60(18)
C(5)	C(6)	C(7)	C(8)	-0.8(3)	C(33)	C(34)	C(35)	C(36)	-179.11(17)
C(5)	C(13)	C(14)	C(8)	0.2(3)	C(33)	C(34)	C(43)	C(44)	179.37(17)
C(6)	C(5)	C(13)	C(14)	0.7(3)	C(34)	C(33)	C(42)	S(2)	95.05(16)
C(6)	C(7)	C(8)	O(3)	176.39(17)	C(34)	C(35)	C(36)	C(37)	-0.3(3)
C(6)	C(7)	C(8)	C(14)	1.6(3)	C(34)	C(43)	C(44)	C(37)	-0.3(3)

C(7)	C(8)	C(14)	C(13)	-1.3(3)	C(35)	C(34)	C(43)	C(44)	-0.3(3)
C(8)	O(3)	C(9)	C(10)	-139.69(18)	C(35)	C(36)	C(37)	C(44)	-0.3(3)
C(8)	O(3)	C(9)	C(16)	44.8(3)	C(36)	C(37)	C(44)	C(43)	0.6(3)
C(9)	O(3)	C(8)	C(7)	36.8(3)	C(39)	O(6)	C(40)	O(4)	1.2(3)
C(9)	O(3)	C(8)	C(14)	-148.24(17)	C(39)	O(6)	C(40)	C(41)	-178.52(15)
C(9)	C(10)	C(11)	C(12)	-1.0(3)	C(40)	O(6)	C(39)	C(38)	166.74(16)
C(10)	C(9)	C(16)	C(15)	0.5(3)	C(41)	S(2)	C(42)	C(33)	37.72(14)
C(10)	C(11)	C(12)	C(15)	0.3(3)	C(41)	N(4)	C(32)	C(31)	-172.43(15)
C(11)	C(12)	C(15)	C(16)	0.8(3)	C(41)	N(4)	C(32)	C(46)	10.2(2)
C(12)	C(15)	C(16)	C(9)	-1.2(3)	C(41)	N(4)	C(33)	C(34)	-122.27(16)
C(13)	C(5)	C(6)	C(7)	-0.4(3)	C(41)	N(4)	C(33)	C(42)	1.7(2)
C(16)	C(9)	C(10)	C(11)	0.6(3)	C(42)	S(2)	C(41)	N(4)	-36.12(13)
C(17)	N(2)	C(4)	S(1)	22.93(18)	C(42)	S(2)	C(41)	C(40)	84.25(14)
C(17)	N(2)	C(4)	C(3)	-95.85(18)	C(42)	C(33)	C(34)	C(35)	81.6(2)
C(17)	N(2)	C(5)	C(6)	174.33(16)	C(42)	C(33)	C(34)	C(43)	-98.0(2)
C(17)	N(2)	C(5)	C(13)	-7.8(2)	C(43)	C(34)	C(35)	C(36)	0.5(3)
C(17)	C(19)	C(20)	C(21)	179.69(17)	C(45)	C(29)	C(30)	C(31)	-0.6(3)
C(17)	C(19)	C(24)	C(23)	-178.51(17)	C(47)	C(25)	C(26)	C(27)	-1.6(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for BARC_RC_3196_0m.

Atom	*x*	*y*	*z*	U(eq)
H(1A)	10870.53	212.82	3632.34	78
H(1B)	9656.19	40.63	4230.42	78
H(1C)	9991.96	1313.03	3955.4	78
H(2A)	7972.56	1028.62	3417.37	57
H(2B)	8965.75	47.22	3028.69	57
H(4)	9856.66	3486.06	1880.99	31
H(6)	10075.42	4235.28	2832.17	31
H(7)	10586.79	5381.4	3630.15	34
H(10)	10066.52	7476.07	5064.09	44
H(11)	12264.54	7588.61	5429.08	52
H(12)	14120.22	7602.02	4588.9	50
H(13)	6843.27	6827.34	2055.95	30
H(14)	7382.1	7968.19	2850.63	33
H(15)	13769.6	7518.66	3370.62	48
H(16)	11552.55	7467.12	2989.06	44
H(17)	6058.62	5401.6	1715.94	30
H(18A)	6163.73	4262.97	647.98	38
H(18B)	6011.74	3630.96	1481.39	38
H(20)	4932.23	6543.42	559.04	37
H(21)	5042.55	8083.57	-397.14	42
H(22)	7169.11	8647.98	-729.06	40
H(23)	9199.82	7614.59	-129.51	39
H(24)	9102.91	6025.51	805.36	34
H(25)	89.91	10466.69	1158.93	49
H(26)	1613.32	10112.22	174.57	44
H(27)	2636.83	8204.59	47.51	34
H(30)	2007.78	4234.09	895.22	31
H(31)	2720.74	2614.95	1798.42	29
H(33)	2529.67	1526.5	2898.74	31
H(35)	2950.23	-286.01	2372.68	43
H(36)	4202.86	-1345.11	1522.17	53
H(37)	6385.57	-985.87	1088.81	52
H(38A)	3972.51	3938.63	6007.41	57
H(38B)	2797.18	5091.53	6034.81	57
H(38C)	4123.54	5143.99	5494.7	57
H(39A)	2045.51	3838.13	5344.83	45
H(39B)	2118.45	5080.94	4848.68	45
H(41)	5174.06	3101.93	3640.6	30
H(42A)	3987.07	-170.62	3799.56	39
H(42B)	2839.46	835.03	4091.99	39
H(43)	6053.85	1494.45	2358.93	38
H(44)	7294.31	440.51	1500.11	46
H(45)	3357.48	6289.98	2092.72	30
H(46)	4046.07	4686.63	3008.47	30
H(47)	-476.56	8903.31	1981.51	44
H(48)	506.2	6983.55	1847.46	34

Experimental

Single crystals of $C_{48}H_{46}N_2O_6S_2$ [BARC_RC_3196_0m; 5ca] were grown from petroleum ether/EtOAc mixture on slow evaporation. A suitable crystal was selected and and diffraction data were collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 168.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic

Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [BARC_RC_3196_0m]

Crystal Data for $C_{48}H_{46}N_2O_6S_2$ (*M* =810.99 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.7838(10) Å, *b* = 11.8694(13) Å, *c* = 18.5982(19) Å, *α* = 79.676(3)°, *β* = 86.767(3)°,
γ = 77.991(3)°, *V* = 2077.9(4) $Å^3$, *Z* = 2, *T* = 168.00 K, μ(MoKα) = 0.181 mm^{-1}, *Dcalc* = 1.296 g/cm^3, 40745 reflections measured (3.56° ≤ 2Θ ≤ 50.24°), 7393 unique (R_{int} = 0.0644, R_{sigma} = 0.0441) which were used in all calculations. The final R_1 was 0.0385 (I > 2σ(I)) and wR_2 was 0.0956 (all data).

Refinement model description
Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of: All C(H) groups, All C(H,H) groups At 1.5 times of: All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates: C4(H4), C17(H17), C33(H33), C41(H41)
2.b Secondary CH2 refined with riding coordinates: C2(H2A,H2B), C18(H18A,H18B), C39(H39A,H39B), C42(H42A,H42B)
2.c Aromatic/amide H refined with riding coordinates: C6(H6), C7(H7), C10(H10), C11(H11), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26), C27(H27), C30(H30), C31(H31), C35(H35), C36(H36), C37(H37), C43(H43), C44(H44), C45(H45), C46(H46), C47(H47), C48(H48)
2.d Idealised Me refined as rotating group: C1(H1A,H1B,H1C), C38(H38A,H38B,H38C).

11. NMR spectra of eosin-Y

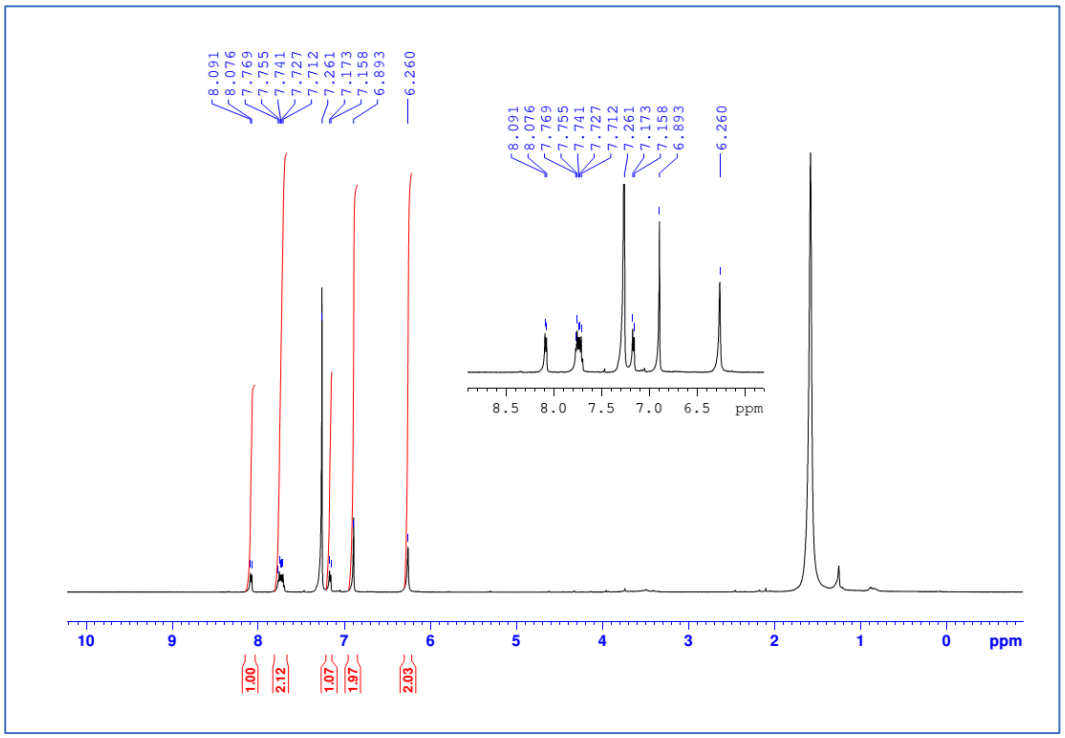
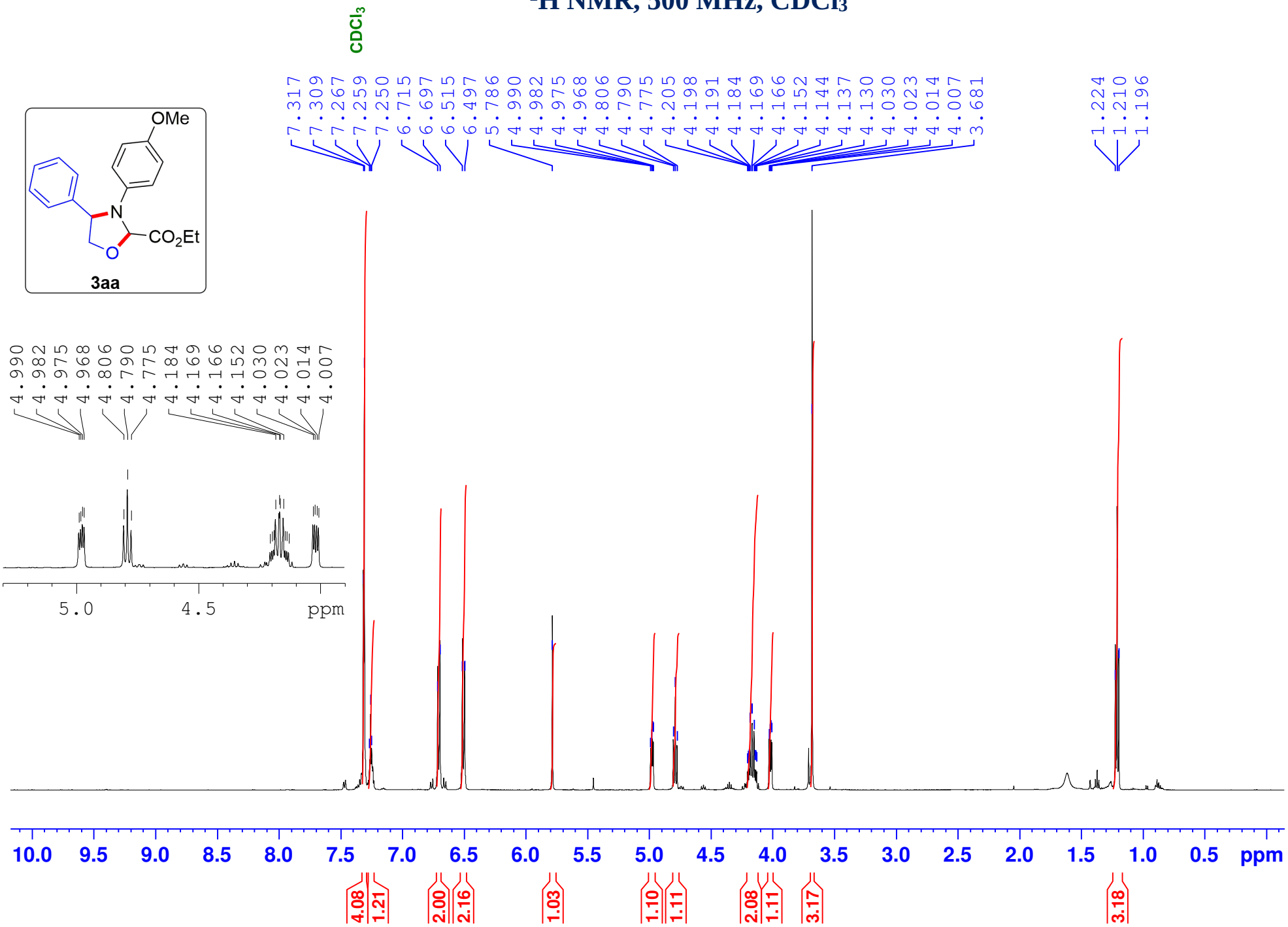


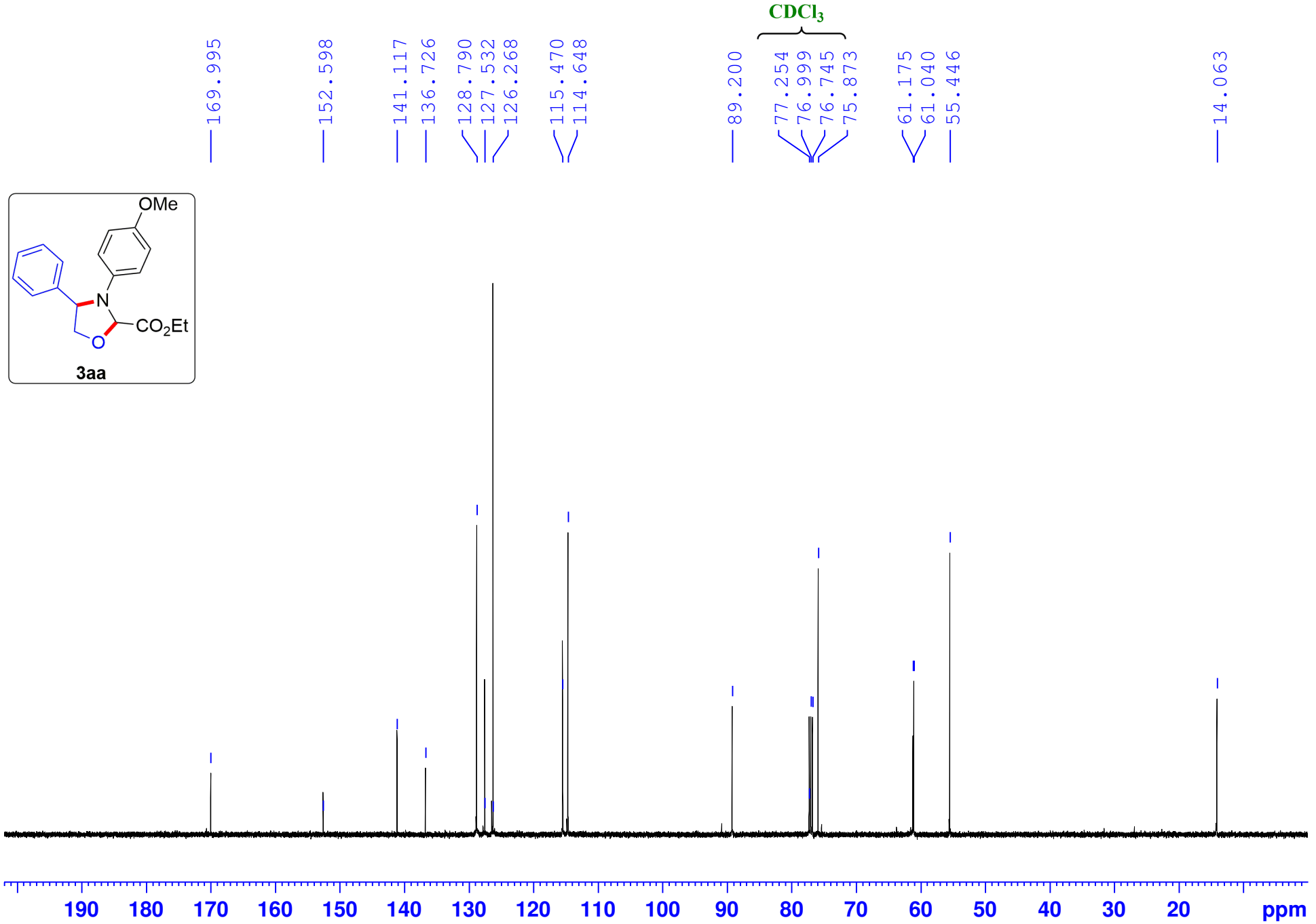
Figure S6. ^{1}H NMR spectra of eosin-Y in $CDCl_3$, 500 MHz

The data is close agreement with the literature: H. Cao, D. Kong, L.-C. Yang, S. Chanmungkalakul, T. Liu, J. L. Piper, Z. Peng, L. Gao, X. Liu, X. Hong and J. Wu, *Nat. Synth* 2022, **1**, 794–803.

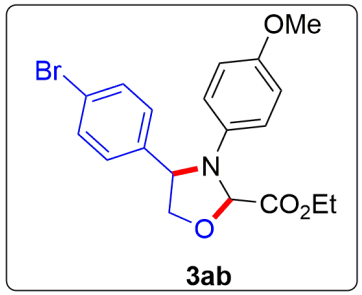
^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C {1H} NMR, 125 MHz, $CDCl_3$

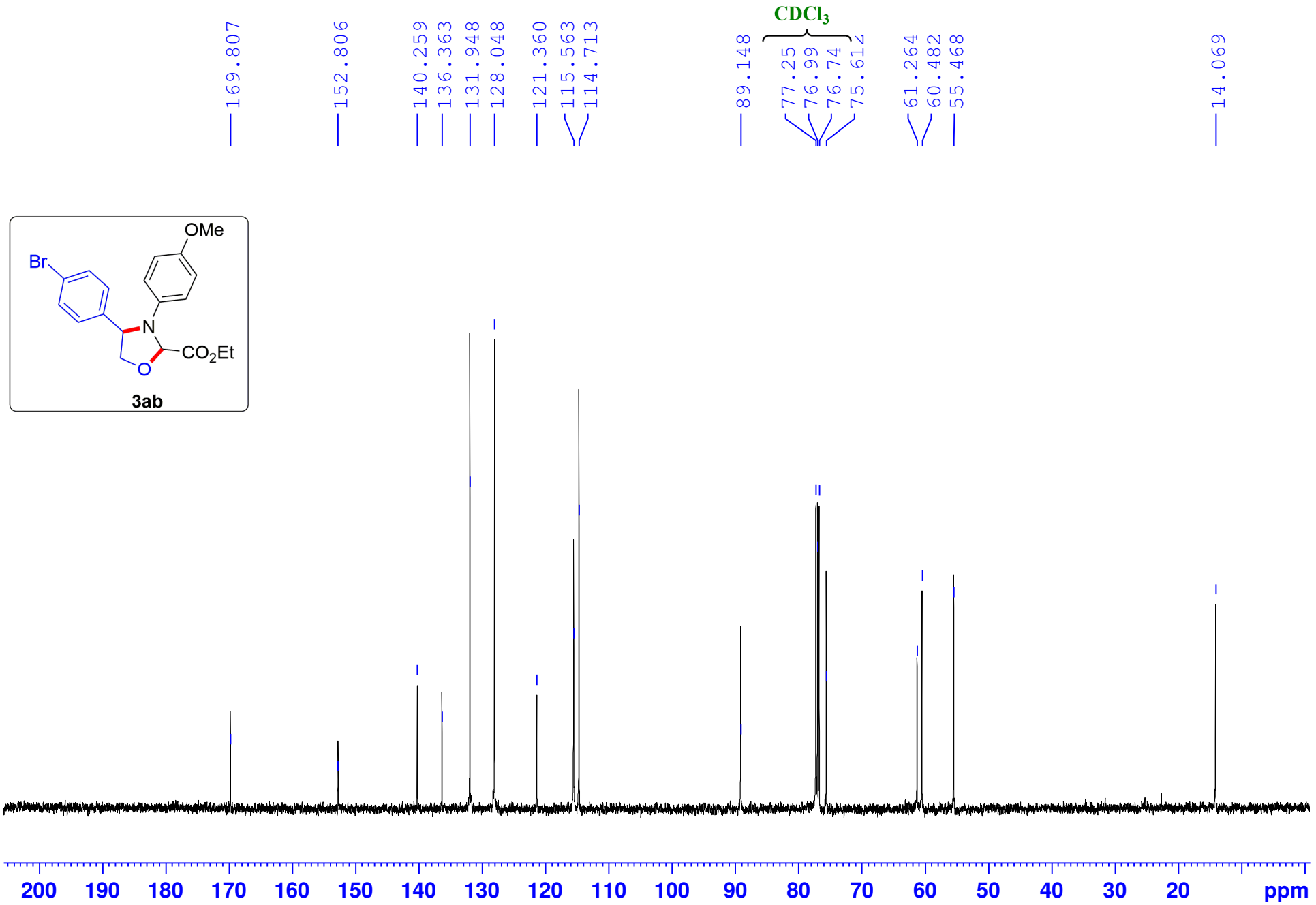


^{1}H NMR, 500 MHz, $CDCl_3$

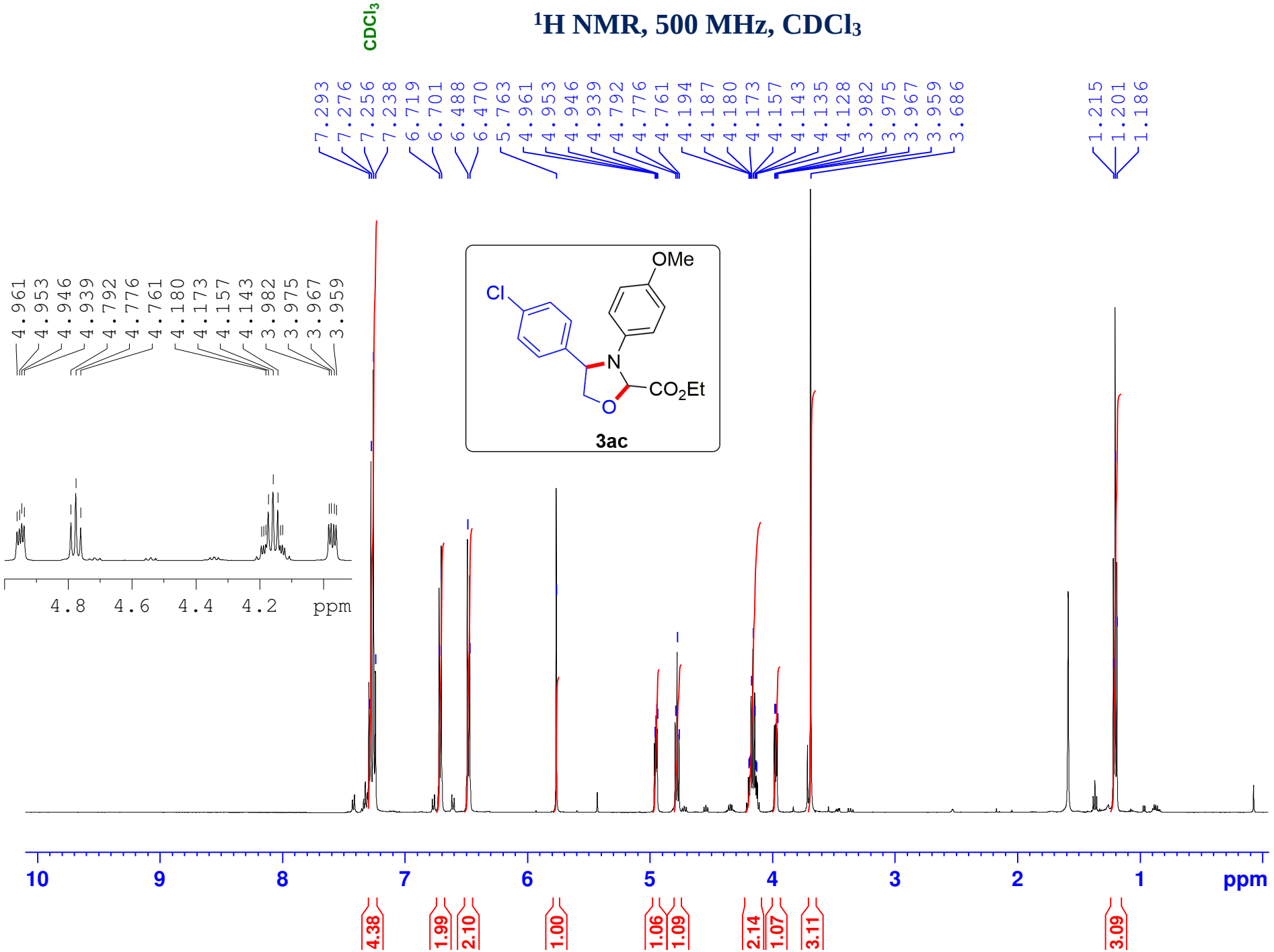


3ab

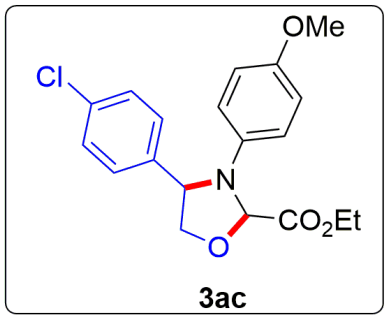
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$

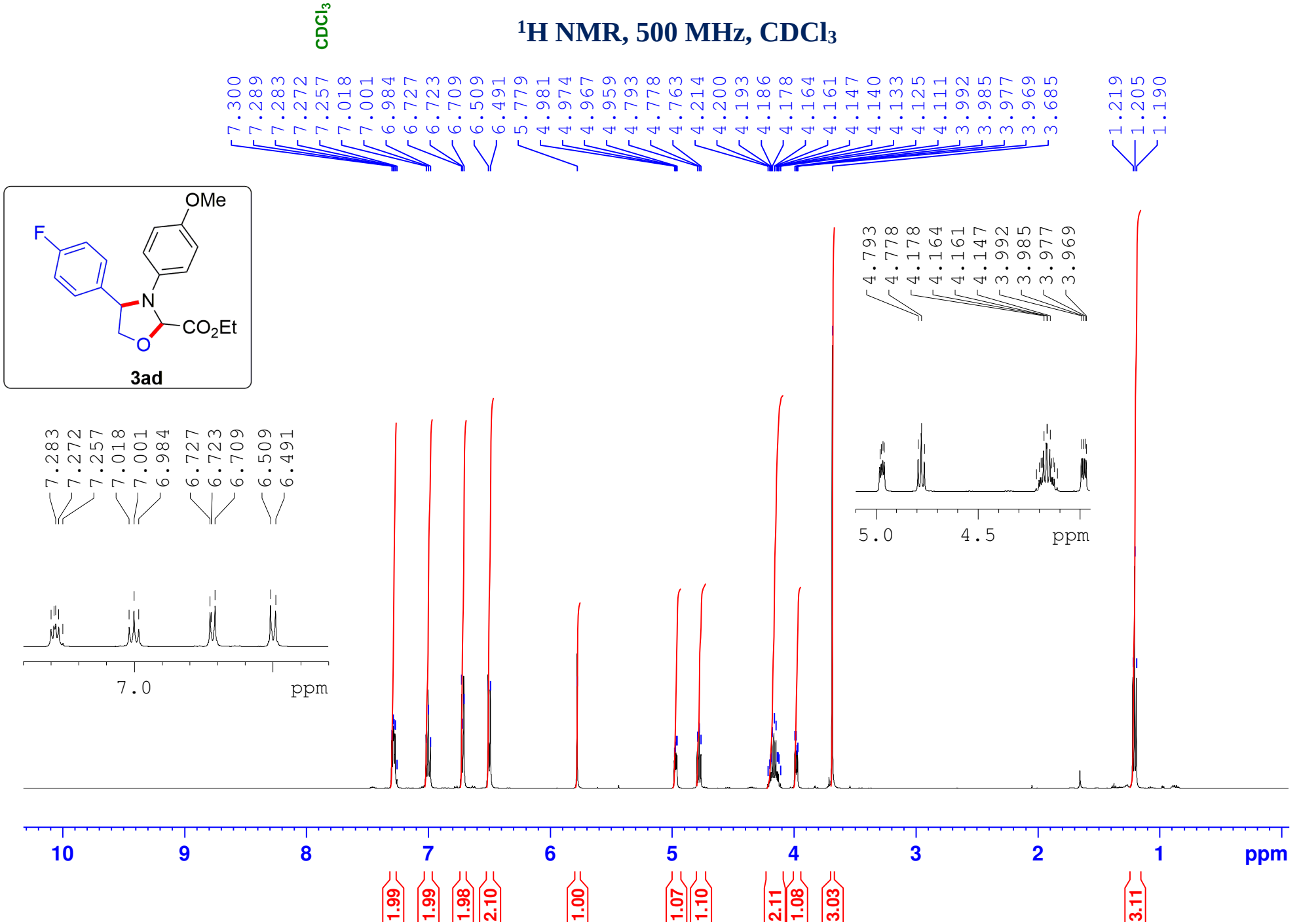


^{13}C {1H} NMR, 125 MHz, $CDCl_3$

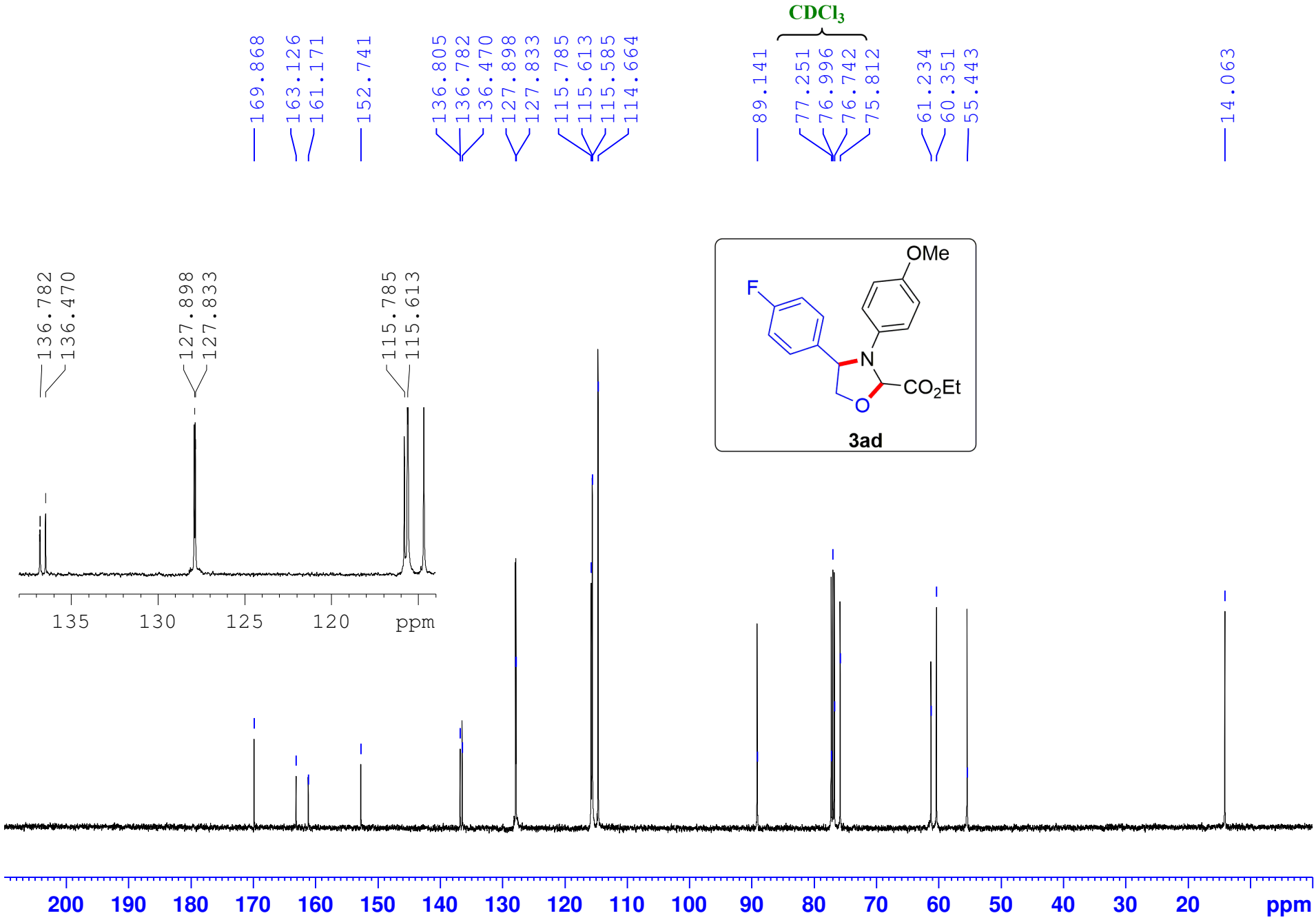


3ac

^{1}H NMR, 500 MHz, $CDCl_3$



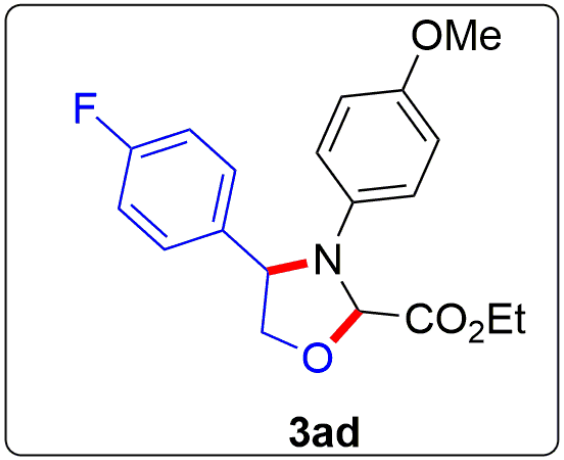
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



^{19}F NMR, 470 MHz, $CDCl_3$

RC_3337

Sample Name **RC_3337**	Pulse sequence **FLUORINE**	Temperature **25**	Study owner **vnmr1**
Date collected **2025-03-05**	Solvent **cdcl3**	Spectrometer **NMR500-vnmrs500**	Operator **vnmr1**



Sample Name **RC_3337**	Pulse sequence **FLUORINE**	Temperature **25**	Study owner **vnmr1**
Date collected **2025-03-05**	Solvent **cdcl3**	Spectrometer **NMR500-vnmrs500**	Operator **vnmr1**

19F NMR

SAMPLE

date	Mar 5 2025
solvent	cdcl3
file	exp

ACQUISITION

sw	108695.7
at	0.603
np	131072
fb	47800
bs	3
d1	1.000
nt	256
ct	256

TRANSMITTER

tn	F19
sfrq	470.292
tof	12070.4
tpwr	57
pw	6.737

DECOUPLER

dn	C13
dof	0
dm	nnn
decwave	W40_AUTOX_DB
dpwr	44
dmf	32258

PRESATURATION

satmode	n
wet	n

SPECIAL

temp	25.0
gain	50
spin	0
hst	0.008
pw90	13.475
alfa	10.000

FLAGS

il	n
in	n
dp	y
hs	nn

PROCESSING

lb	1.00
fn	not used

DISPLAY

sp	-94606.6
wp	108694.0
rfl	94608.3
rfp	0
rp	-57.0
lp	0

PLOT

wc	252
sc	8
vs	47
th	4
ai ph	

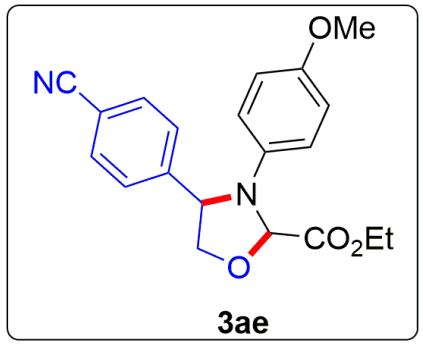
INTEGRAL VALUES

Integral	start(ppm)	end	value
1	29.9519	-114.832	-20.841
2	-114.832	-115.065	108.255
3	-115.065	-201.149	12.587

PEAK FREQUENCIES

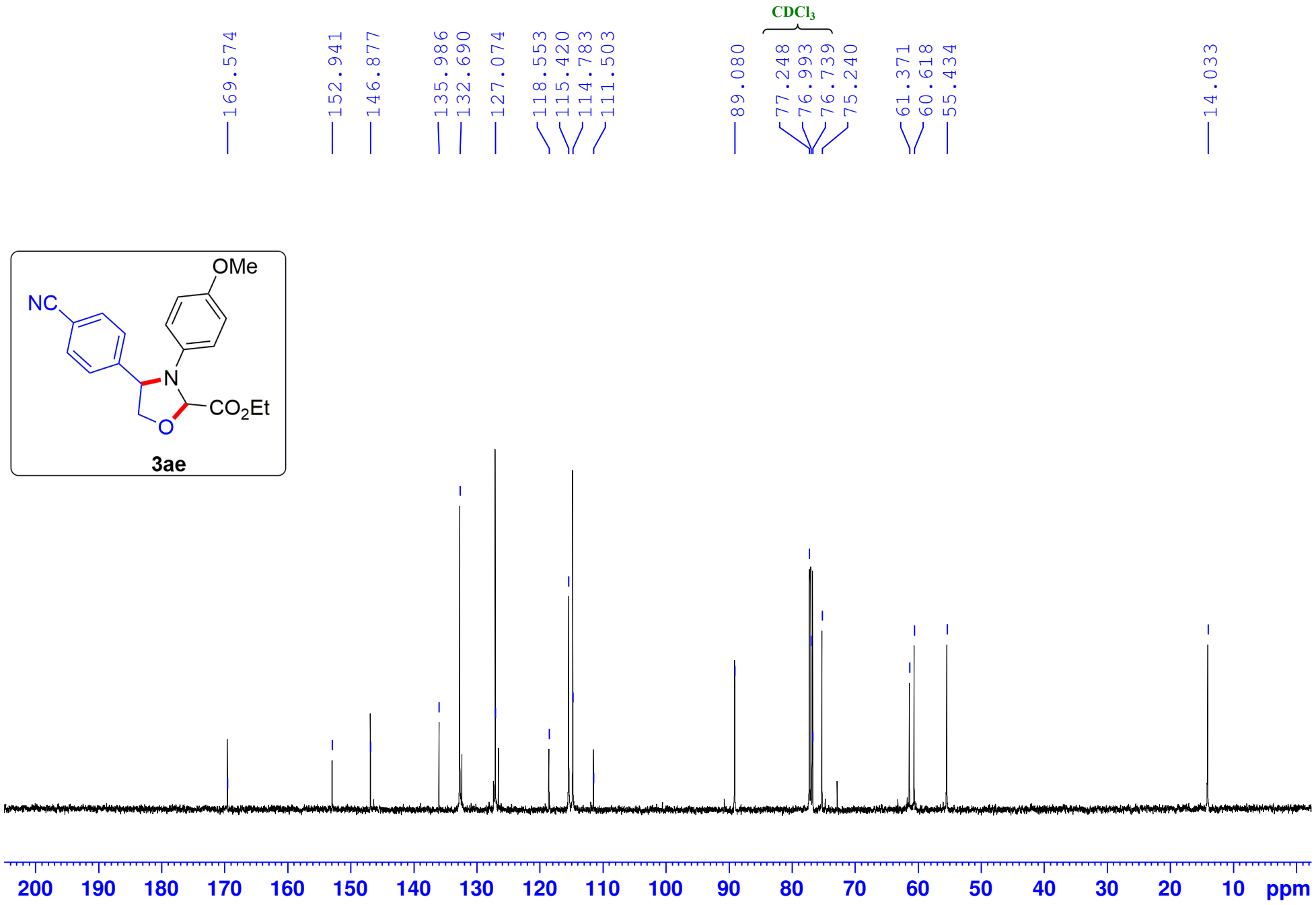
index	freq(ppm)	intensity
1	-114.908	18.5373
2	-114.922	42.1065
3	-114.929	51.6688
4	-114.939	90.0826
5	-114.95	58.599
6	-114.957	52.8015
7	-114.968	25.4325

^{1}H NMR, 500 MHz, $CDCl_3$

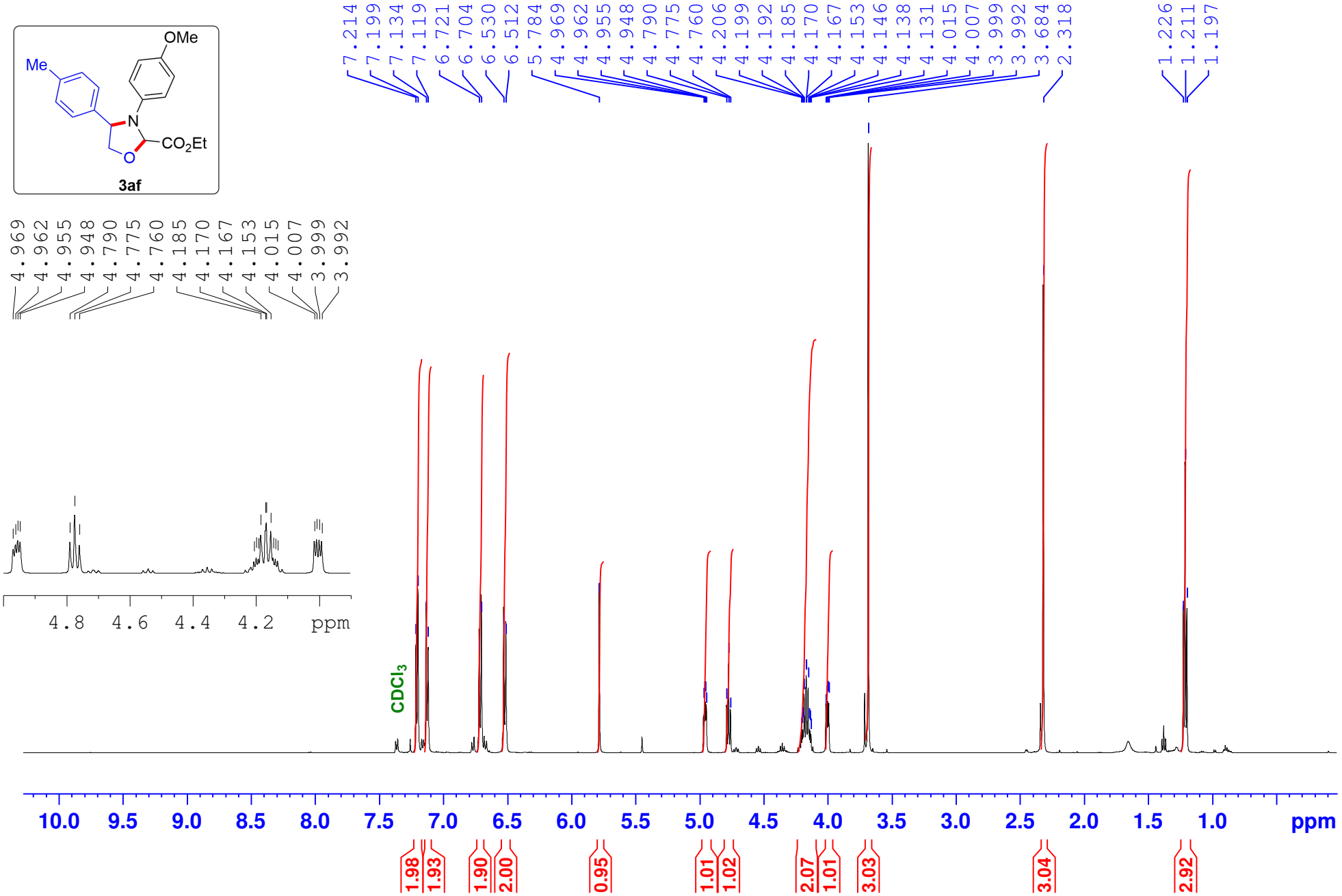


3ae

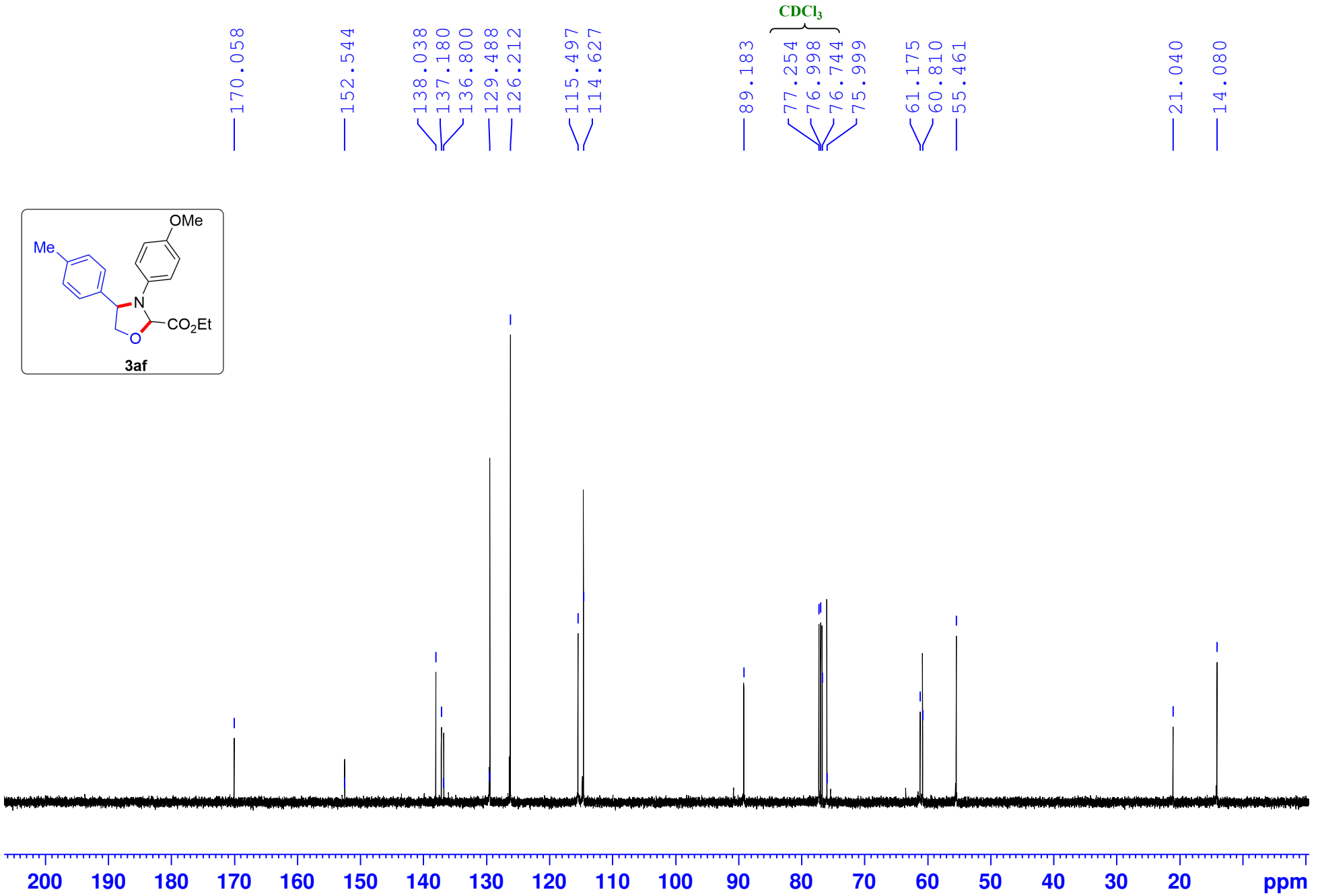
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



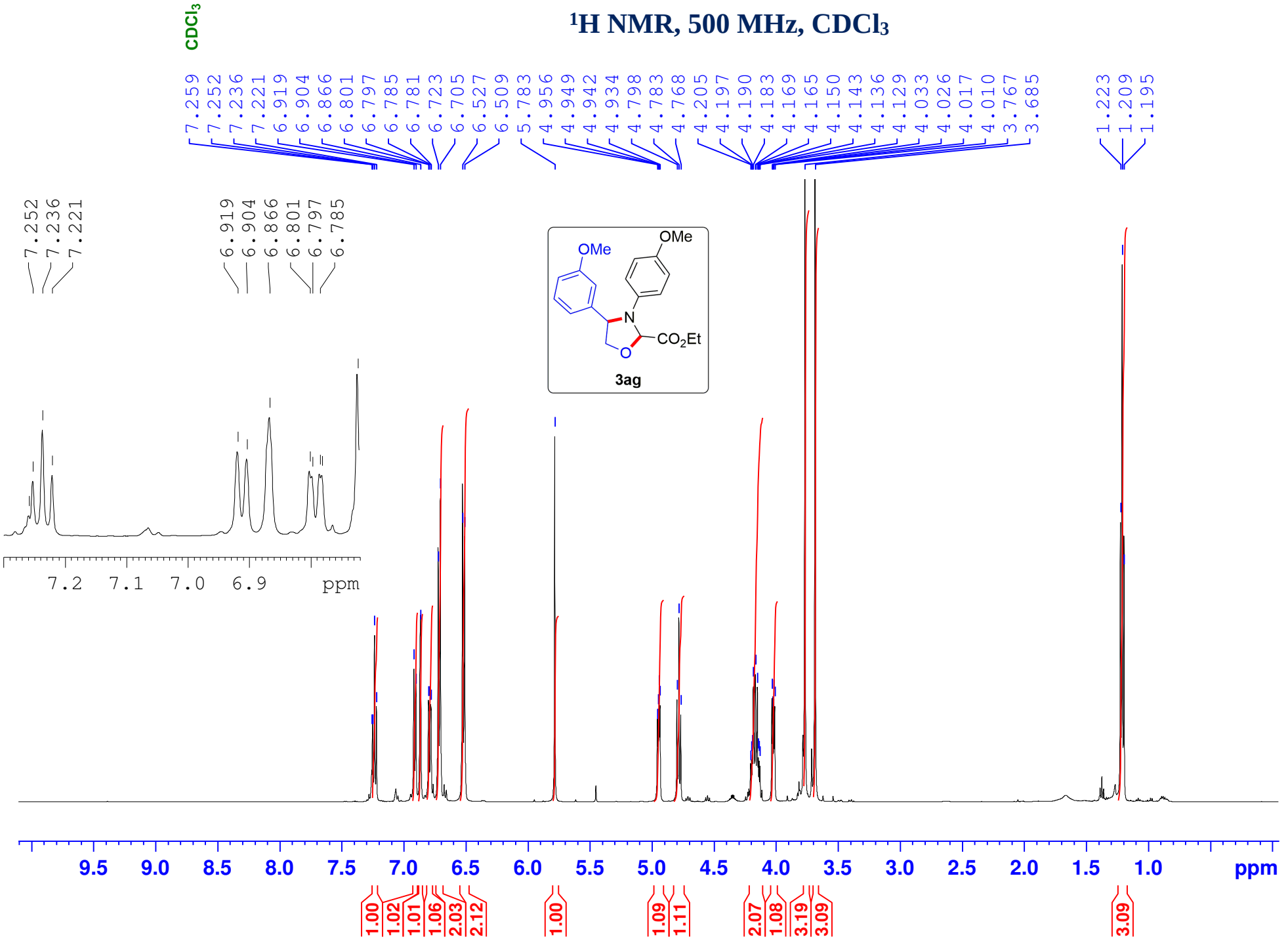
^{1}H NMR, 500 MHz, $CDCl_3$



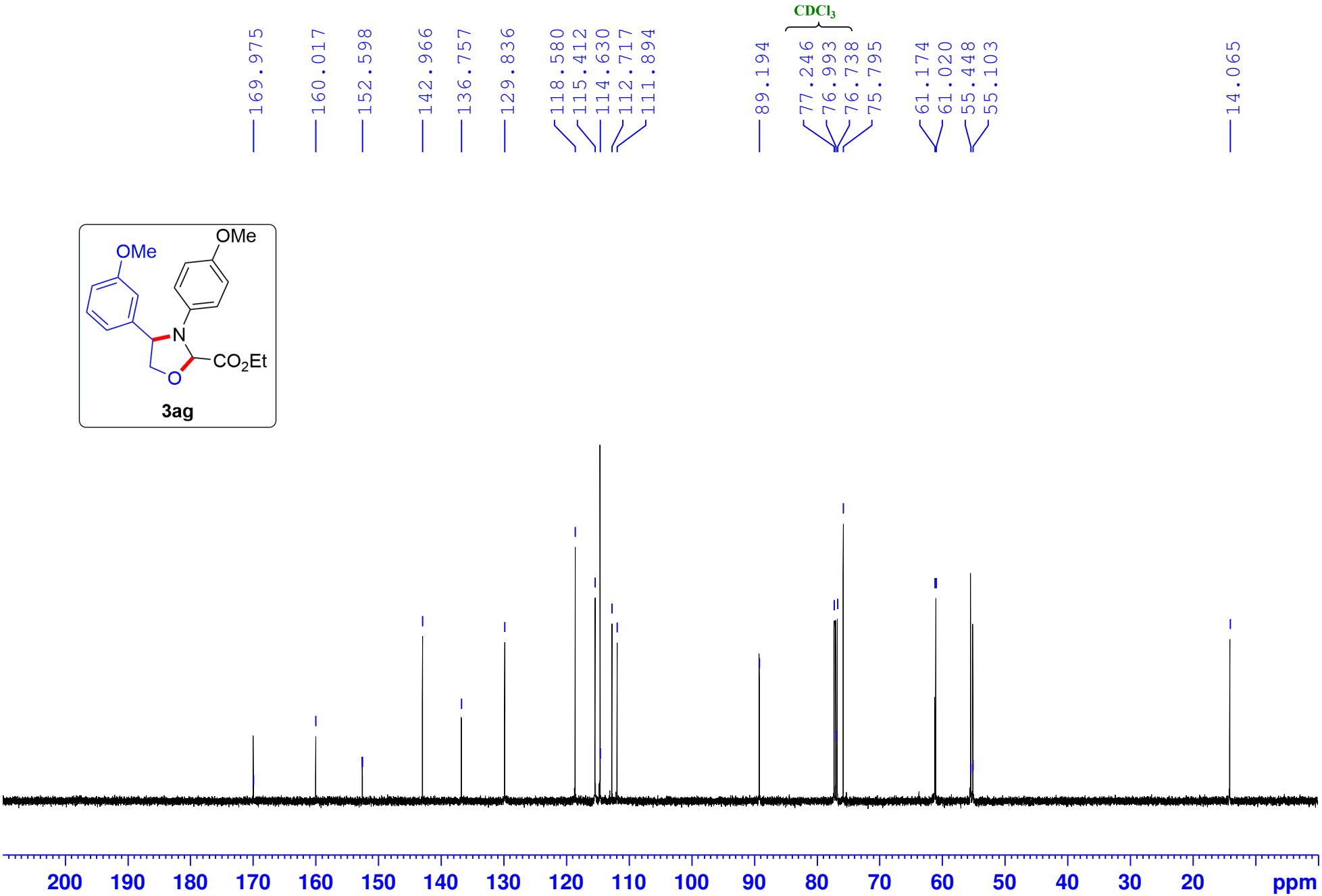
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



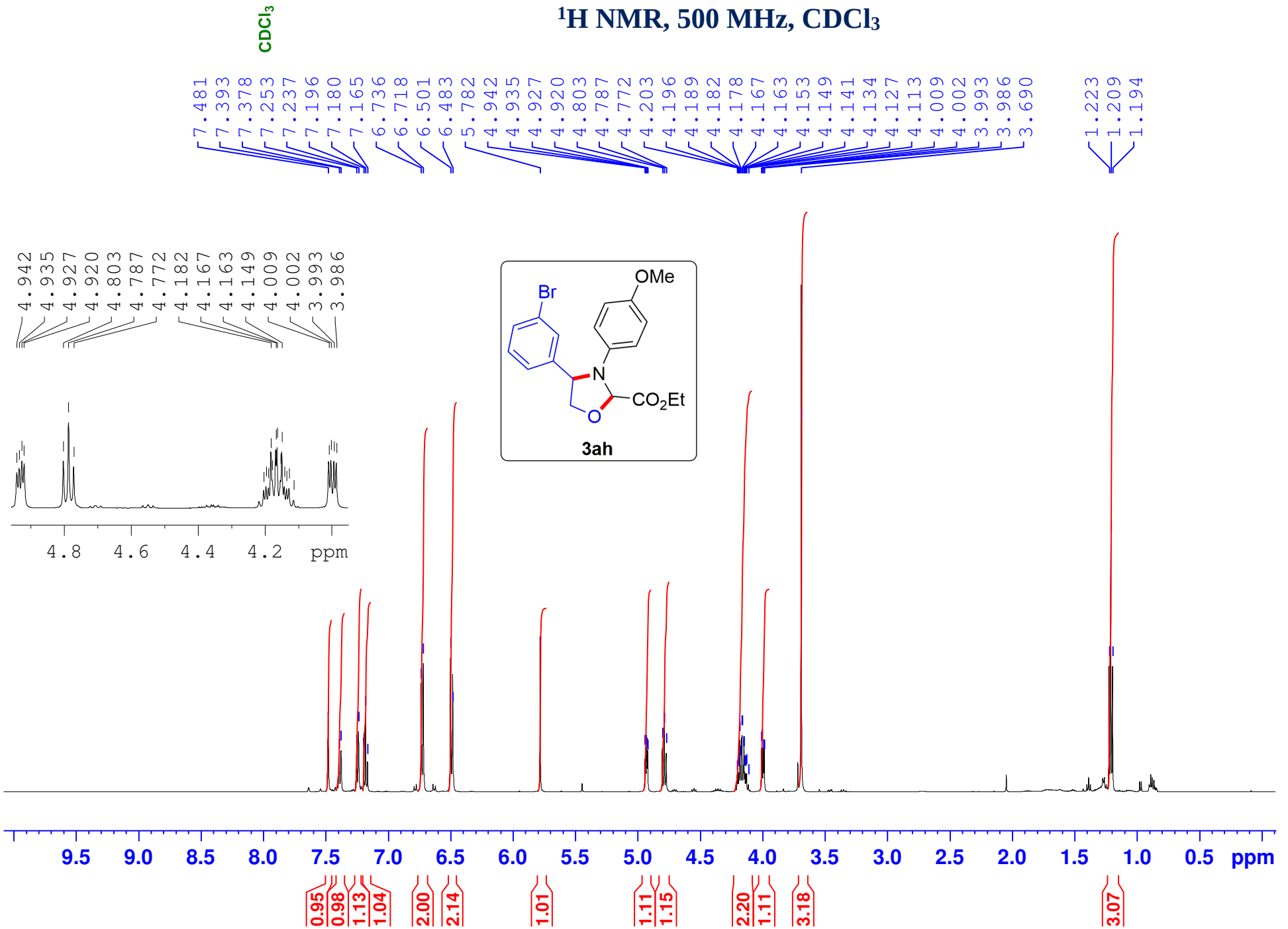
^{1}H NMR, 500 MHz, $CDCl_3$



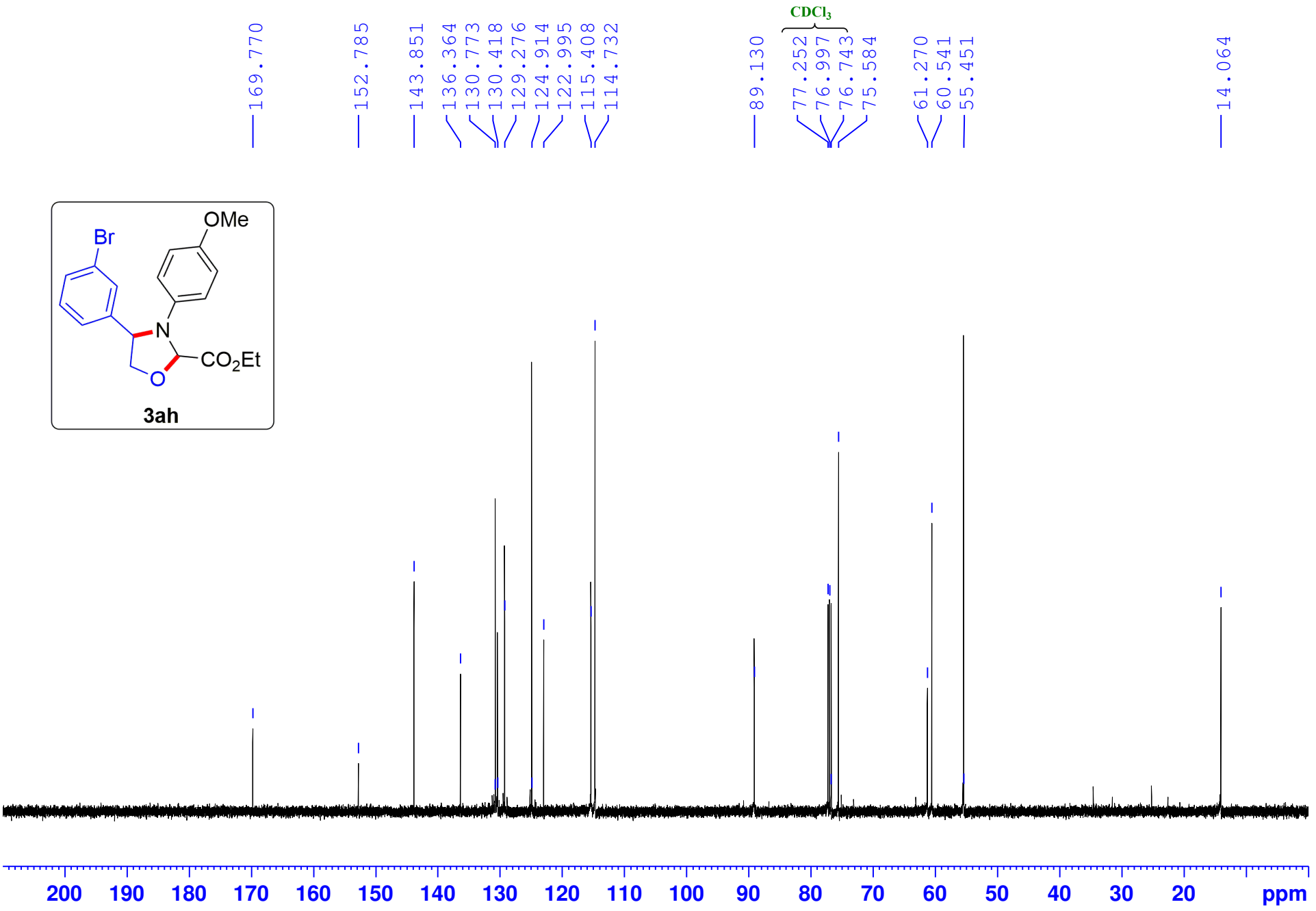
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



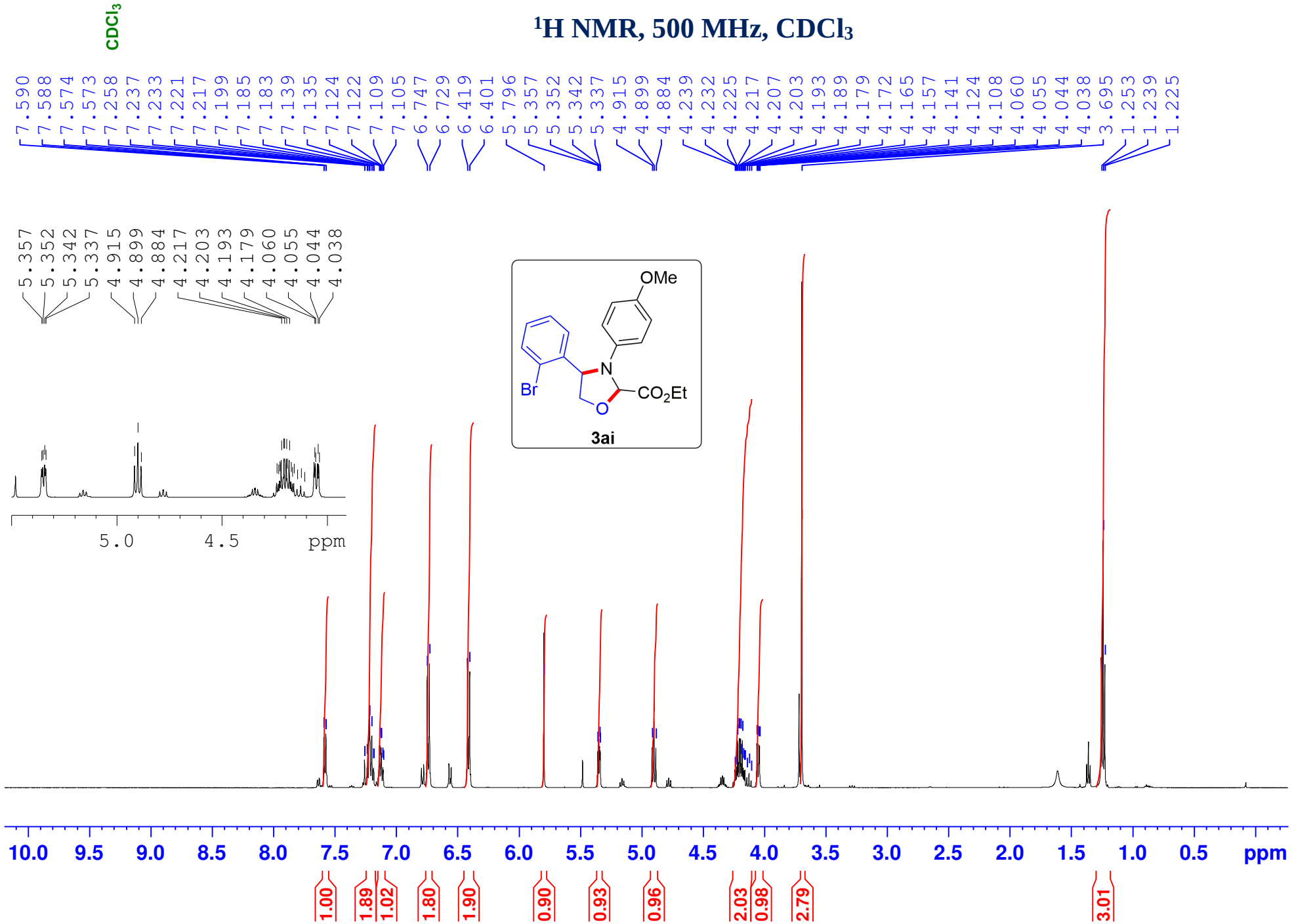
^{1}H NMR, 500 MHz, $CDCl_3$



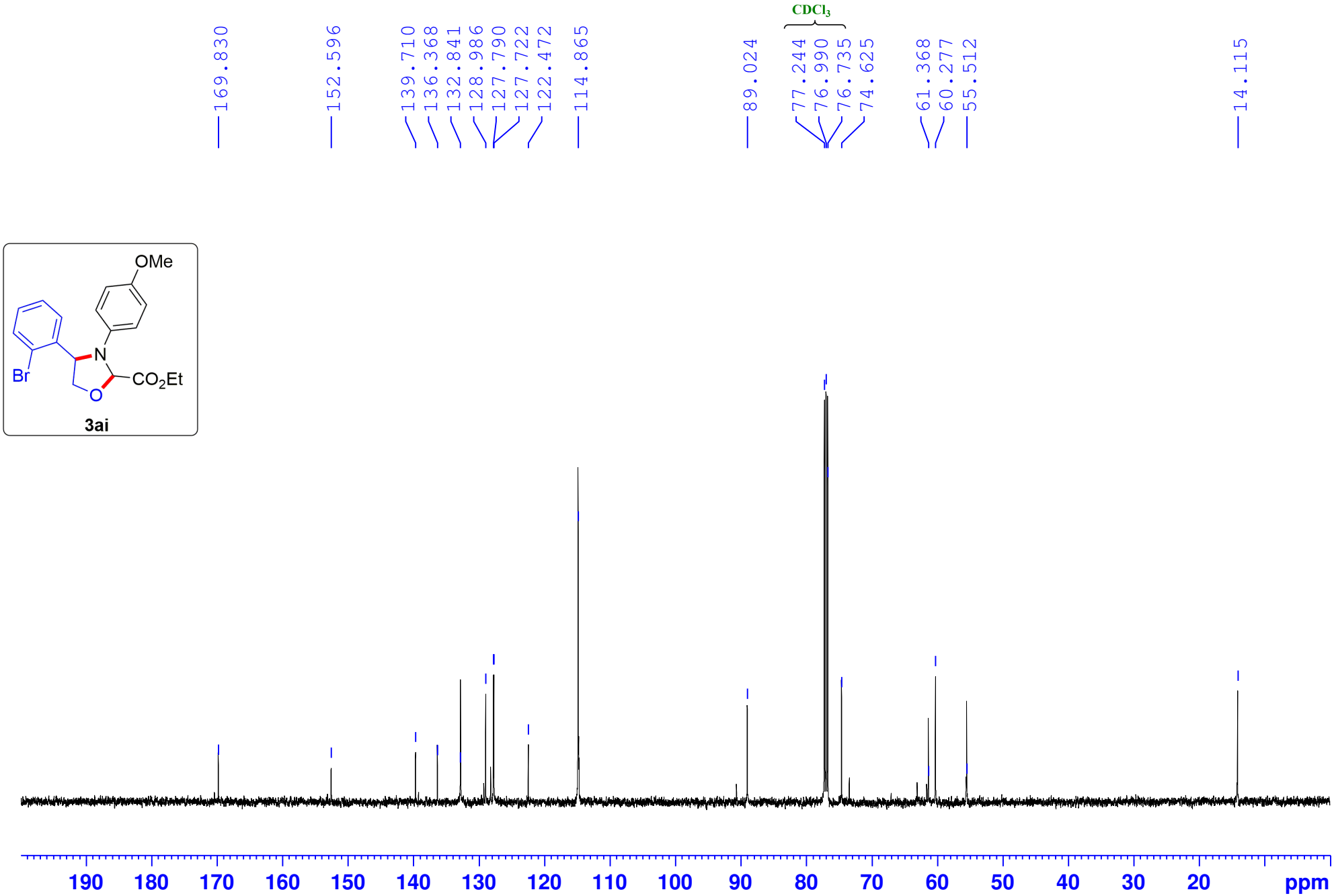
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



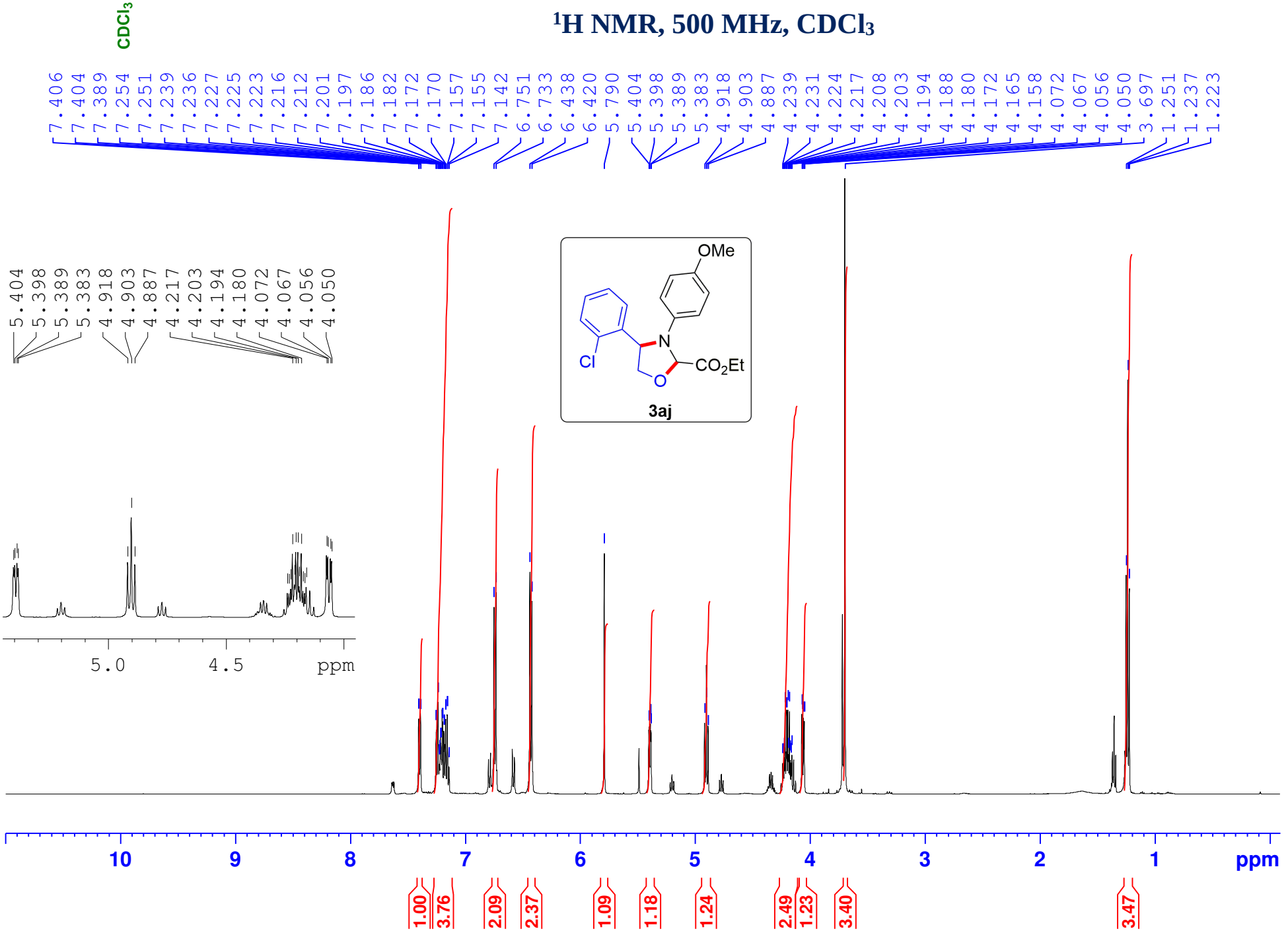
^{1}H NMR, 500 MHz, $CDCl_3$



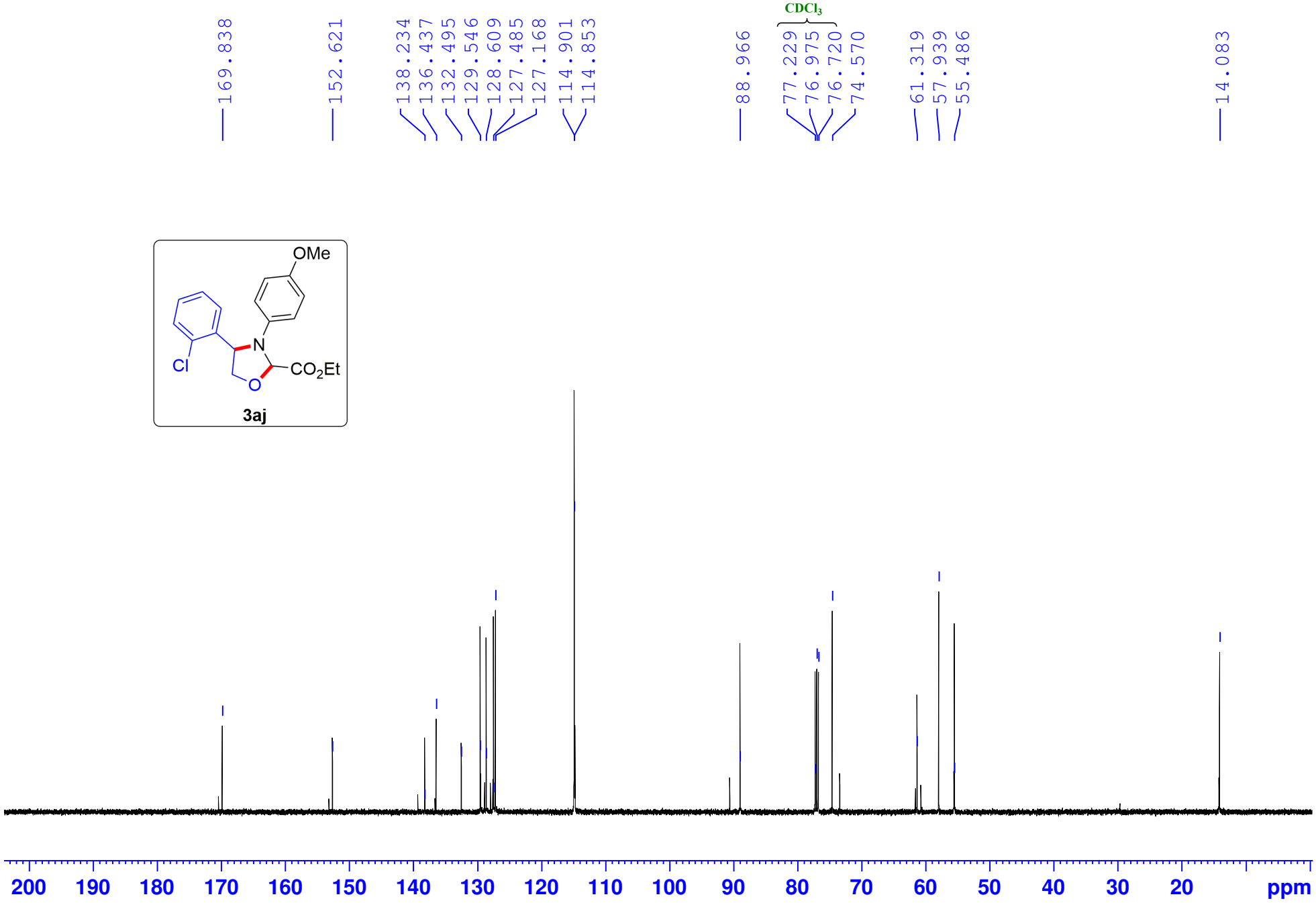
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



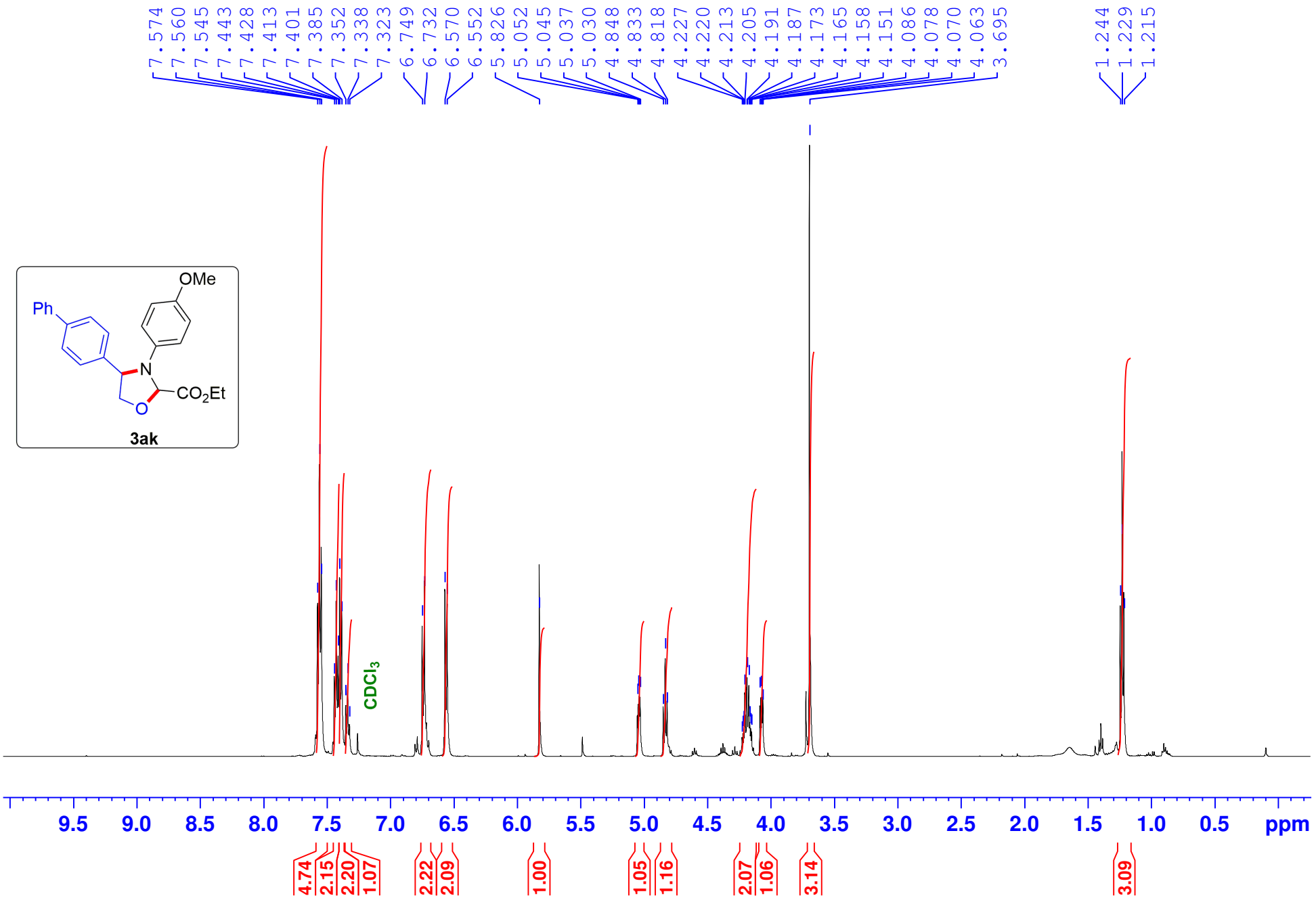
^{1}H NMR, 500 MHz, $CDCl_3$



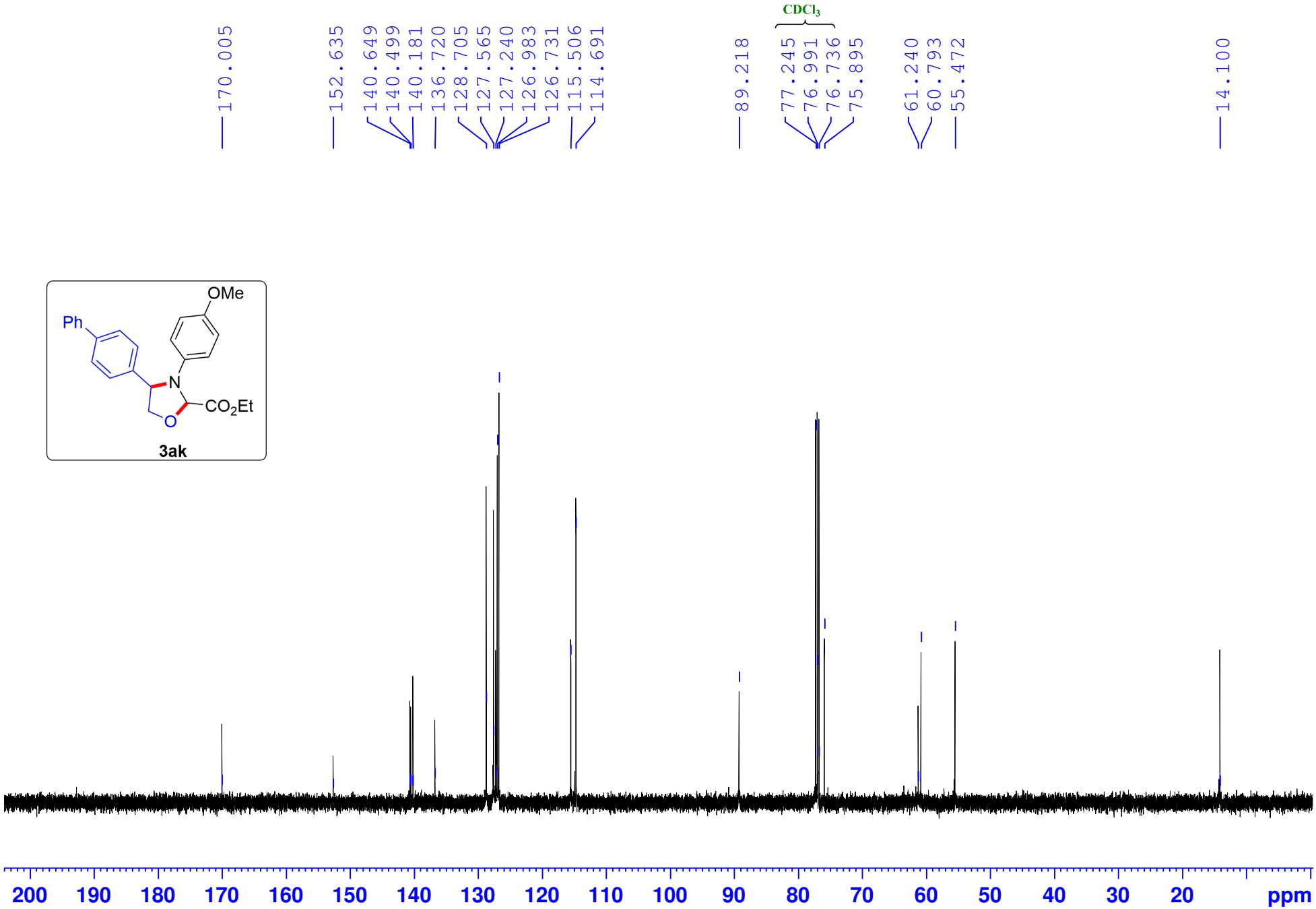
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



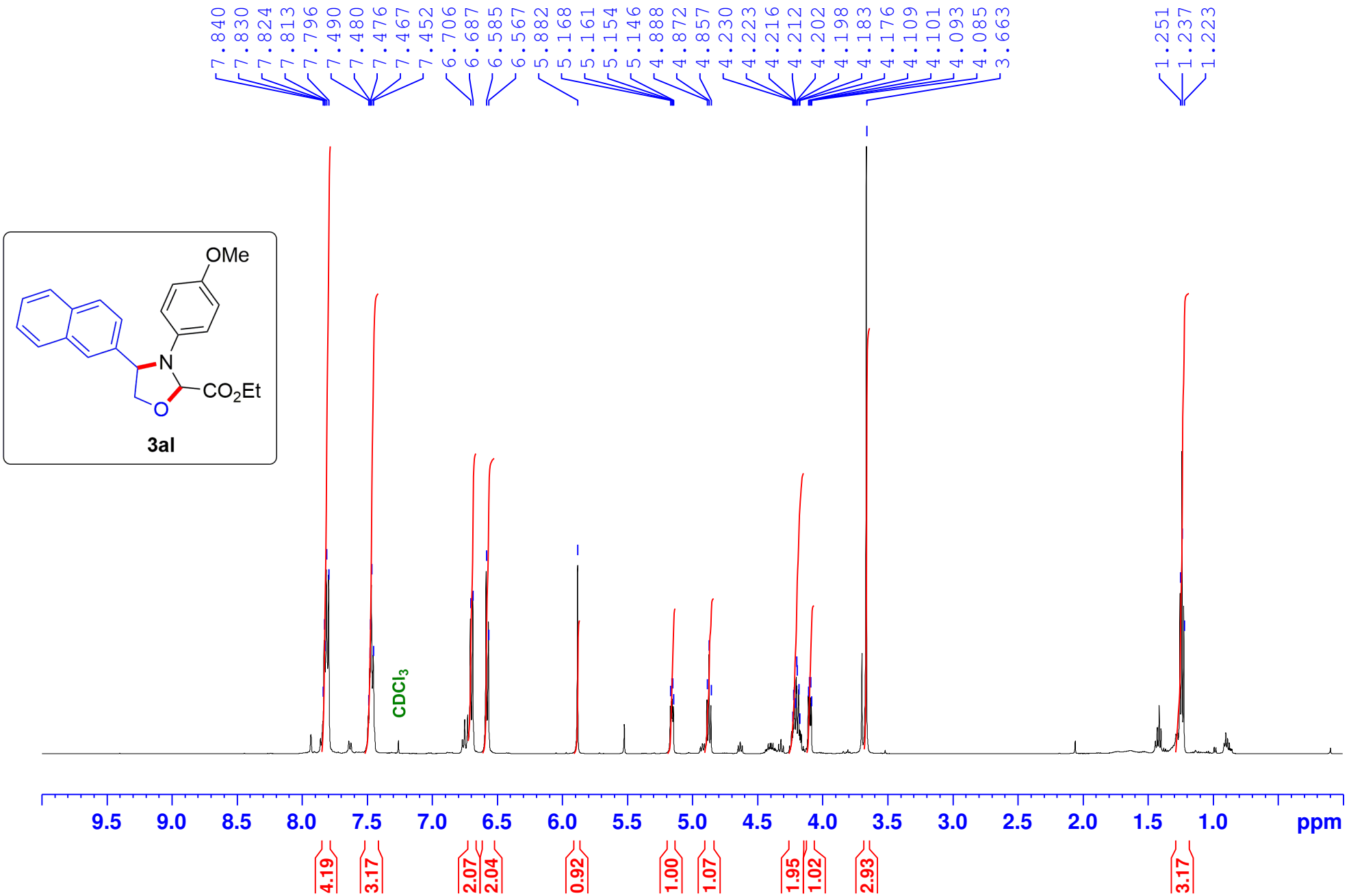
^{1}H NMR, 500 MHz, $CDCl_3$



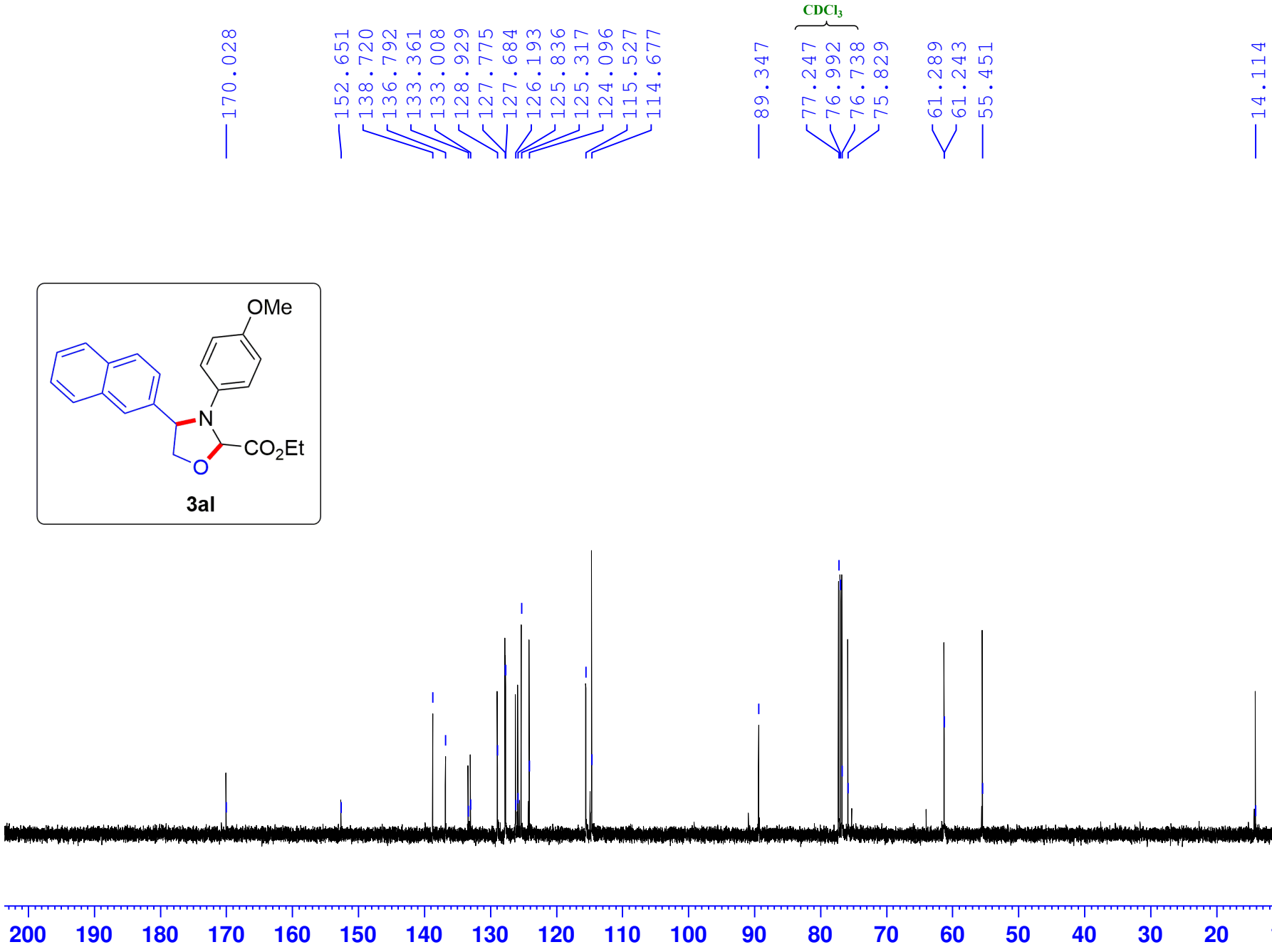
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



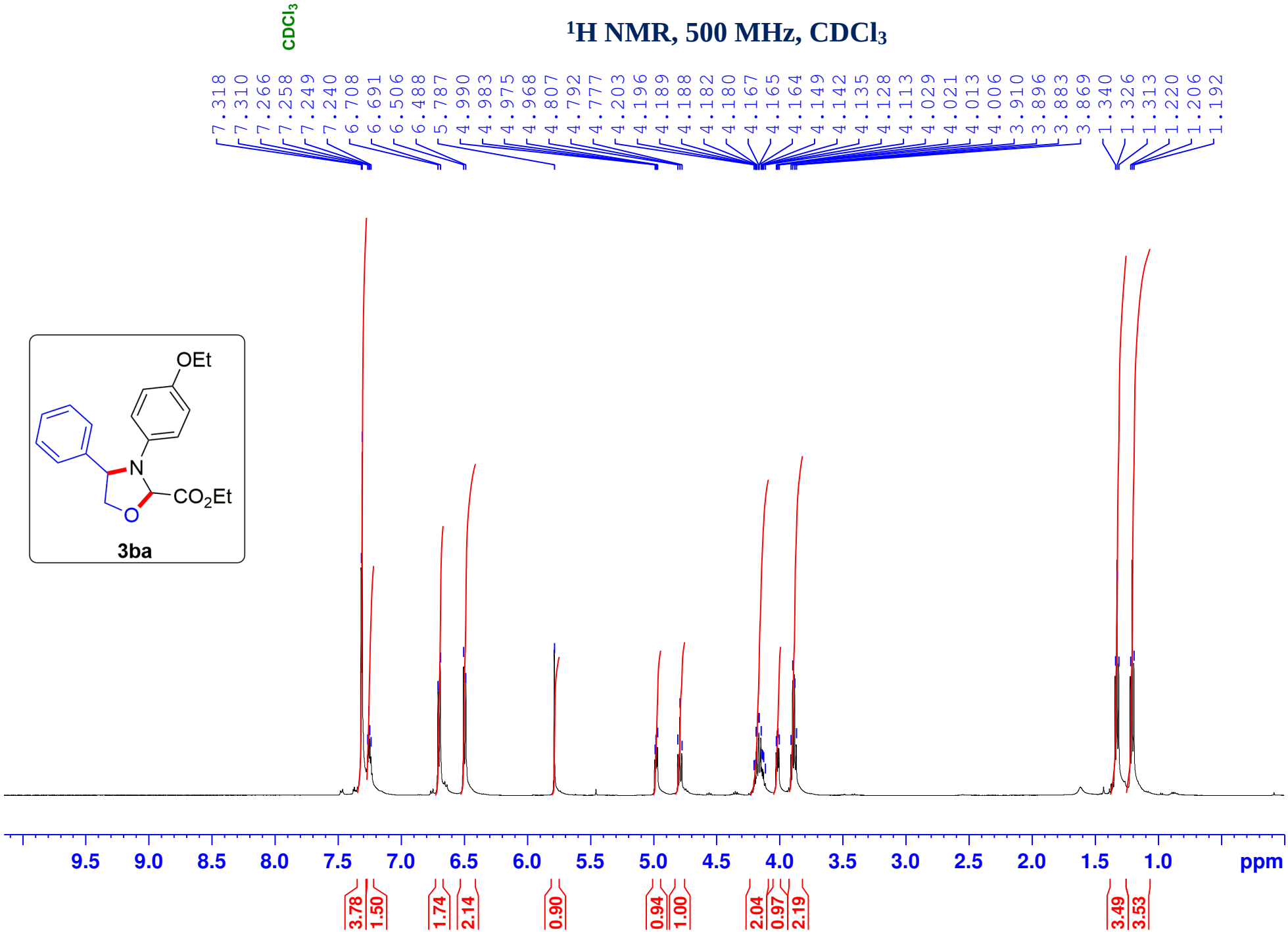
^{1}H NMR, 500 MHz, $CDCl_3$



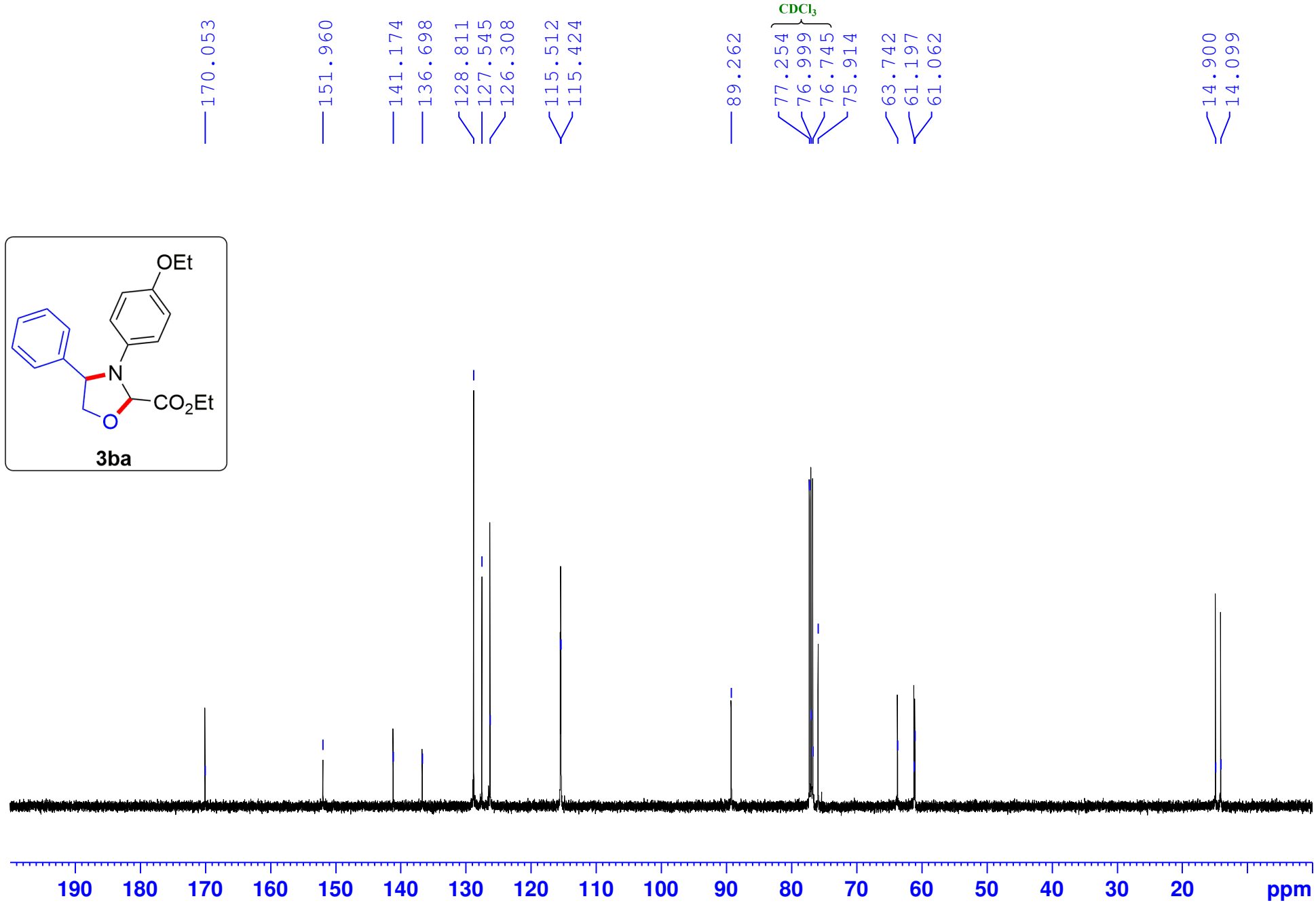
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



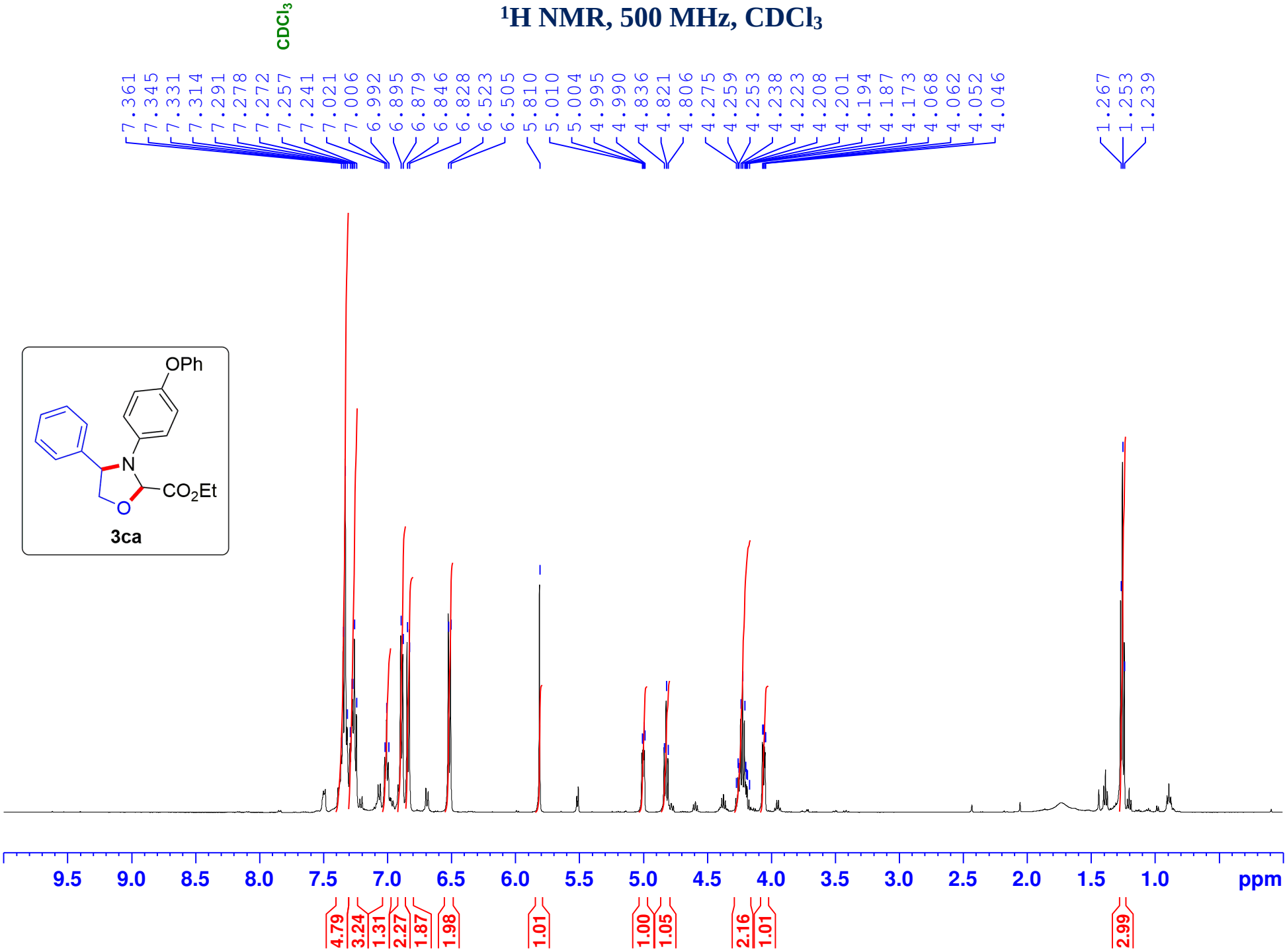
^{1}H NMR, 500 MHz, $CDCl_3$



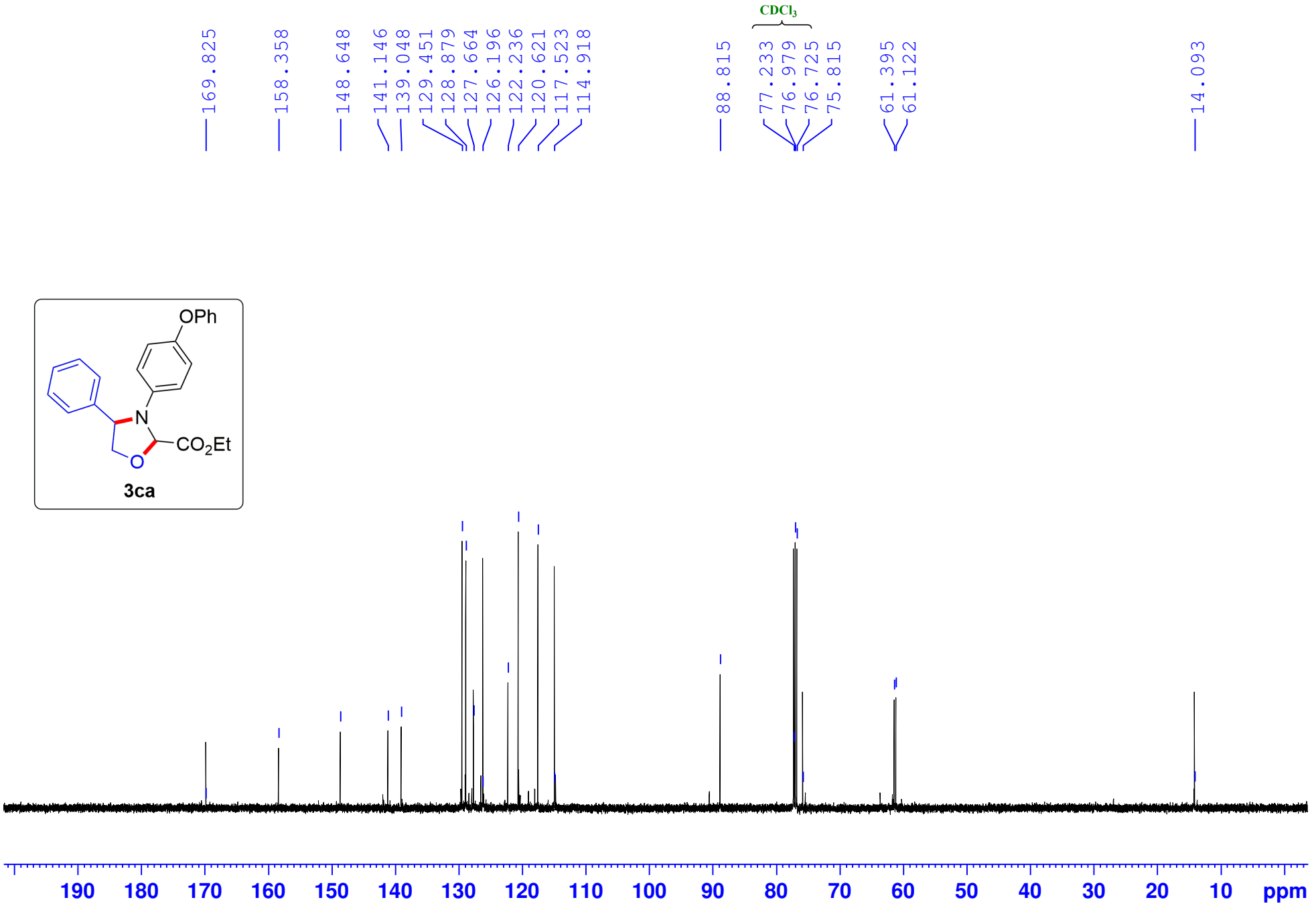
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



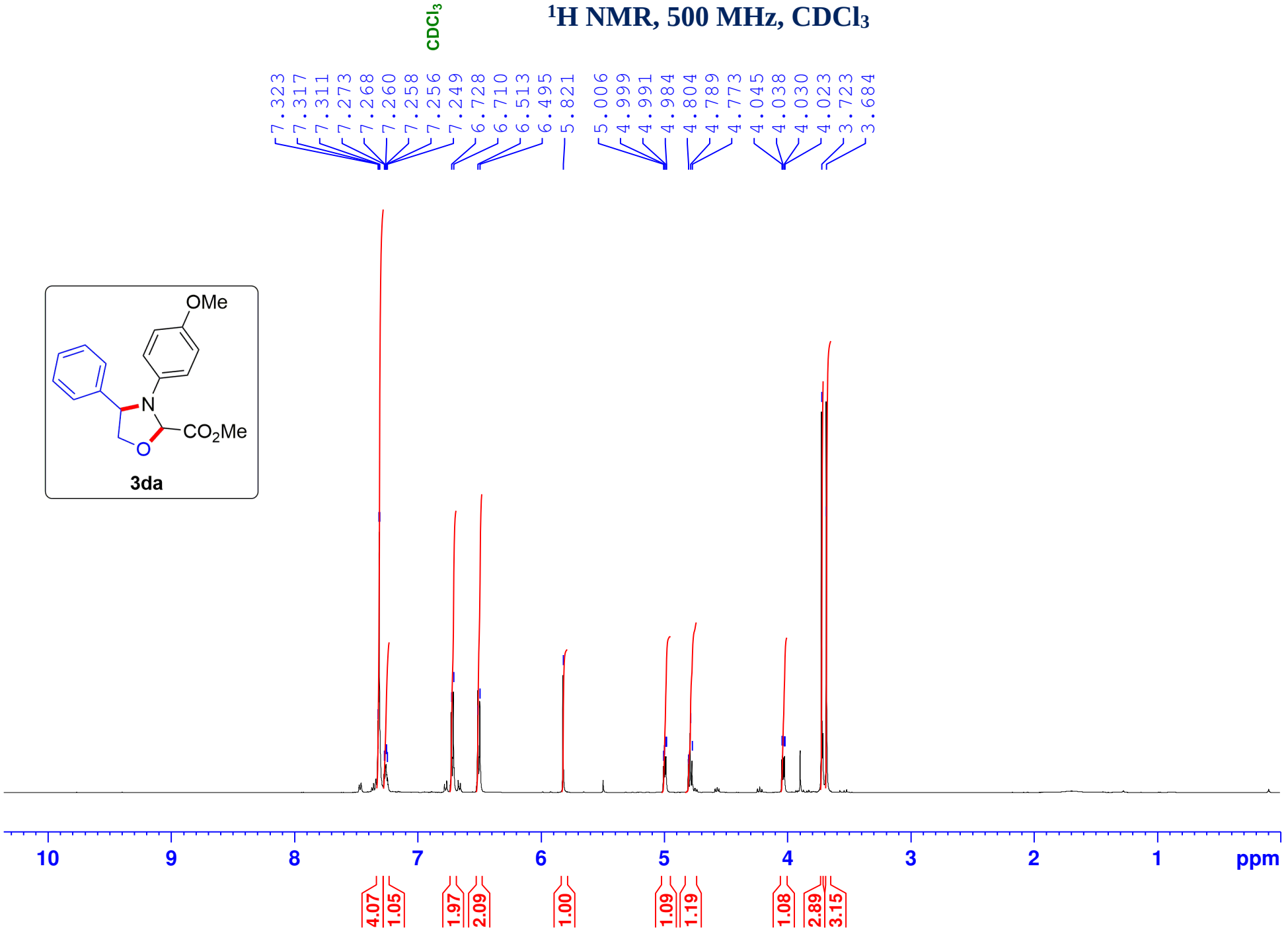
^{1}H NMR, 500 MHz, $CDCl_3$



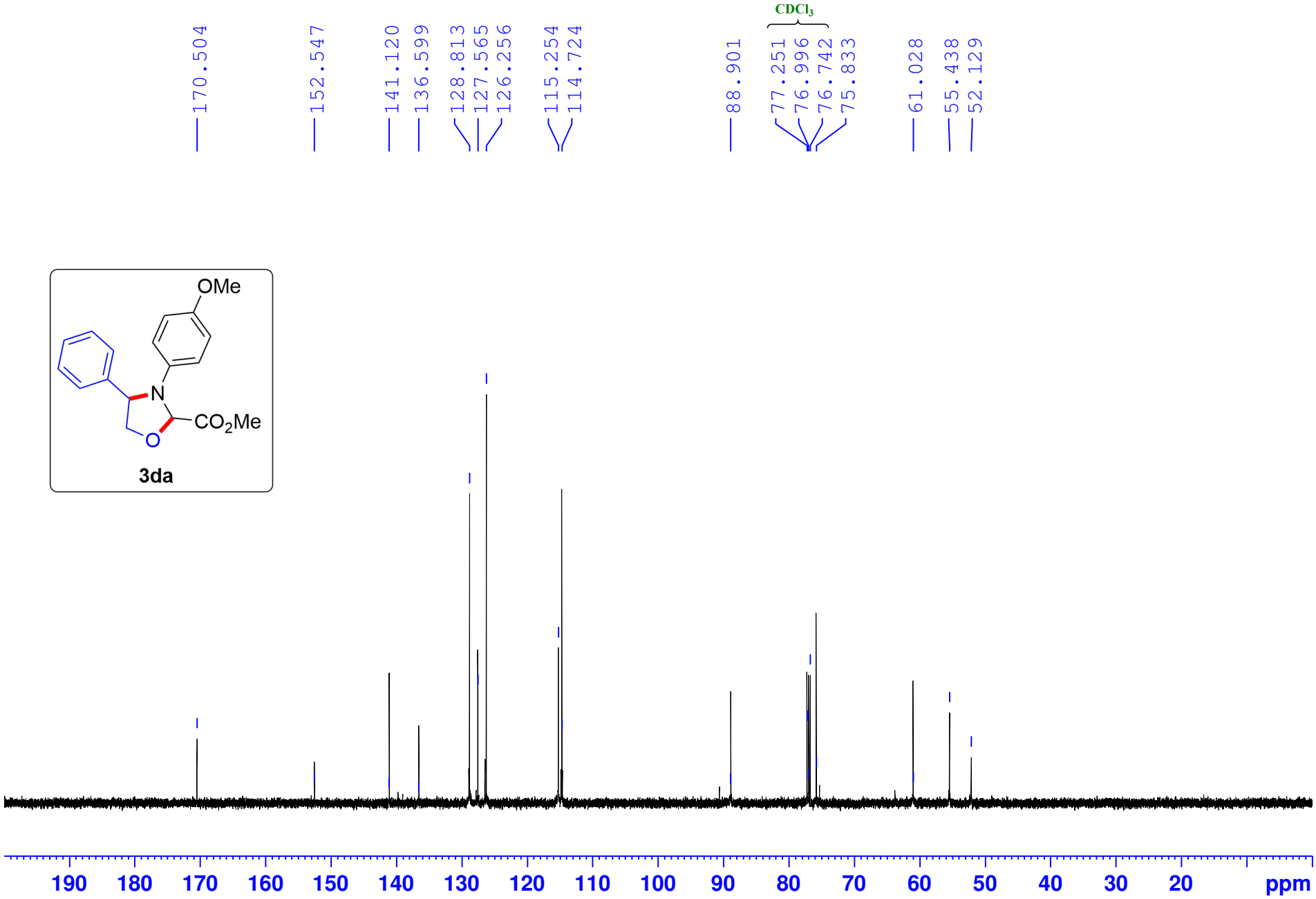
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



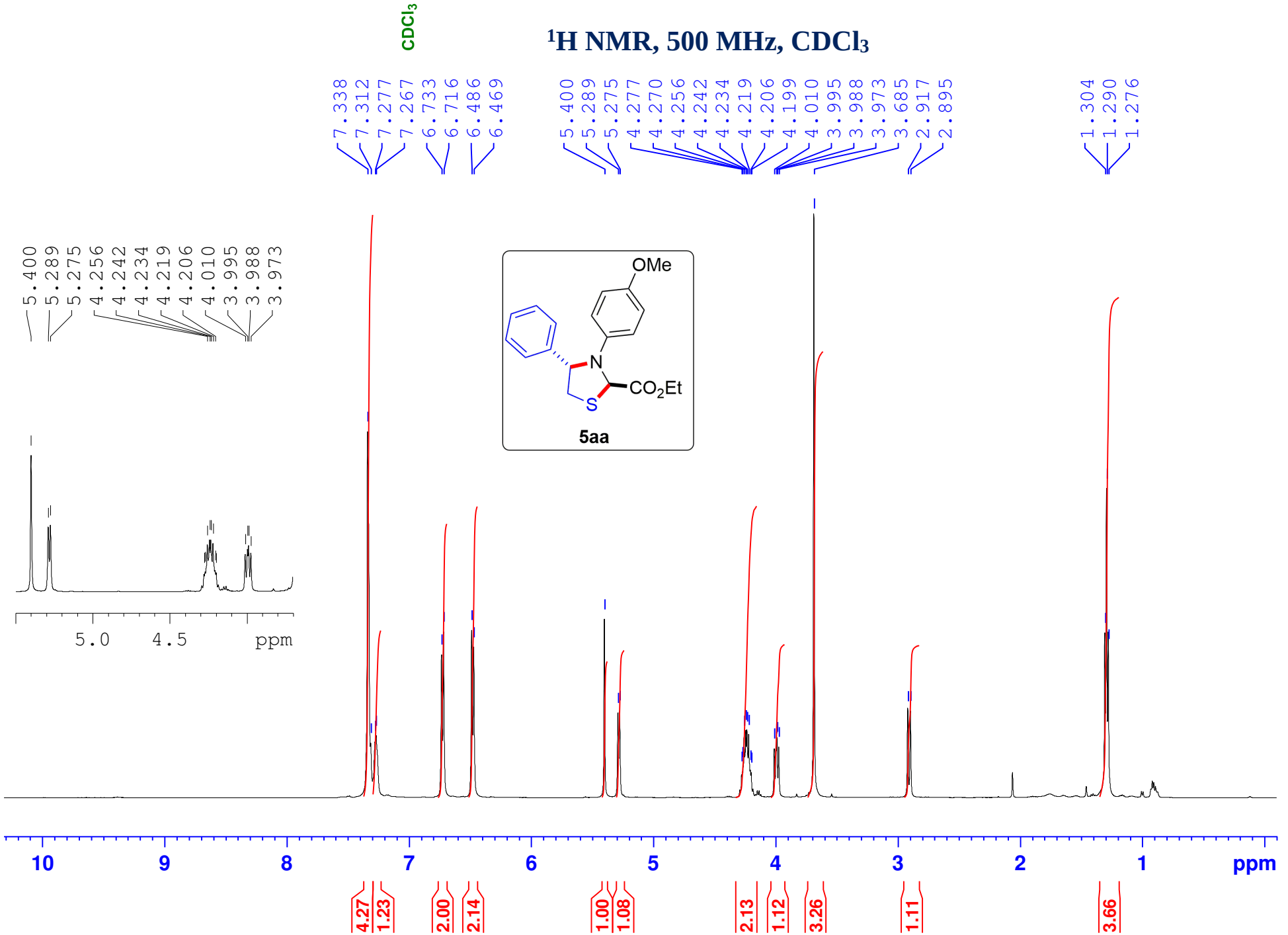
^{1}H NMR, 500 MHz, $CDCl_3$



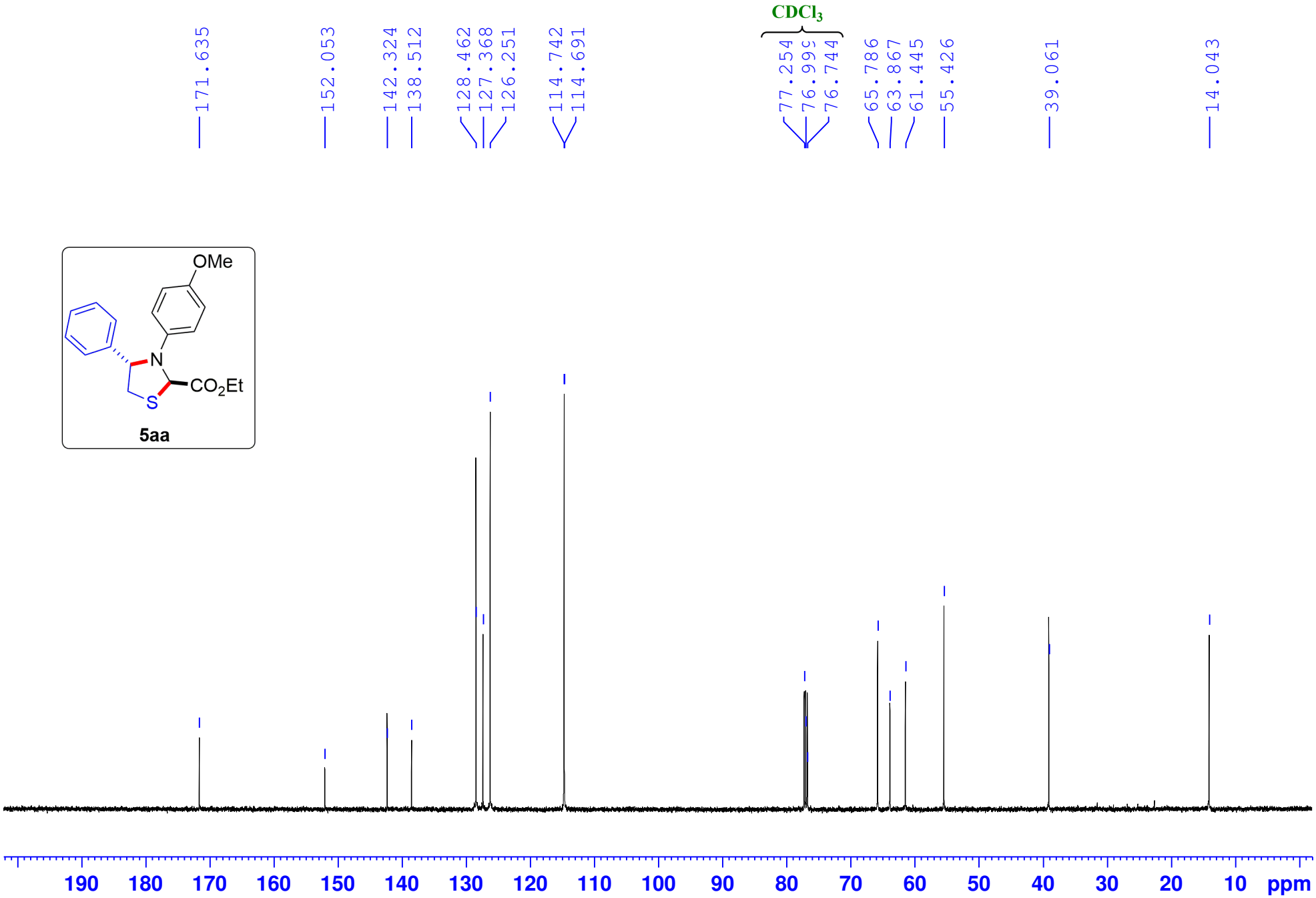
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



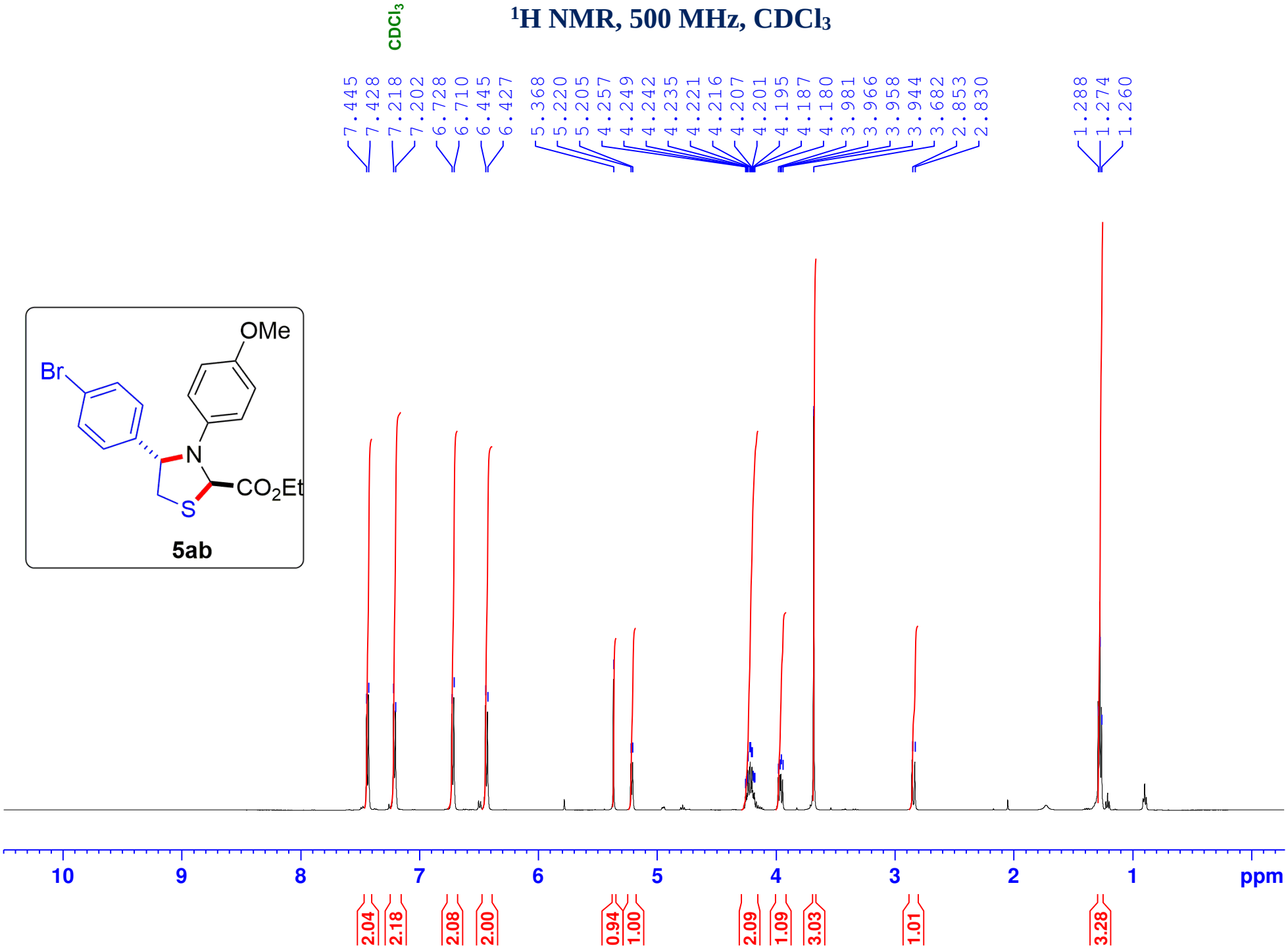
^{1}H NMR, 500 MHz, $CDCl_3$



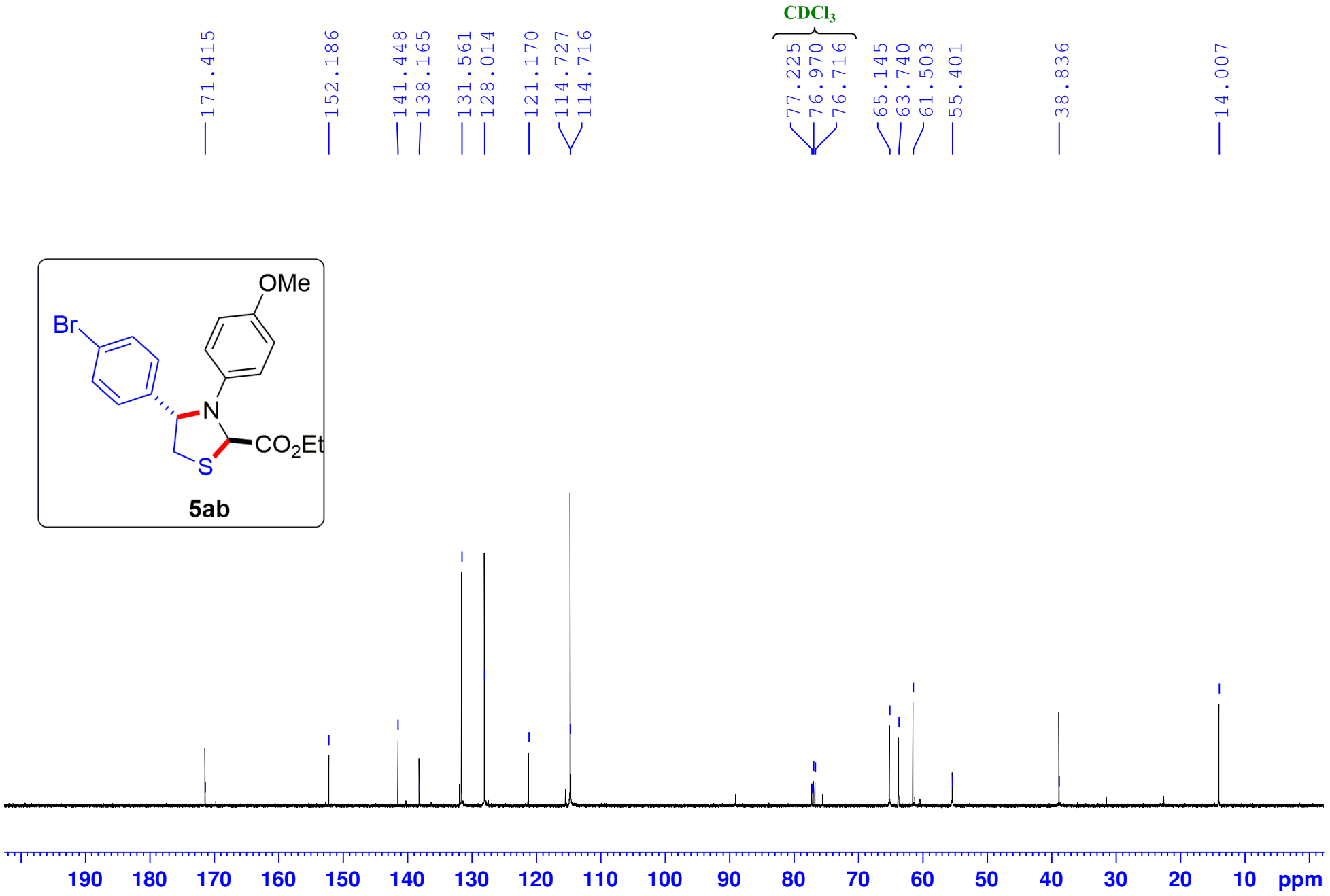
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



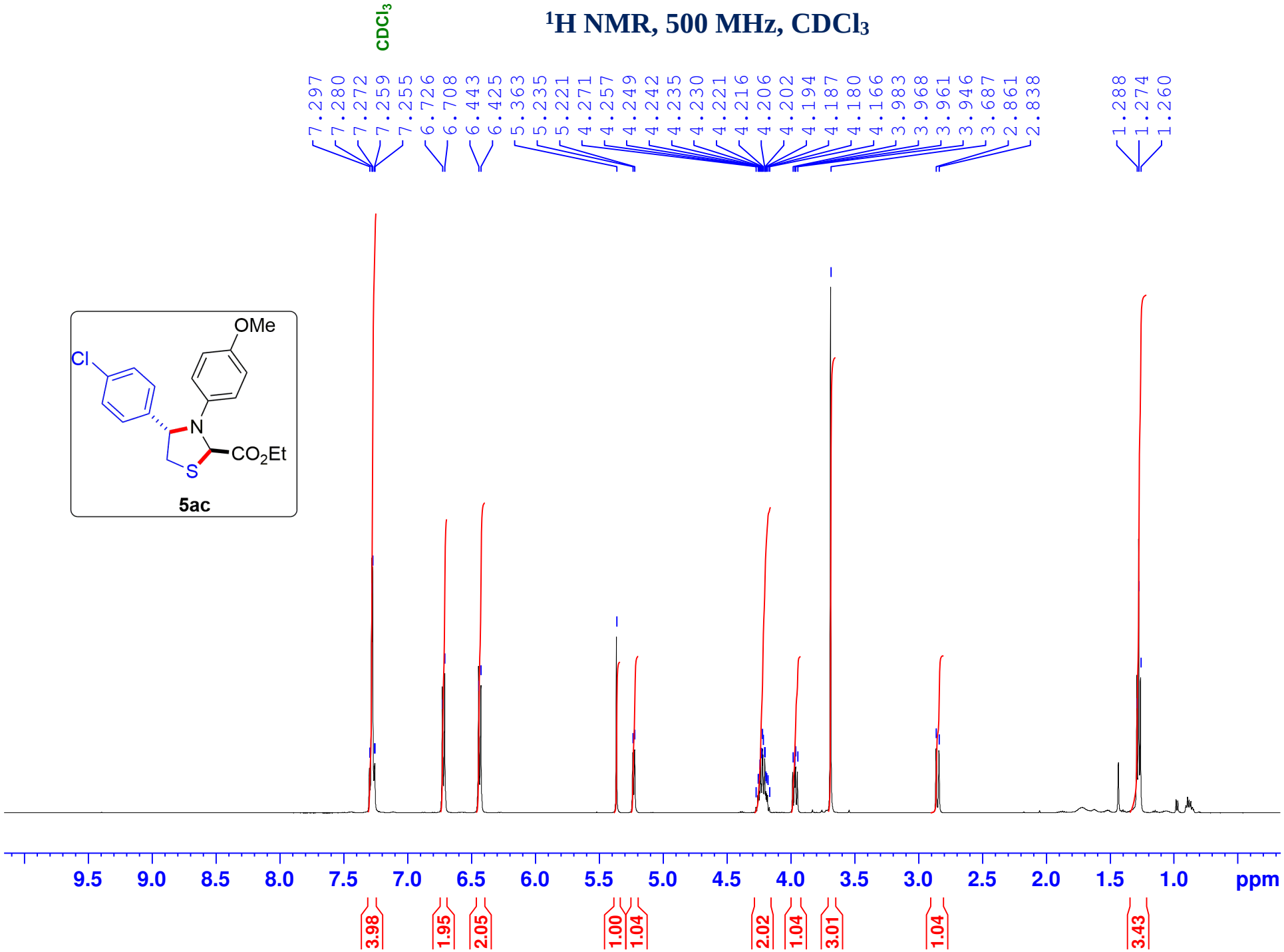
^{1}H NMR, 500 MHz, $CDCl_3$



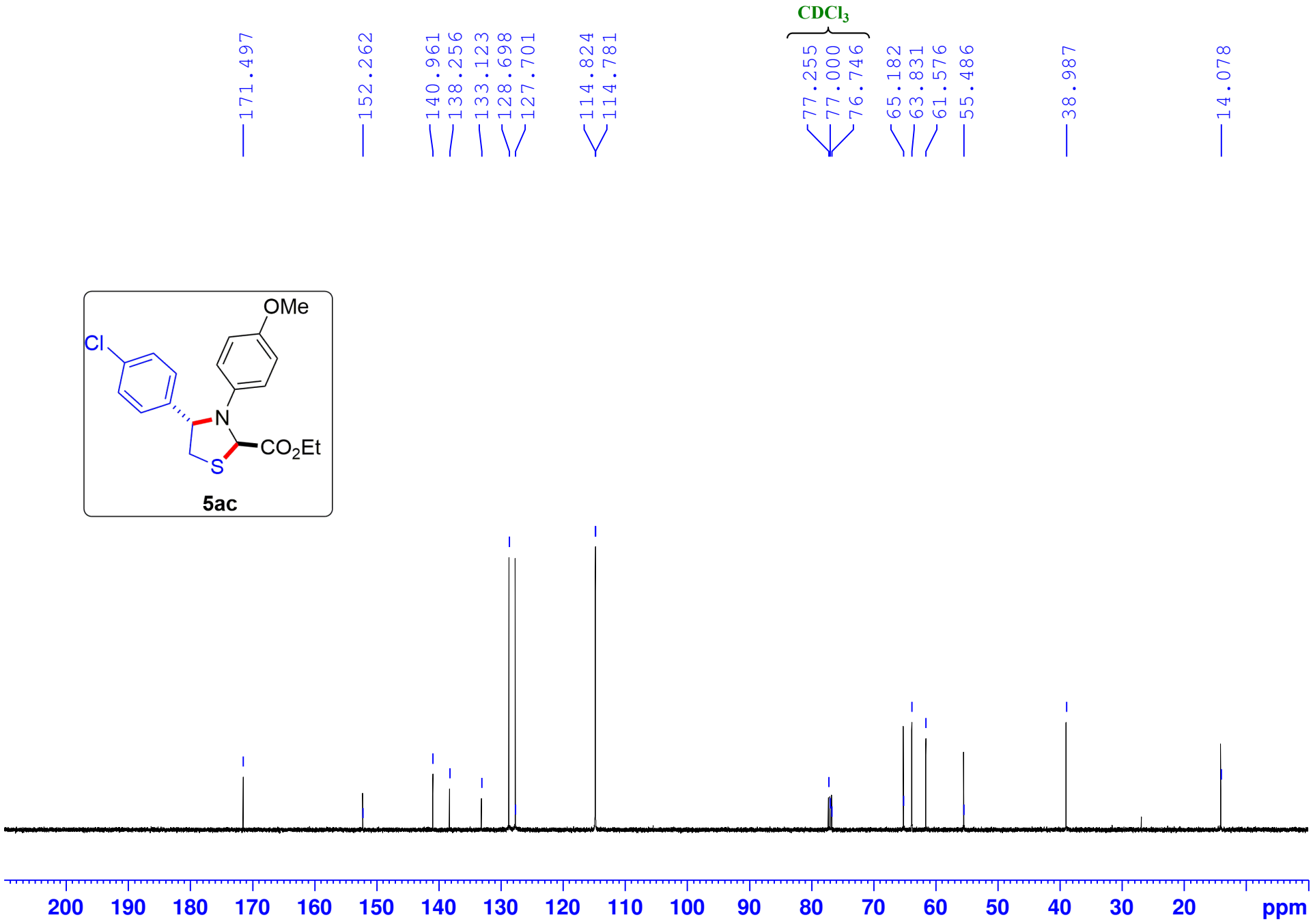
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



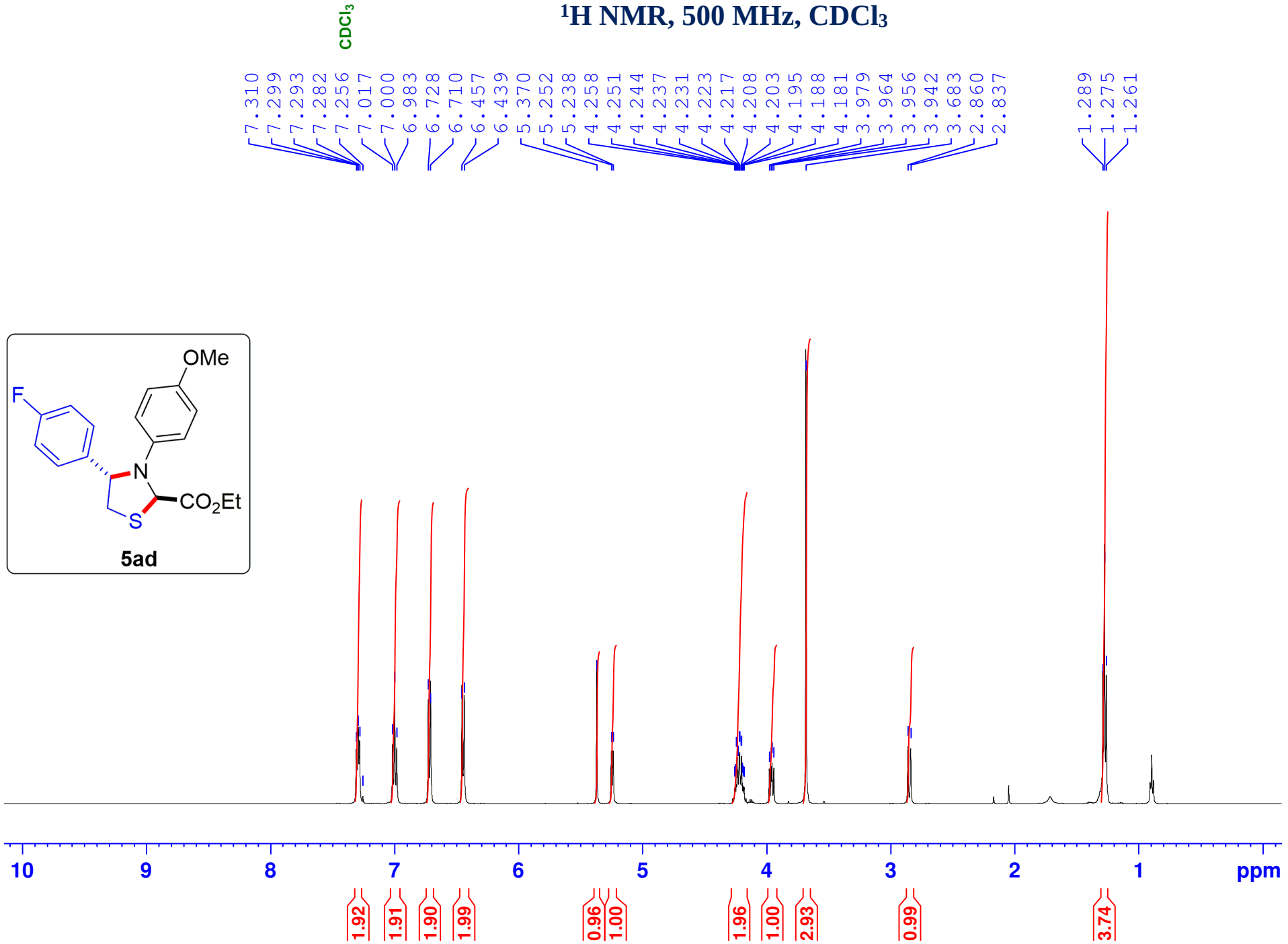
^{1}H NMR, 500 MHz, $CDCl_3$

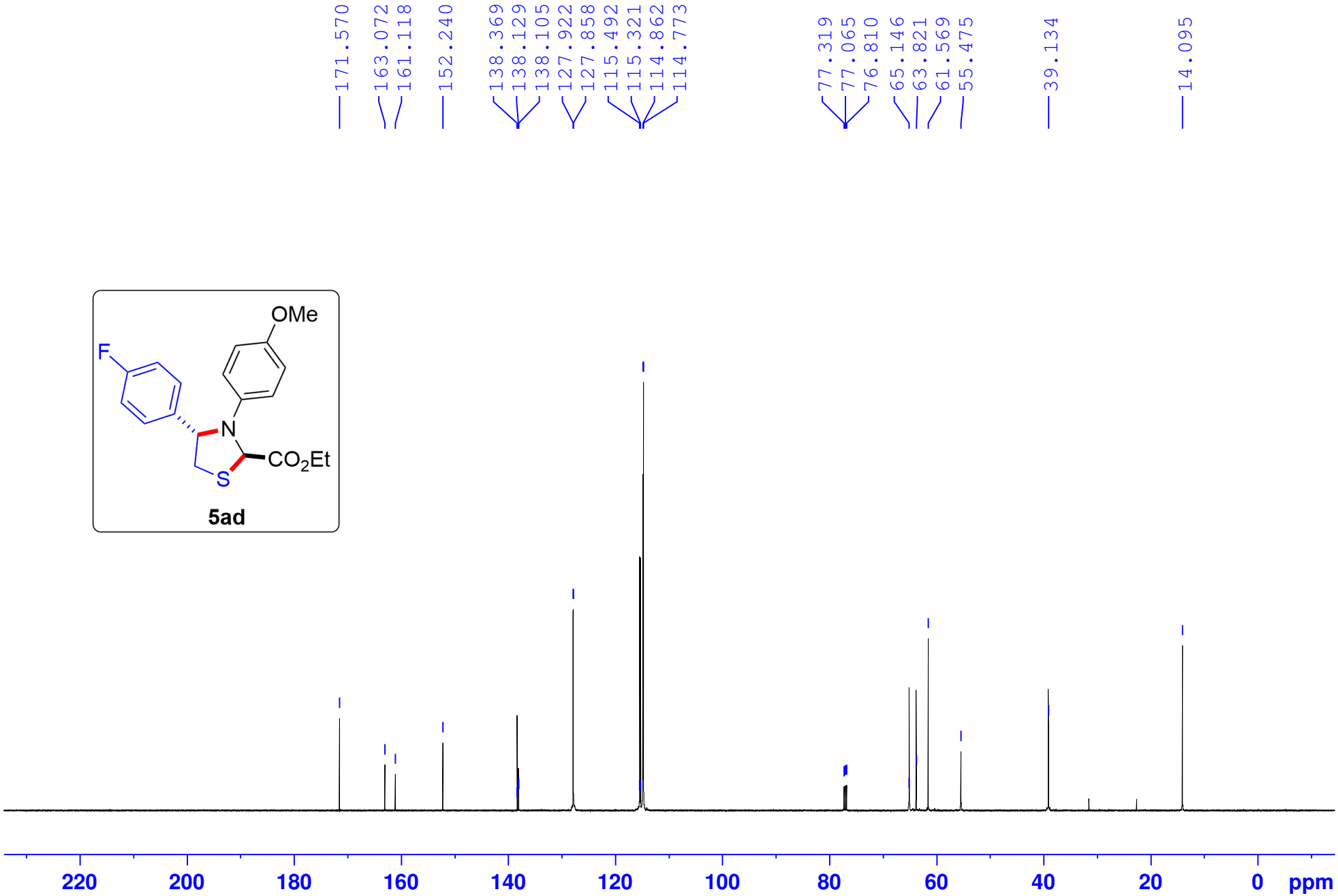


^{13}C {1H} NMR, 125 MHz, $CDCl_3$

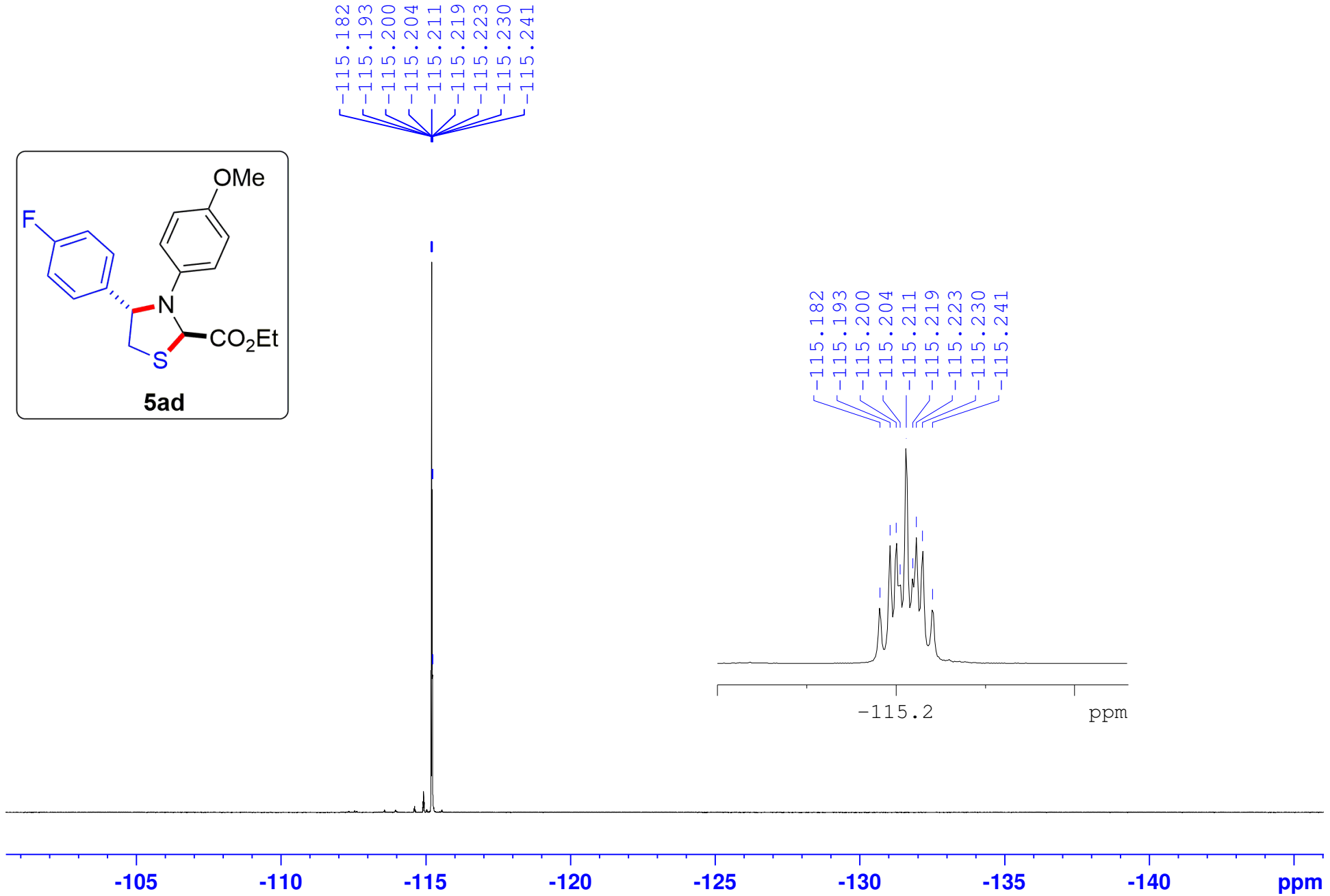


^{1}H NMR, 500 MHz, $CDCl_3$

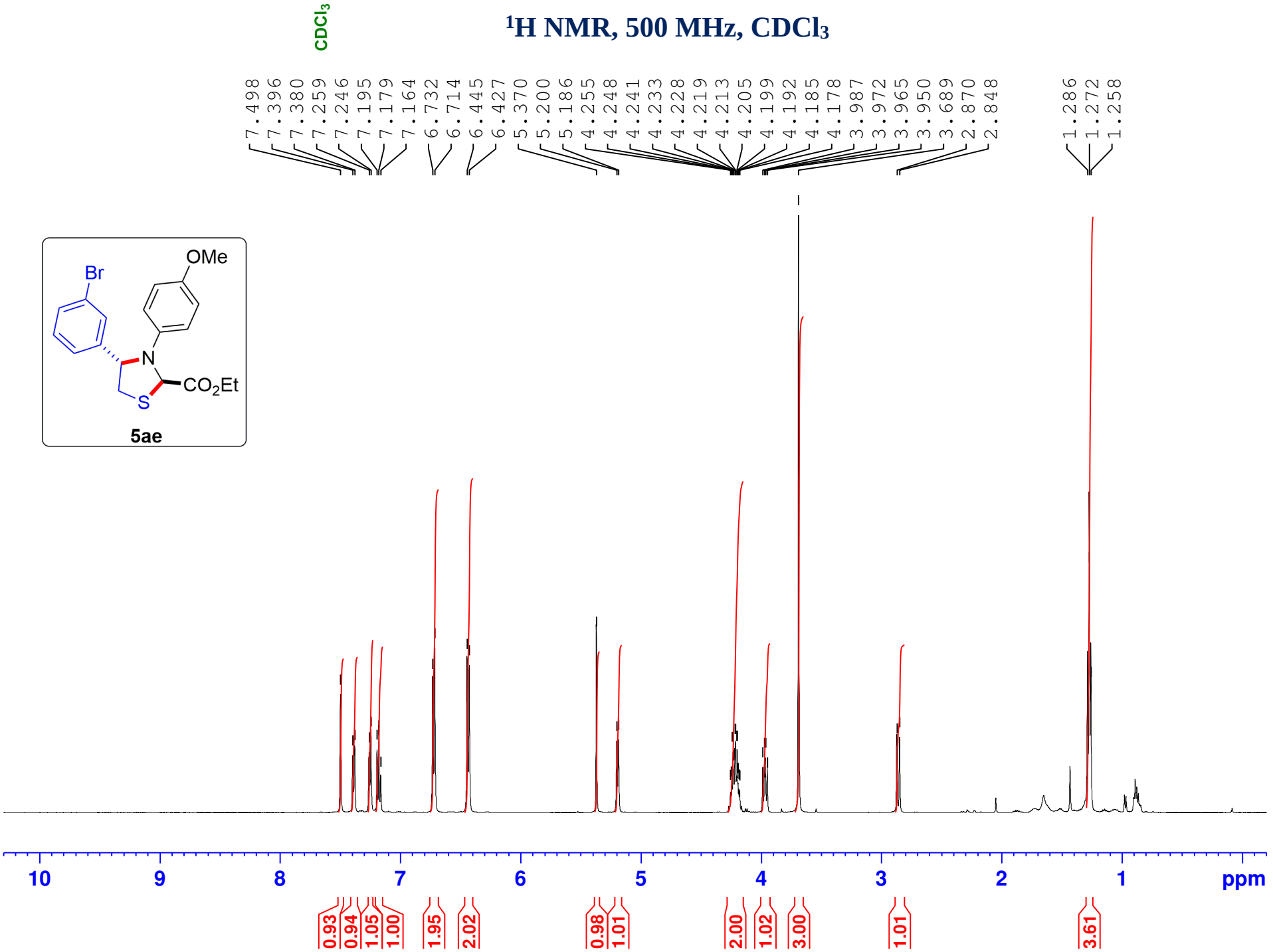



171.570
163.072
161.118
152.240
138.369
138.129
138.105
127.922
127.858
115.492
115.321
114.862
114.773
77.319
77.065
76.810
65.146
63.821
61.569
55.475
39.134
14.095
OMe
F
N
S
CO2Et
5ad
220
200
180
160
140
120
100
80
60
40
20
0
ppm

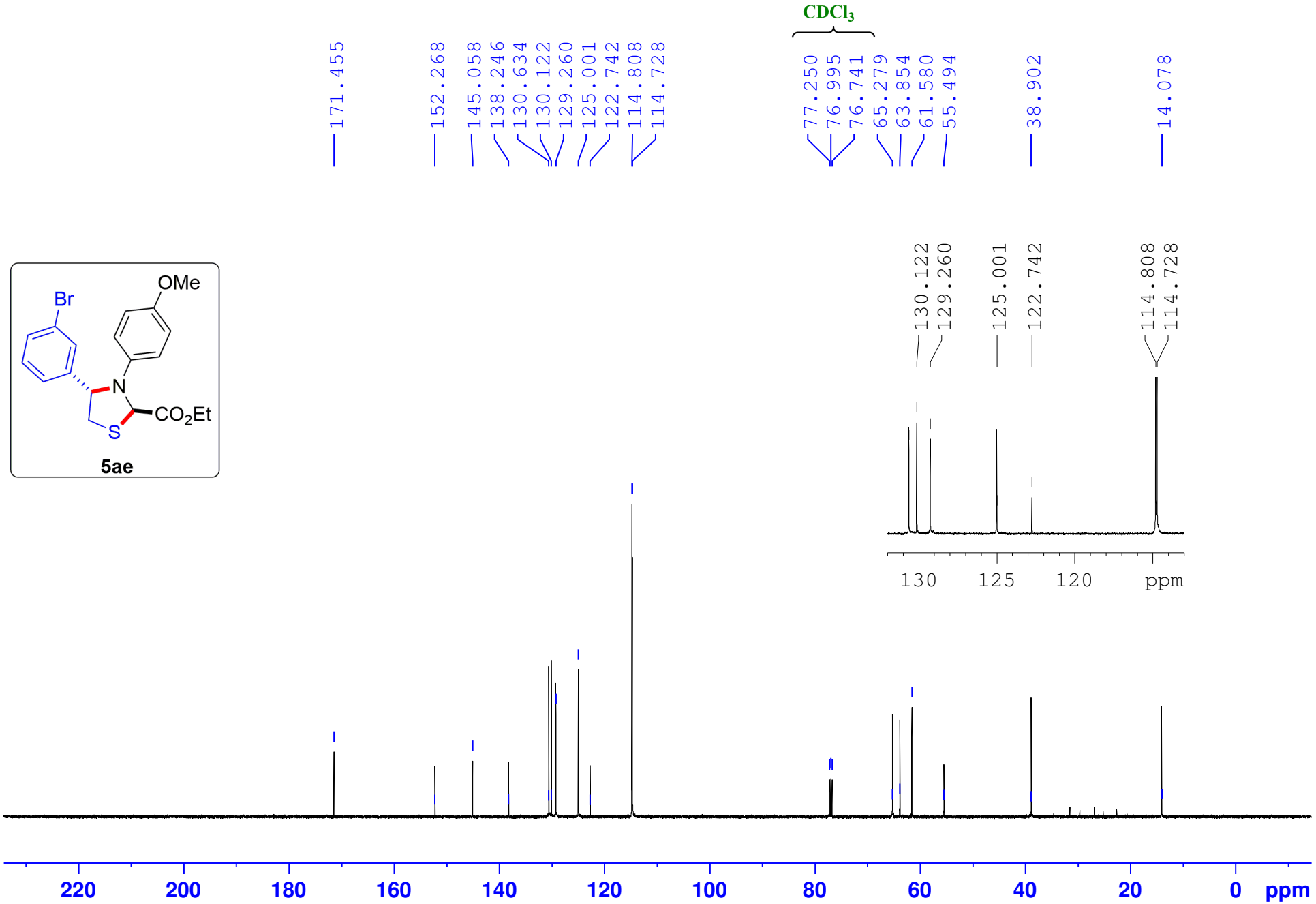
^{19}F NMR, 470 MHz, $CDCl_3$



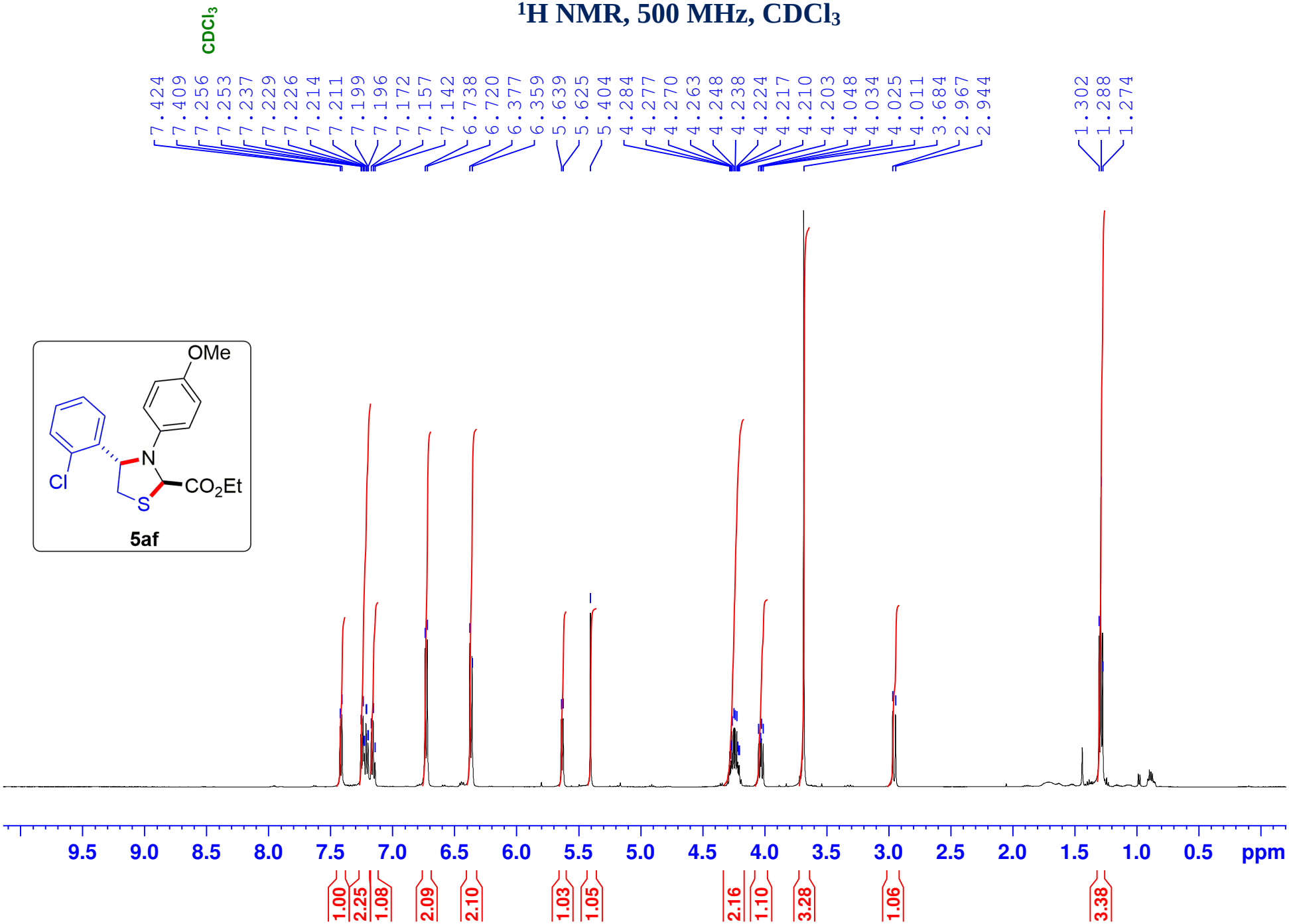
^{1}H NMR, 500 MHz, $CDCl_3$



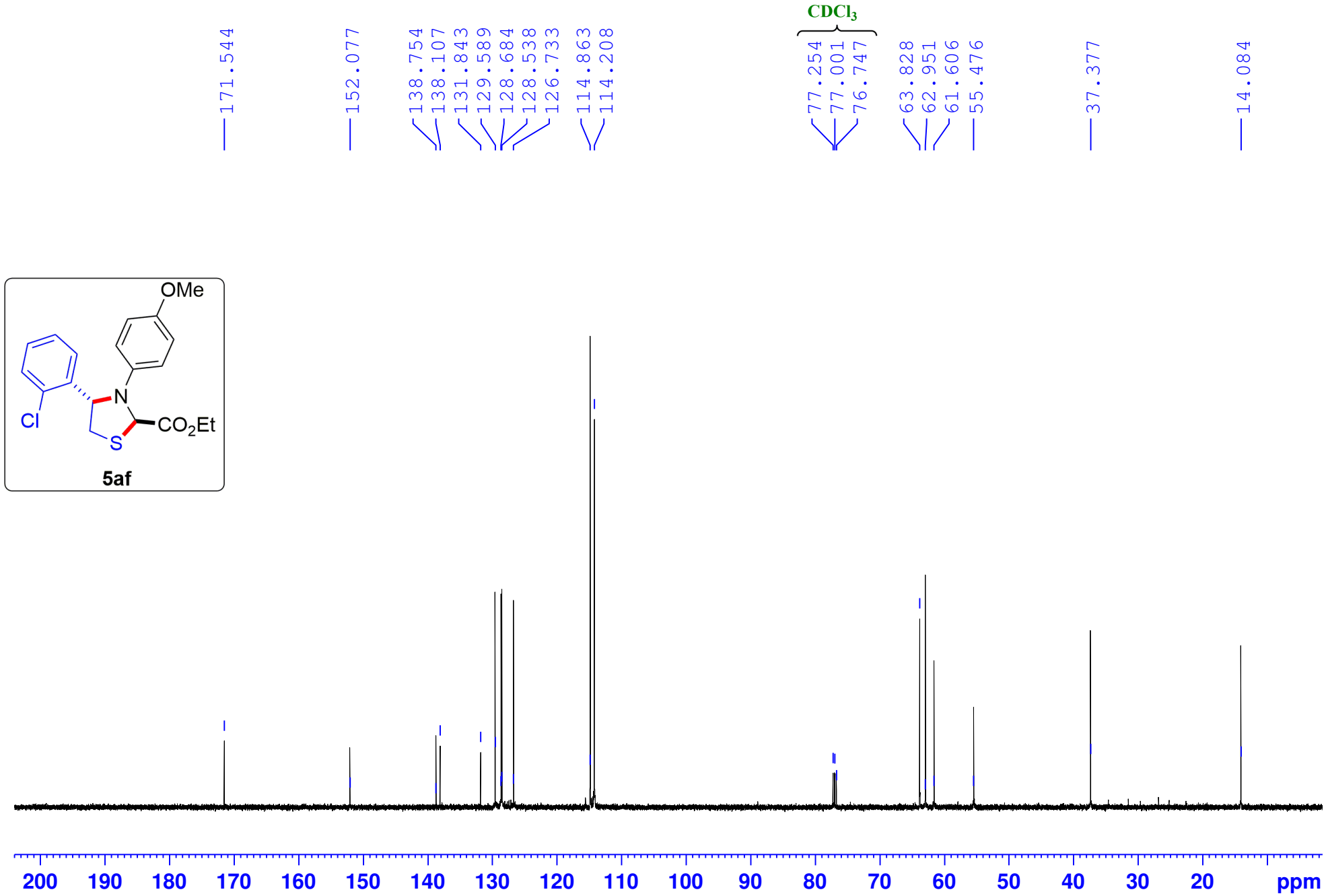
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



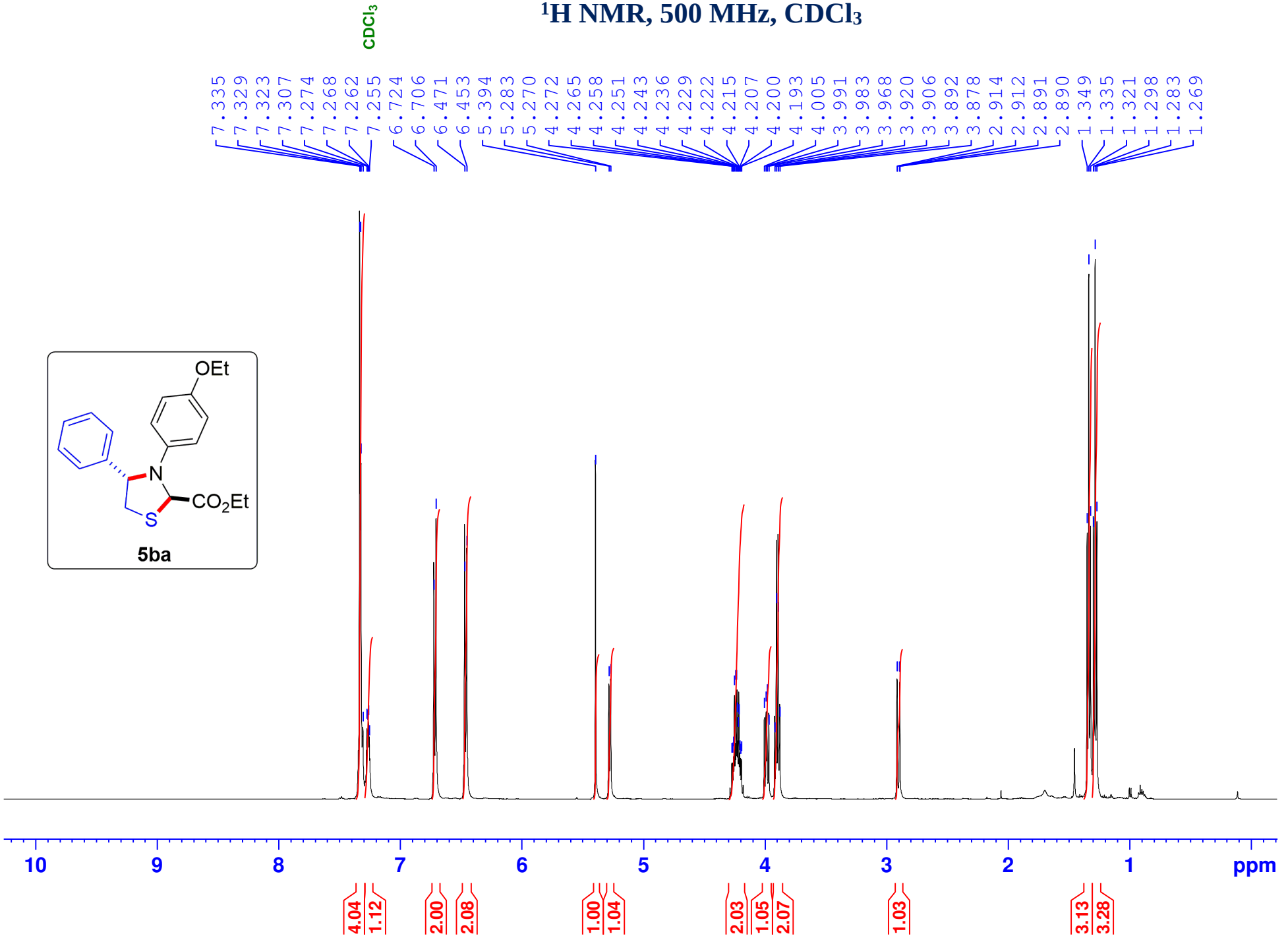
^{1}H NMR, 500 MHz, $CDCl_3$



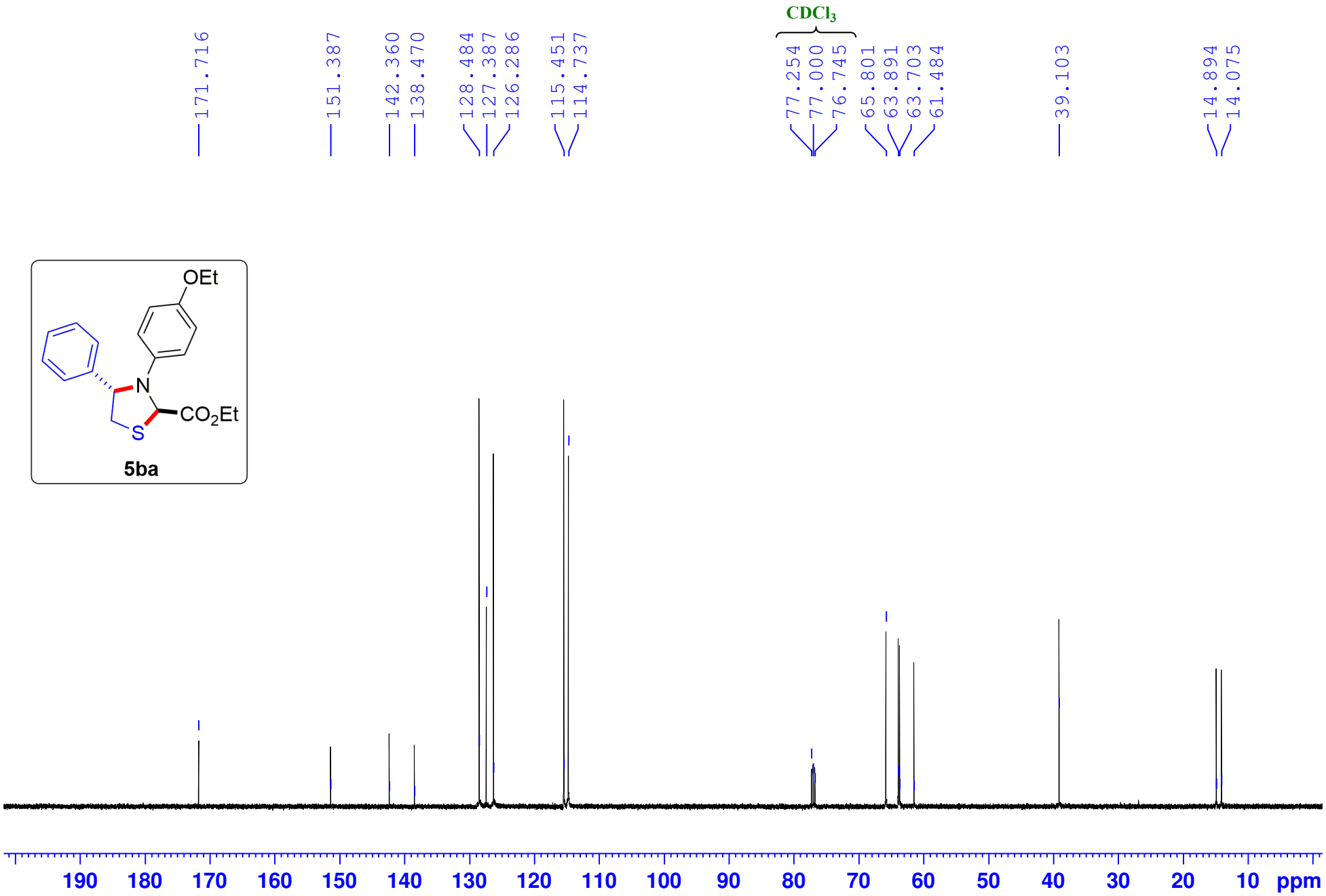
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



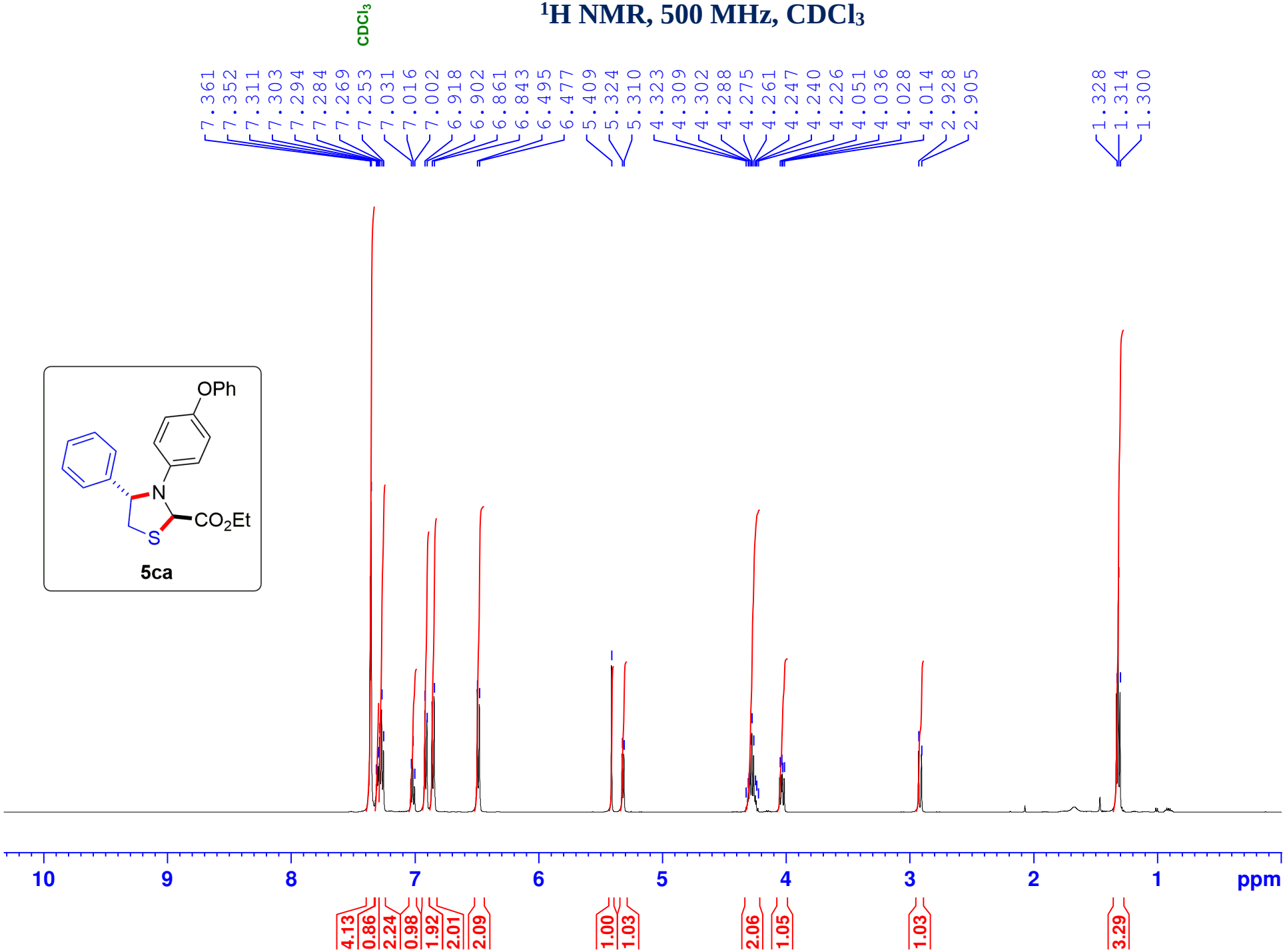
^{1}H NMR, 500 MHz, $CDCl_3$



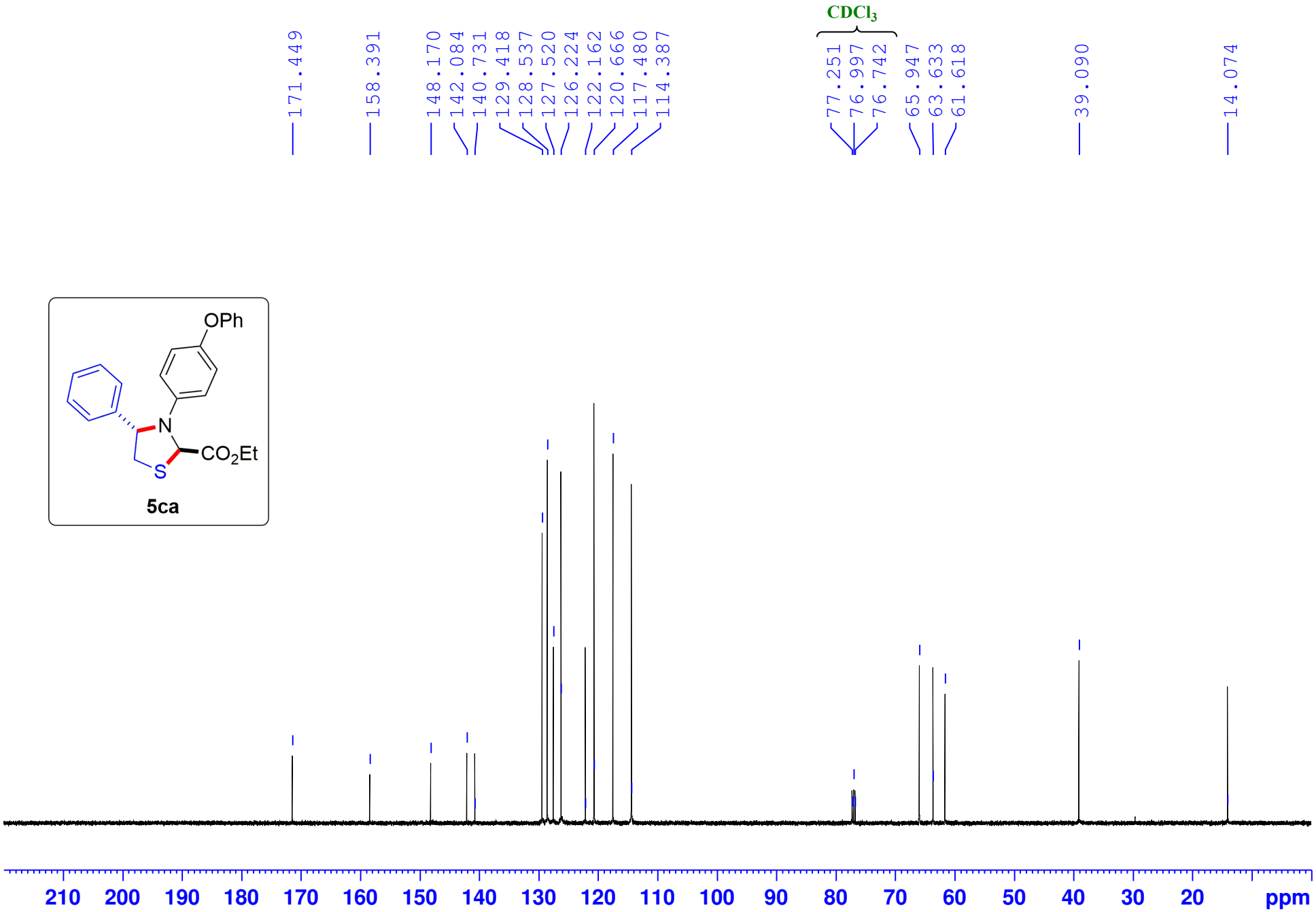
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



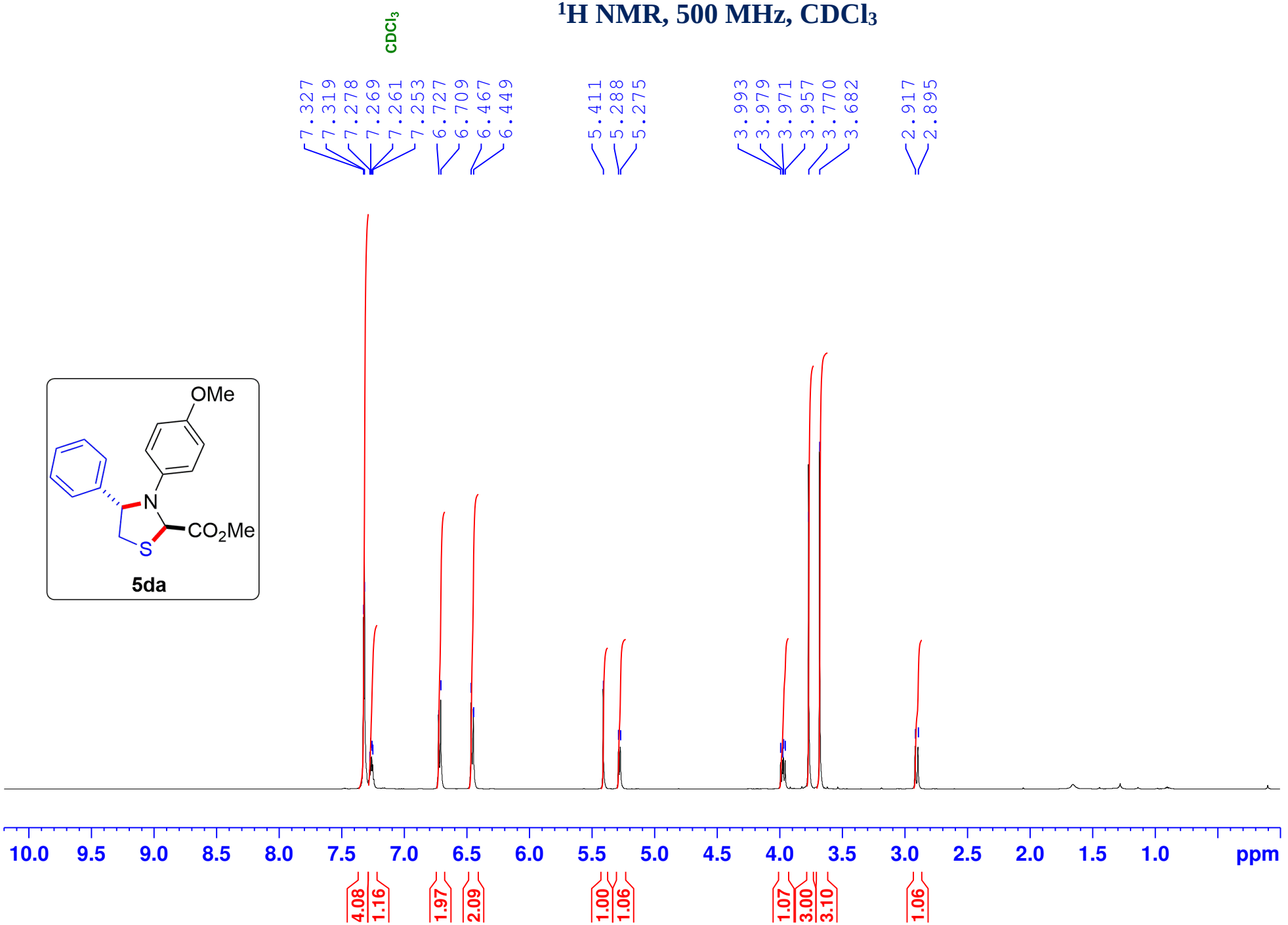
^{1}H NMR, 500 MHz, $CDCl_3$



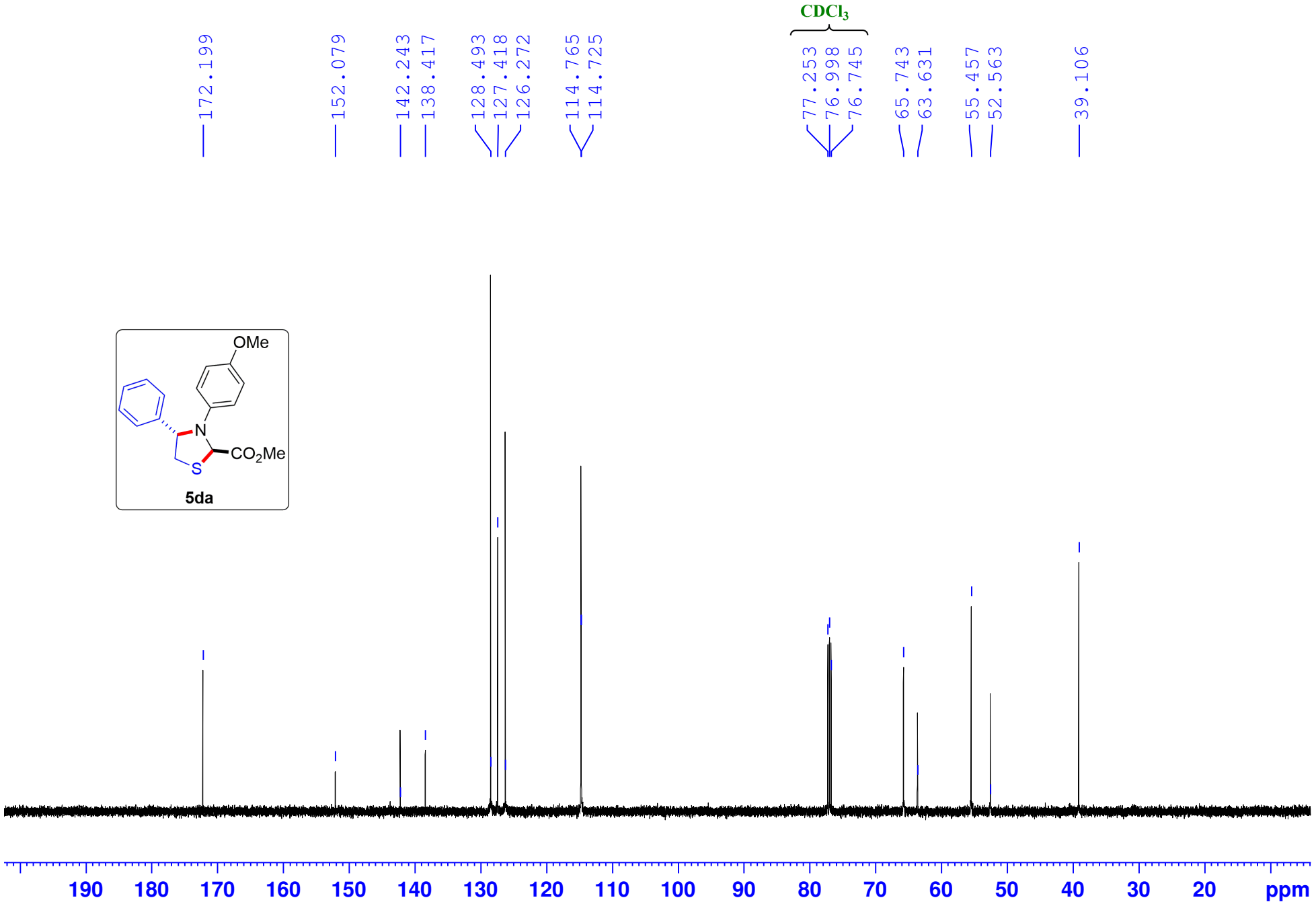
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



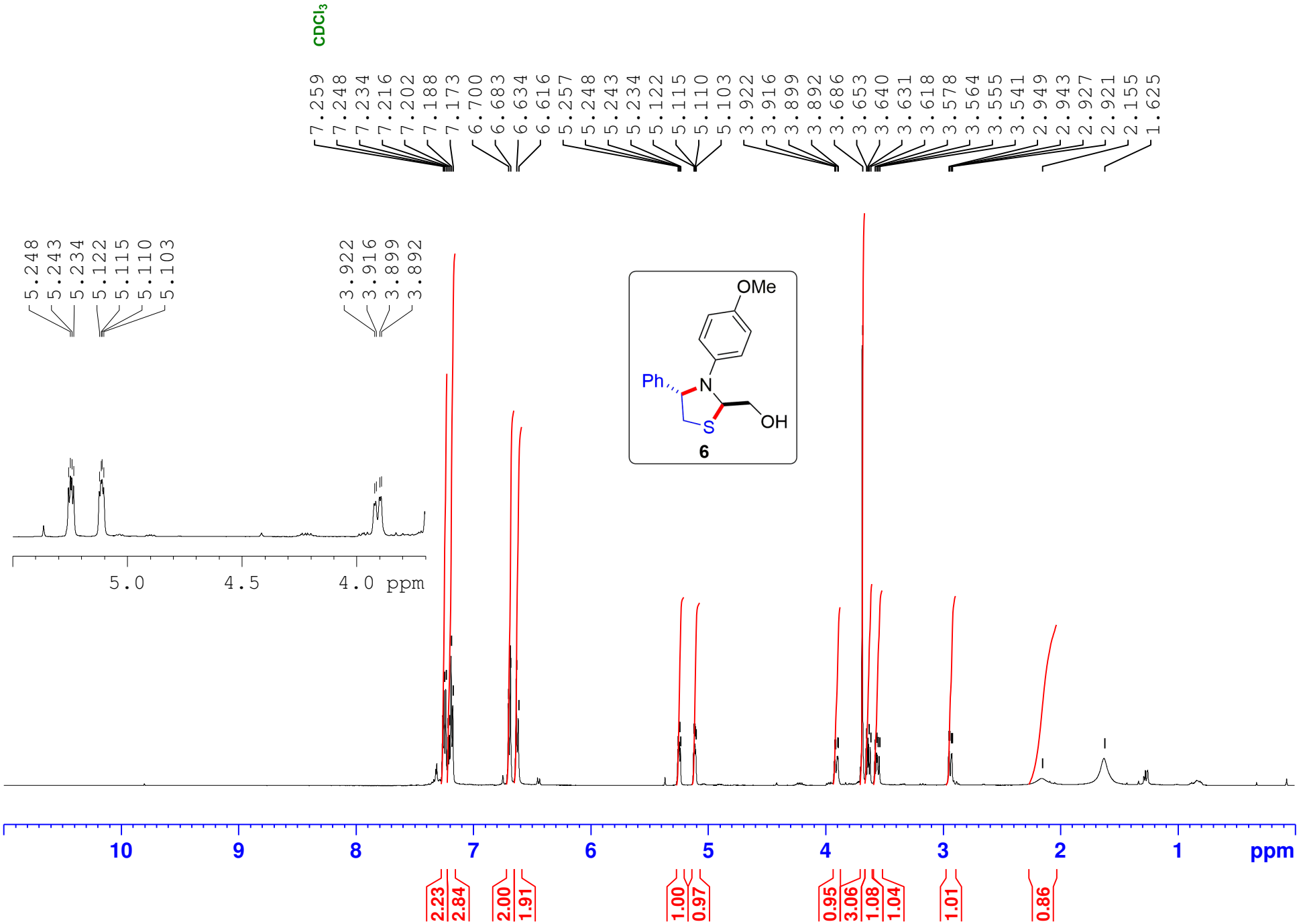
^{1}H NMR, 500 MHz, $CDCl_3$



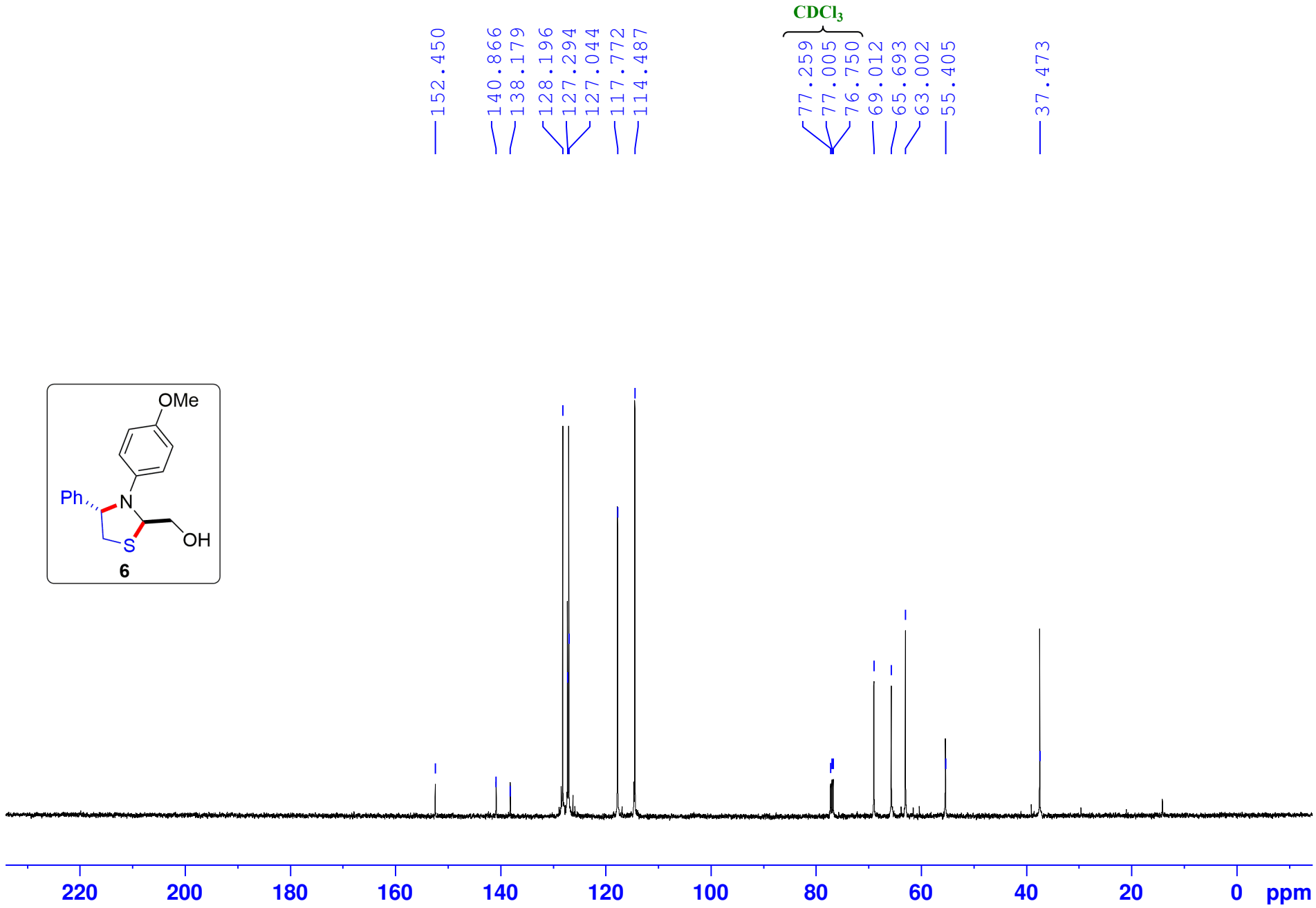
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



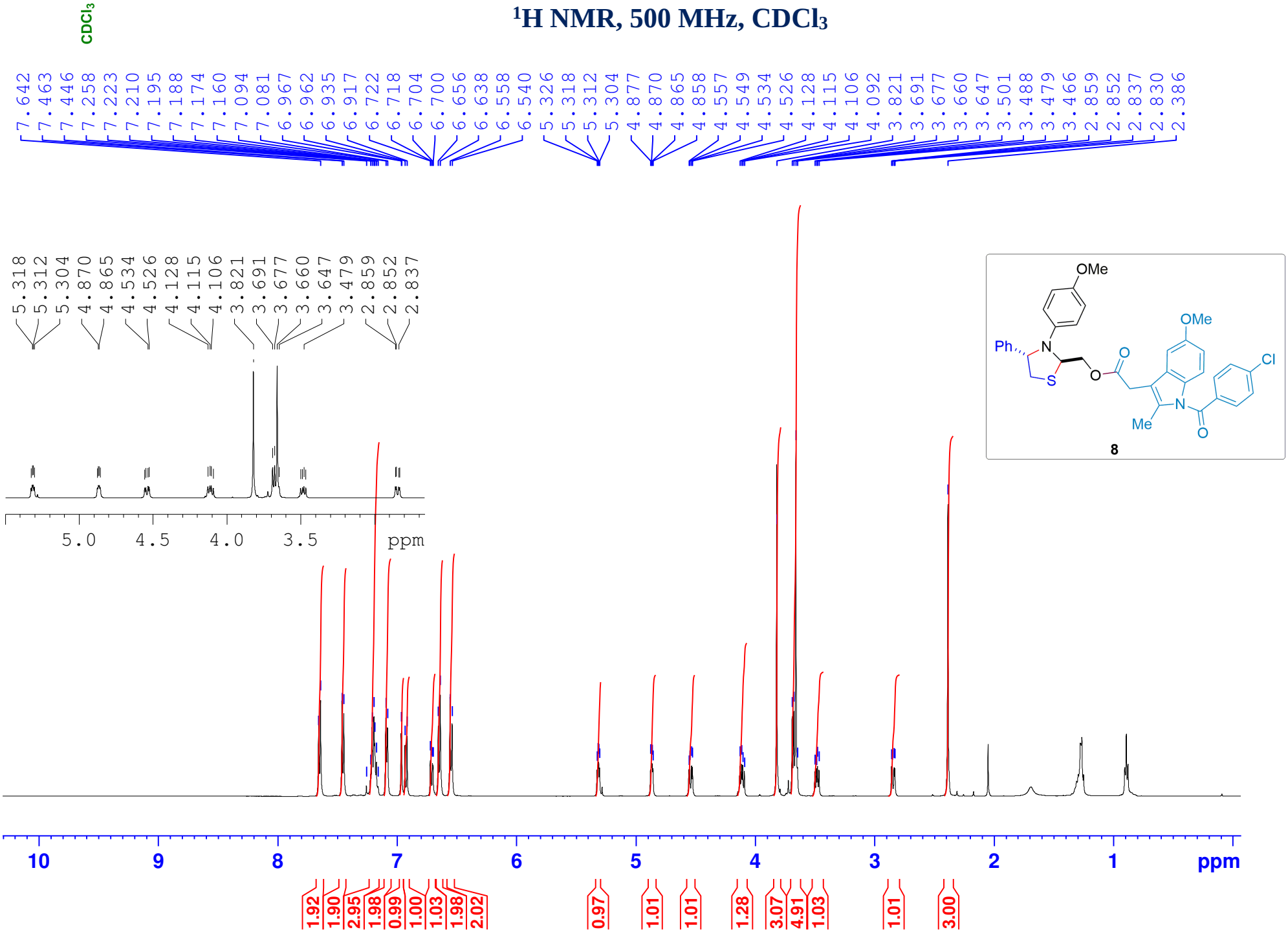
^{1}H NMR, 500 MHz, $CDCl_3$



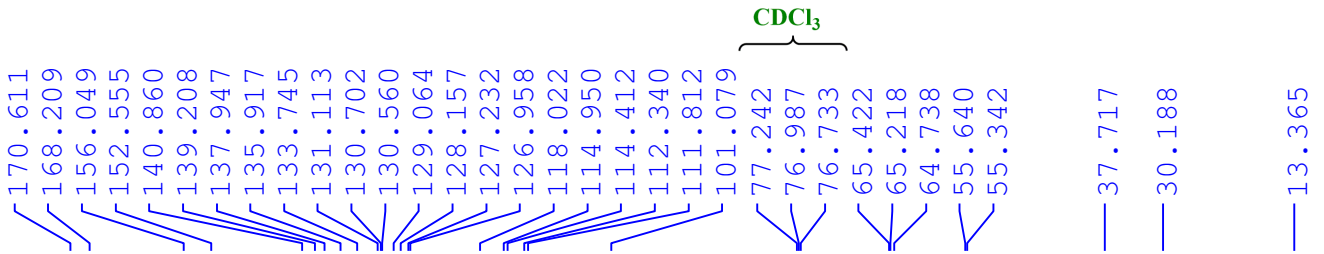
^{13}C {1H} NMR, 125 MHz, $CDCl_3$

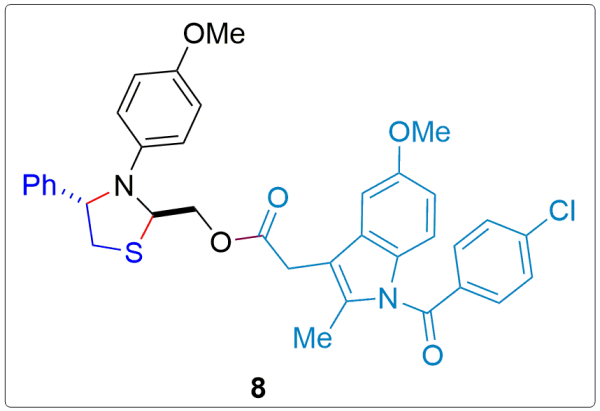


^{1}H NMR, 500 MHz, $CDCl_3$

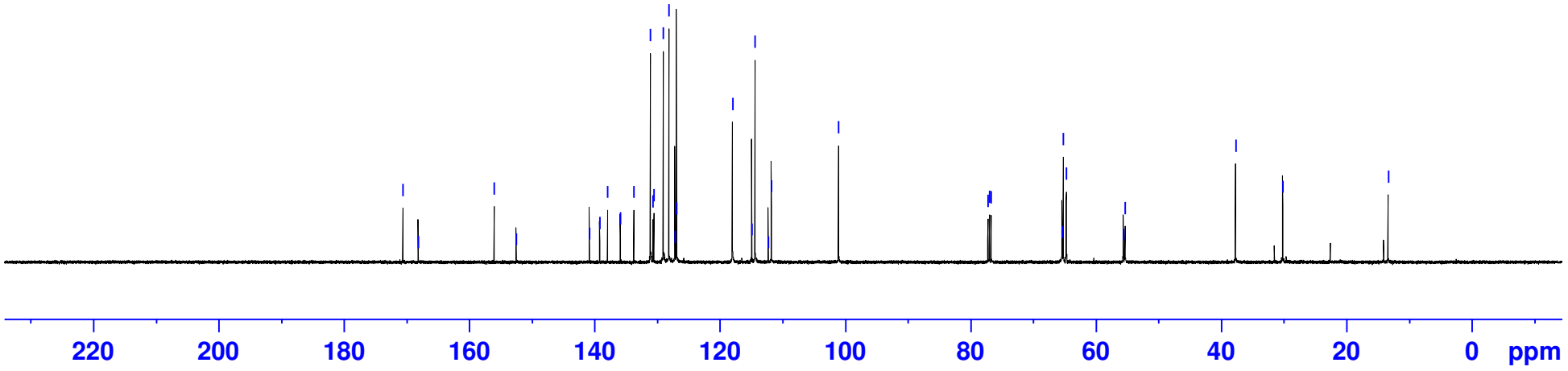


^{13}C {1H} NMR, 125 MHz, $CDCl_3$

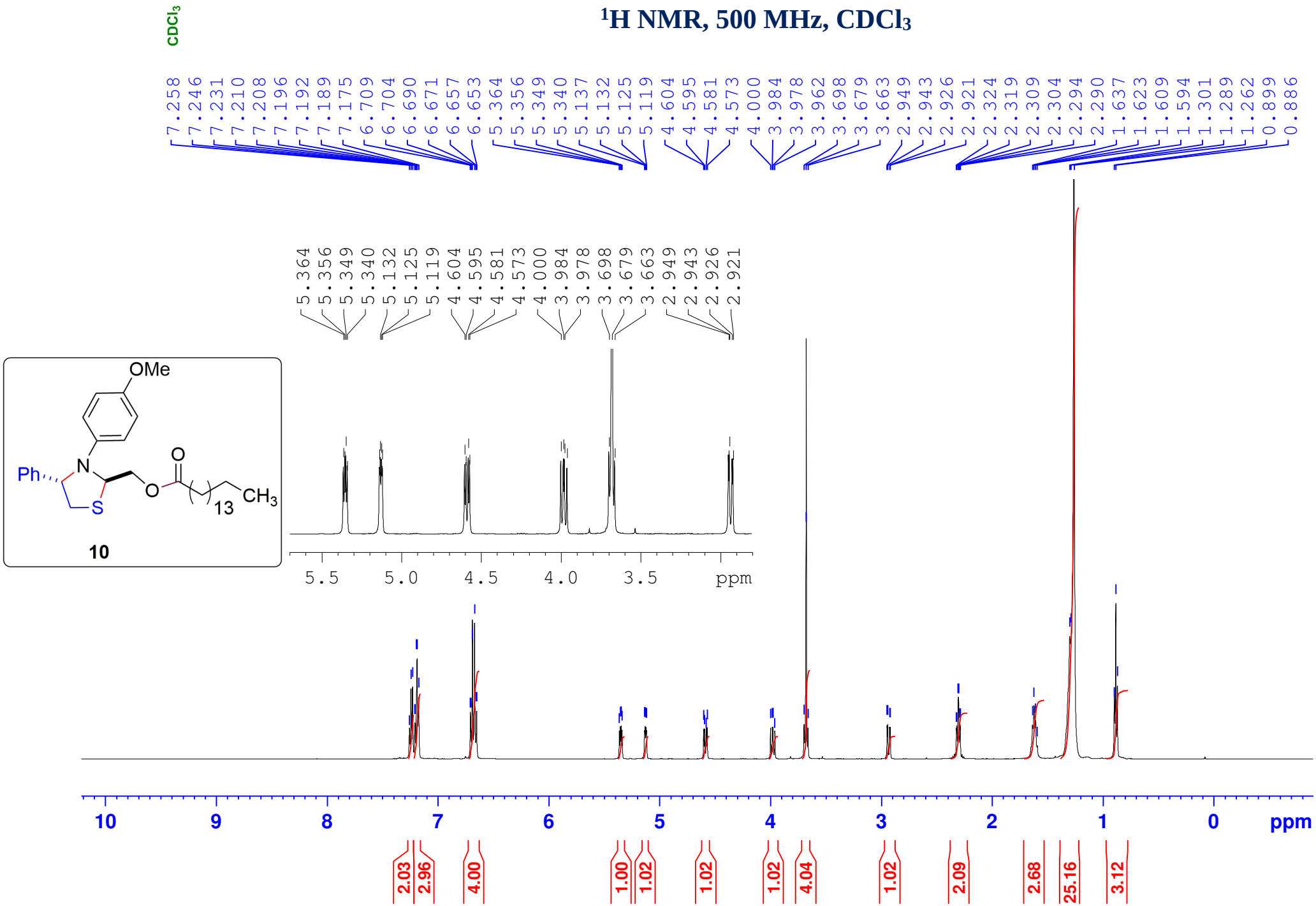




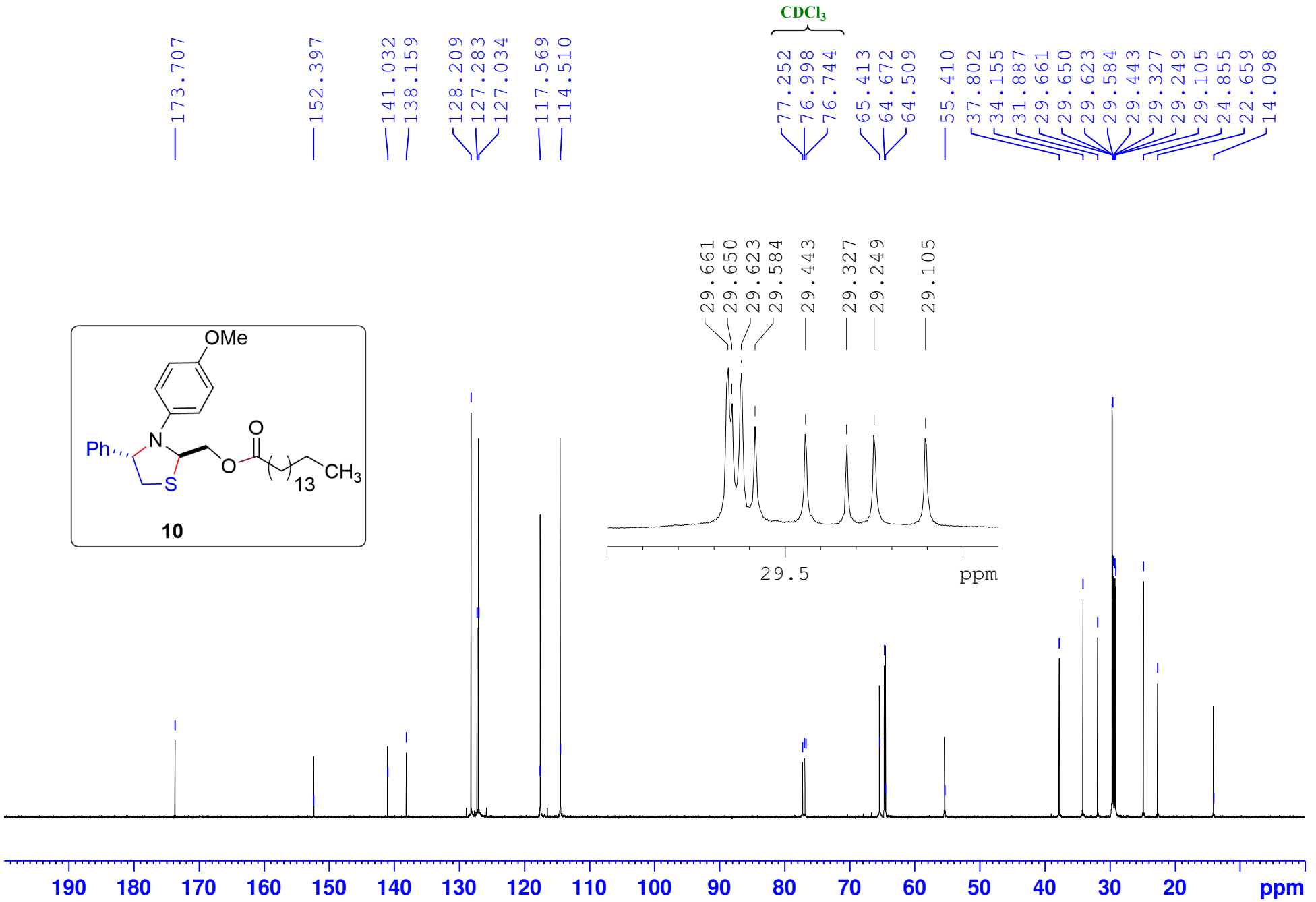
8



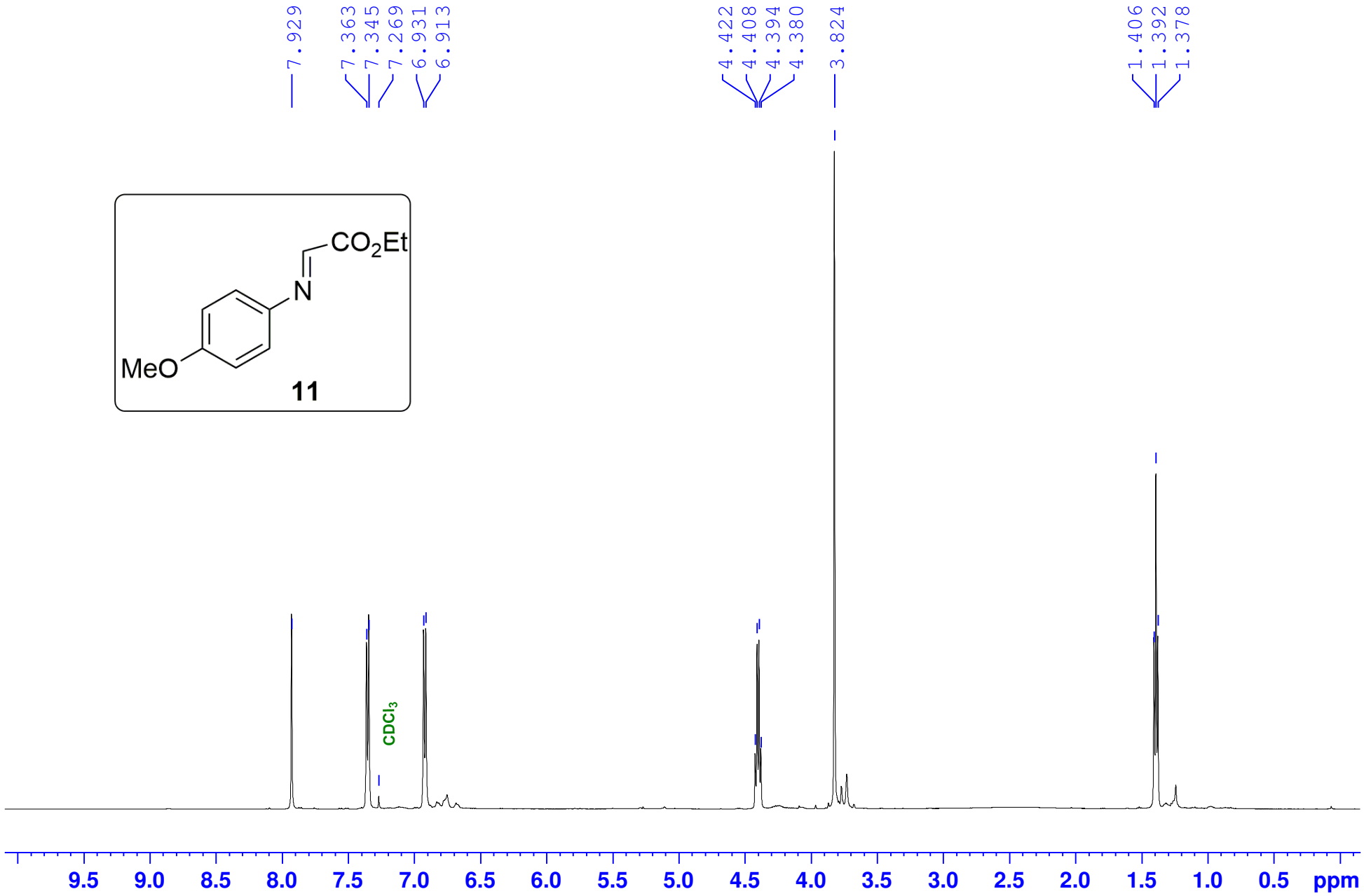
^{1}H NMR, 500 MHz, $CDCl_3$



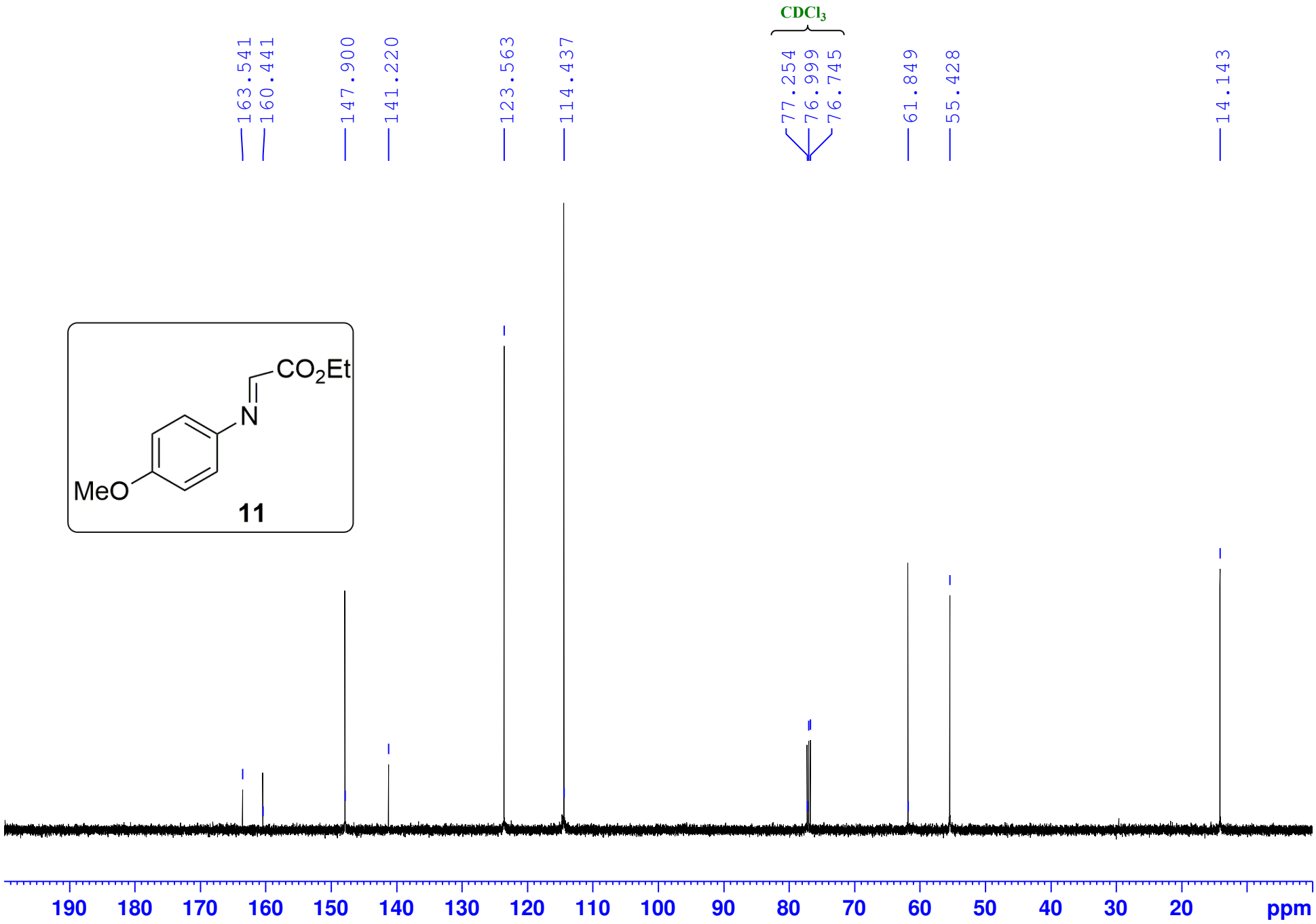
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



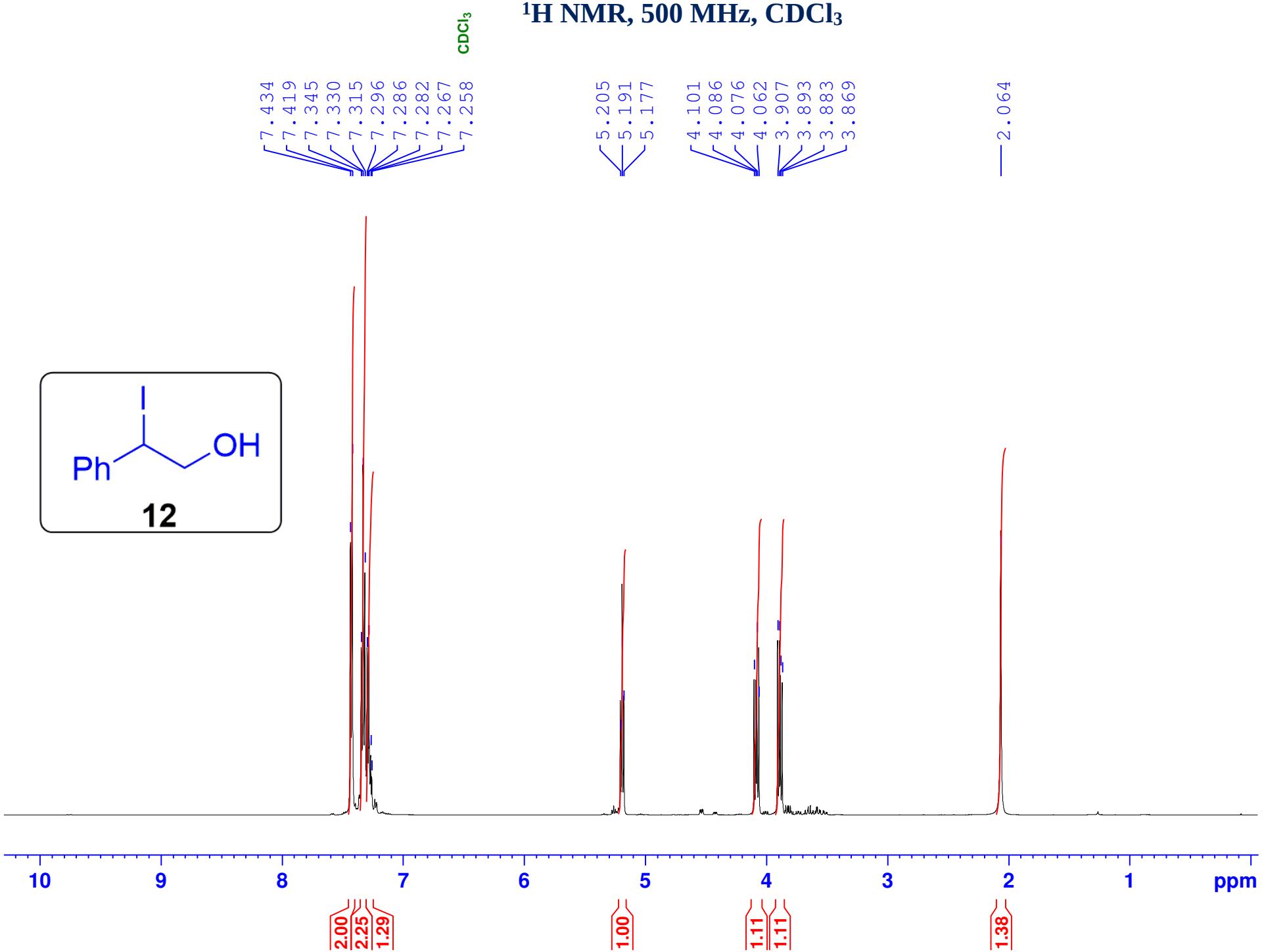
^{1}H NMR, 500 MHz, $CDCl_3$



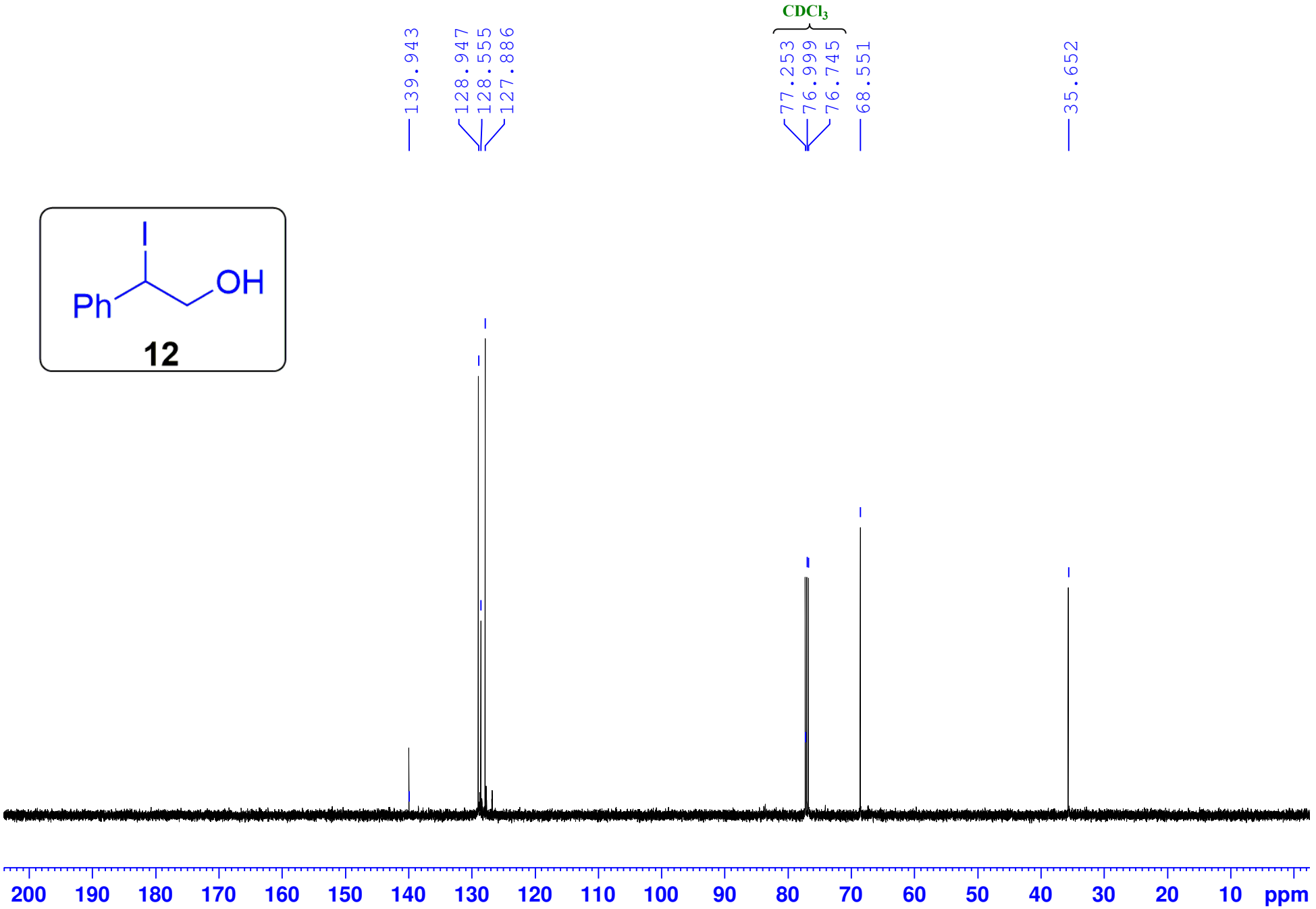
^{13}C {1H} NMR, 125 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C {1H} NMR, 125 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$