Supporting Information for

Fe-Catalyzed Fukuyama-type Indole Synthesis Triggered by Hydrogen Atom Transfer

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CONTENTS

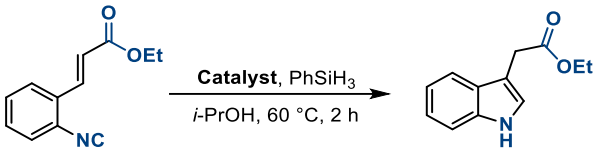
1. General experiment details and materials

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI). All commercially available compounds were purchased from Adamas or Energy Chemical. Flash column chromatography was performed using 200-300 mesh silica gels. Methyl (Me), ethyl (Et), iso-propyl (*i*-Pr), tert-butyl (*t*-Bu), acetylacetone (acac), diisobutyrylmethane (dibm), dipivaloylmethane (dpm), $(EtO)_2MeSiH$ (DEMS), $(MeO)_2MeSiH$ (DMMS), oxalate (ox).

2. Optimization of the reaction conditions

Ethyl (*E*)-3-(2-isocyanophenyl)acrylate **1aa** (40 mg, 0.20 mmol), catalyst (0.01 mmol, 5 mol%), solvent (1.2 mL) and hydrosilane (0.40 mmol, 2.0 equiv.) were added to a 25 mL flame-dried Young-type tube. The reaction mixture was stirred at 35 ℃ for 2 hours, then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 5/1) to give the desired product **2aa**.

Table S1. Screening of catalysts[a]

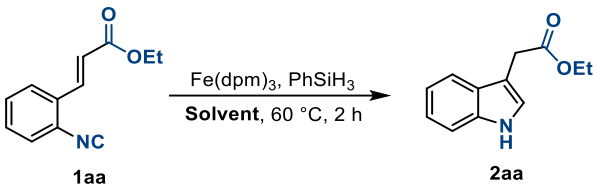


1aa 2aa

Entry	Catalyst	yield
1	$Fe(acac)_3$	25%
2	$Fe(acac)_2$	ND
3	$Fe(dibm)_3$	59%
4	$Fe(dpm)_3$	75%
5	$Fe(tfac)_3$	trace
6	$Fe(hfac)_3$	trace
7	$Co(acac)_2$	21%
8	$Co(acac)_3$	21%
9	$Co(dpm)_2$	21%
10	$Mn(dpm)_3$	46%
11	$Fe_2(ox)_3$	NR
12[b]	$Fe(dpm)_3$	82%
13[c]	$Fe(dpm)_3$	81%
12[b, d]	$Fe(dpm)_3$	82%

[a] Reaction conditions: **1** (40 mg, 0.20 mmol), **catalyst** (0.060 mmol, 30 mol%), $PhSiH_3$ (44 mg, 0.40 mmol), *i*-PrOH (1.2 mL). 60 °C, 2h. Yield determined by GC using *n*-hexadecane as internal standard. [b] Used 5 mol% $Fe(dpm)_3$. [c] Used 2 mol% $Fe(dpm)_3$. [d] Reaction performed under N_2 atmosphere.

Table S2. Screening of solvents[a]

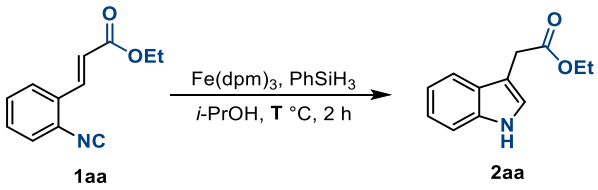


1aa 2aa

Entry	Solvent	yield
1	MeOH	trace
2	EtOH	56%
3	*i*-PrOH	82%
4	*n*-BuOH	38%
5	*t*-BuOH	77%
6	THF	NR
7	DCE	NR
8	THF/*i*-PrOH (1:1)	57%
9	DCE/*i*-PrOH (1:1)	82%

[a] Reaction conditions: **1** (40 mg, 0.20 mmol), $Fe(dpm)_3$ (6 mg, 0.02 mmol, 5 mol%), $PhSiH_3$ (44 mg, 0.40 mmol), **solvent** (1.2 mL). 60 ℃, 2h. Yield determined by GC using *n*-hexadecane as internal standard.

Table S3. Screening of temperature[a]

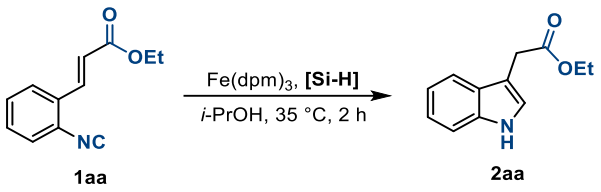


1aa 2aa

Entry	T	yield[a]
1	rt (23 °C)	51%
2	35 °C	82%
3	50 °C	77%
4	60 °C	82%
5	70 °C	80%

[a] Reaction conditions: **1** (40 mg, 0.20 mmol), $Fe(dpm)_3$ (6 mg, 0.02 mmol, 5 mol%), $PhSiH_3$ (44 mg, 0.40 mmol), *i*-PrOH (1.2 mL). **T** °C, 2h. Yield determined by GC using *n*-hexadecane as internal standard.

Table S4. Screening of hydrosilanes[a]



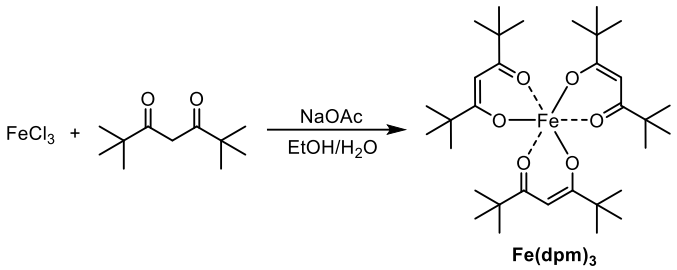
1aa 2aa

Entry	Hydrosilane	yield[a]
1	$PhSiH_3$	82%
2[b]	Ph_2SiH_2	80%
3[b]	Et_3SiH	12%
4	$(EtO)_3SiH$	28%
5[b]	DMMS	79%
6[b]	DEMS	79%
7[c]	$PhSiH_3$	77%

[a] Reaction conditions: **1** (40 mg, 0.20 mmol), $Fe(dpm)_3$ (6 mg, 0.02 mmol, 5 mol%), $PhSiH_3$ (44 mg, 0.40 mmol), *i*-PrOH (1.2 mL). 35 °C, 2h. Yield determined by GC using *n*-hexadecane as internal standard. [b] Reaction at 60 ℃ for 5 h. [c] Used 1.5 equiv. $PhSiH_3$.

3. General procedure for the catalytic reaction

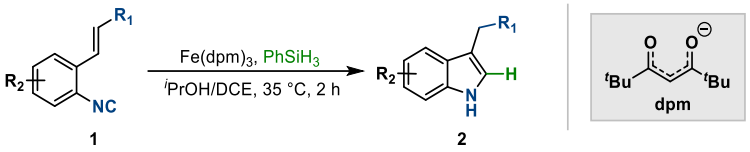
3.1. Synthesis of catalyst $Fe(dpm)_3$:



To a biphasic mixture of 2,2,6,6-tetramethyl-3,5-heptanedionate (3.1 g, 16.6 mmol, 3.0 equiv.) and $NaOAc•3H_2O$ (2.3 g, 16.6 mmol, 3.0 equiv.) in an aqueous solution of EtOH (1:1 EtOH:H_2O, 50 mL) was added anhydrous $FeCl_3$ (0.89 g, 5.6 mmol, 1.0 equiv.). A red slurry formed and the reaction mixture was heated at 60 ℃ with stirring for 2 hours, at this time the orange precipitate was formed. The slurry was cooled to room temperature, then cooled in refrigerator (-18 ℃) for 2 hours, and filtered to give an orange powder. The orange powder was rinsed with EtOH (10 mL) and H_2O (10 mL), collected, and dried under high vacuum.

Recrystallization: The above obtained orange solid was dissolved in 50 mL of hexane to give a red, homogenous solution. Filtered the hexane solution through a filter paper and the resulting filtrate was concentrated under reduced pressure to afford pure $Fe(dpm)_3$ as a red powder (2.8 g) in 83% yield.

3.2. General procedure for the catalytic reaction

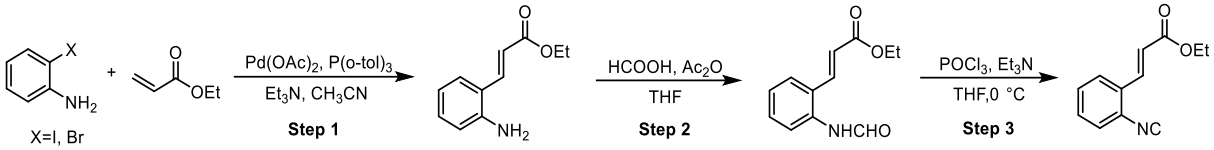


Ethyl (*E*)-3-(2-isocyanophenyl)acrylate **1** (100 mg, 0.50 mmol), $Fe(dpm)_3$ (16.0 mg, 5 mol%), *i*-PrOH (2 mL), DCE (1 mL) and $PhSiH_3$ (108 mg, 1.0 mmol, 2.0 equiv.) were added to a 25 mL flame-dried Young-type tube. The reaction mixture was stirred at 35 ℃ for 2 hours, then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 5/1) to give the desired product **2**.

4. Experimental characterization data

4.1. Preparation and spectral data of isonitrile substrates

Procedure A: Synthesis of substrate **1aa~1ag**, **1aj**, **1ak**, **1ba~1da**, **1fa~1ja**, **1la~1pa**



Step 1.

The starting aniline (15 mmol, 1.0 equiv.), $Pd(OAc)_2$ (35 mg, 1 mol%), P(*o*-Tol)$_3$ (0.40 g, 8 mol%) were added to a 100 mL flame-dried Young-type tube containing a stir bar. The tube was evacuated and back-filled with nitrogen for three times, then olefin (18 mmol, 1.2 equiv.), anhydrous acetonitrile (20 mL) and triethylamine (3 mL) were added. The resulting mixture was stirred at 120 ℃ overnight. After cooling to room temperature, the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylaniline as a bright yellow solid (2.4 g, 84% yield).

1aa~1ag, **1aj**, **1ak**, **1da**, **1ga**, **1ha**, **1ia** and **1na** were obtained from the corresponding 2-iodoaniline and olefin.

1ba, **1ca**, **1fa**, **1ja**, **1la**, **1ma**, **1oa** and **1pa** were obtained from the corresponding 2-bromoaniline and olefin.

Step 2.

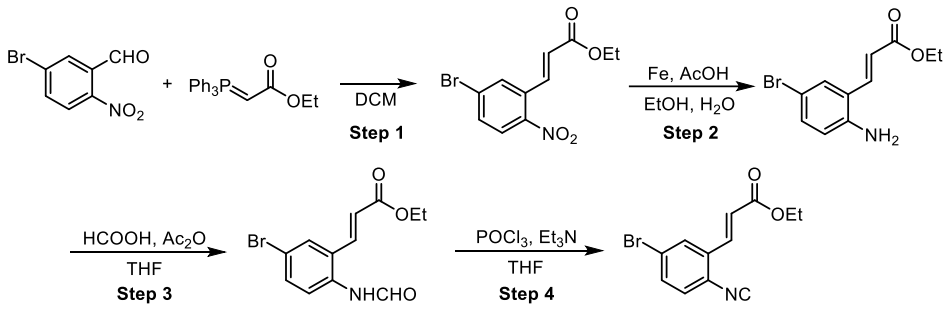
Acetic anhydride (1.5 equiv.) and formic acid (1.6 equiv.) were stirred at 50 ℃ in a sealed tube for 2 hours. The resulting mixed anhydride was cooled to room temperature and was added dropwise to a stirred solution of 2-alkenyl aniline (8 mmol, 1.0 equiv.) in anhydrous THF (16 mL). The solution was stirred at room temperature for 30 min. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) and then the organic layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was utilized in the subsequent step without further purification.

Step 3.

The crude formamide was mixed with anhydrous THF (16 mL) in a dry reaction flask under nitrogen. Anhydrous triethylamine (6.0 equiv.) was added, and the mixture (solution or suspension) was cooled to 0 ℃. Then, neat $POCl_3$ (2.0 equiv.) was added dropwise while

maintaining the reaction temperature at 0 ℃. The mixture was stirred at 0 ℃ for an additional 2 hours, and then quenched with saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) at 0 ℃. After the gas evolution subsided, the mixture was extracted with ethyl acetate (3 × 30 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylisocyanide (1.2 g, 75% yield).

Procedure B: Synthesis of substrate **1ea**, **1ka**



Step 1.

The wittig reagent (18 mmol, 1.2 equiv.) was added to a solution of 2-nitrobenzaldehyde (15 mmol, 1.0 equiv.) in DCM (35 mL). The mixture was stir at room temperature for 1 hour, and then quenched with H_2O. The mixture was extracted with DCM (3 × 20 mL) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding 2-nitrocinnamate as a white solid (4.0 g, 89% yield).

Step 2.

Iron powder (60 mmol, 6.0 equiv.) and AcOH (10 mL) were added to a solution of nitroaromatic substrate (10 mmol, 1.0 equiv.) in EtOH (10 mL) and water (5 mL). The mixture was heated to 60 ℃ with vigorous stirring for 1 hour. The reaction mixture was cooled to room temperature and filtered through a Celite pad, and the filtrate was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylaniline as a bright yellow solid (2.3 g, 78% yield).

Step 3.

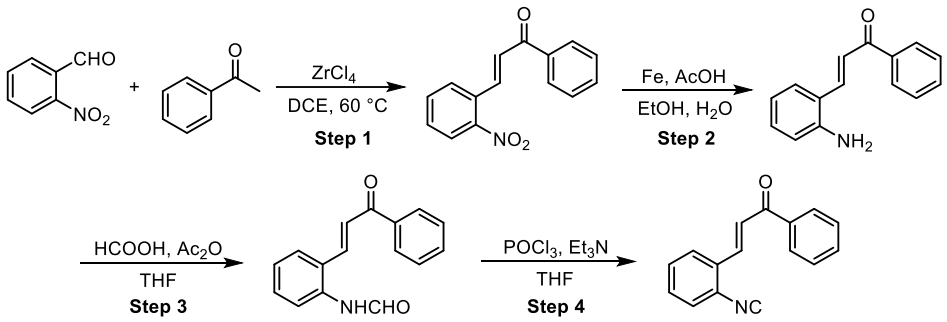
Acetic anhydride (1.5 equiv.) and formic acid (1.6 equiv.) were stirred at 50 ℃ in a sealed tube for 2 hours. The resulting mixed anhydride was cooled to room temperature and was added dropwise to a stirred solution of 2-alkenyl aniline (8 mmol, 1.0 equiv.) in anhydrous THF (16 mL). The solution was stirred at room temperature for 30 min. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) and then

the organic layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was utilized in the subsequent step without further purification.

Step 4.

The crude formamide was mixed with anhydrous THF (16 mL) in a dry reaction flask under nitrogen. Anhydrous triethylamine (6.0 equiv.) was added, and the mixture (solution or suspension) was cooled to 0 ℃. Then, neat $POCl_3$ (2.0 equiv.) was added dropwise while maintaining the reaction temperature at 0 ℃. The mixture was stirred at 0 ℃ for an additional 2 hours, and then quenched with saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) at 0 ℃. After the gas evolution subsided, the mixture was extracted with ethyl acetate (3 × 30 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylisocyanide (1.9 g, 80% yield in two steps).

Procedure C: Synthesis of substrate **1ah, 1ai**



Step 1.

Following a modification of the method of Patti[1], to a dry flask was added 2-nitrobenzaldehyde (16 mmol, 1.0 equiv.) under N_2 atmosphere. Then ketone (9.6 mmol, 1.2 equiv.), $ZrCl_4$ (1.5 g, 40 mol%) and anyhydrous DCE (80 mL) were added. The mixture was maintained at 60 ℃ for 20 h. The reaction mixture was quenched with H_2O and then extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the corresponding 2-nitrochalcone.

Step 2.

Iron powder (60 mmol, 6.0 equiv.) and AcOH (10 mL) were added to a solution of nitroaromatic substrate (10 mmol, 1.0 equiv.) in EtOH (10 mL) and water (5 mL). The mixture was heated to 60 ℃ with vigorous stirring for 1 hour. The reaction mixture was cooled to room temperature and filtered through a Celite pad, and the filtrate was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and

brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylaniline (1.7 g, 56% yield in two steps).

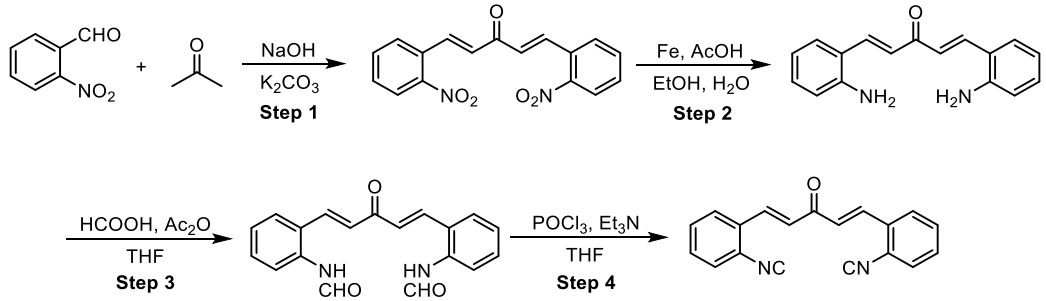
Step 3.

Acetic anhydride (1.5 equiv.) and formic acid (1.6 equiv.) were stirred at 50 ℃ in a sealed tube for 2 hours. The resulting mixed anhydride was cooled to room temperature and was added dropwise to a stirred solution of 2-alkenyl aniline (8 mmol, 1.0 equiv.) in anhydrous THF (16 mL). The solution was stirred at room temperature for 30 min. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) and then extracted with ethyl acetate (3 ×20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was utilized in the subsequent step without further purification.

Step 4.

The crude formamide was mixed with anhydrous THF (16 mL) in a dry reaction flask under nitrogen. Anhydrous triethylamine (6.0 equiv.) was added, and the mixture (solution or suspension) was cooled to 0 ℃. Then, neat $POCl_3$ (2.0 equiv.) was added dropwise while maintaining the reaction temperature at 0 ℃. The mixture was stirred at 0 ℃ for an additional 2 hours, and then quenched with saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) at 0 ℃. After the gas evolution subsided, the mixture was extracted with ethyl acetate (3 × 30 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding 2-alkenylarylisocyanide (1.2 g, 76% yield in two steps).

Procedure D: Synthesis of substrate **1al**



Step 1.

To a dry flask was added 2-nitrobenzaldehyde (20 mmol, 2.0 equiv.), NaOH (80 mg, 10 mol%) and K_2CO_3 (0.28 g, 10 mol%). Then acetone (0.70 g, 1.2 equiv.) was added dropwise while maintaining the reaction temperature at 0 ℃, and the mixture was stirred at room temperature for additional 30 minutes to give a suspension. The precipitate was filtered, washed

with a cold mixture of EtOH/H_2O to afford the dibenzalacetone derivative as a green yellow solid (1.3 g, 40% yield).

Step 2.

Iron powder (50 mmol, 12.0 equiv.) and AcOH (10 mL) were added to a solution of nitroaromatic substrate (4 mmol, 1.0 equiv.) in EtOH (10 mL) and water (5 mL). The mixture was heated to 60 ℃ with vigorous stirring for 1 hour. The reaction mixture was cooled to room temperature and filtered through a Celite pad, and the filtrate was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding product (0.5 g, 47% yield).

Step 3.

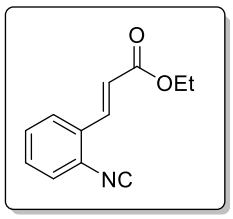
Acetic anhydride (3.0 equiv.) and formic acid (3.2 equiv.) were stirred at 50 ℃ in a sealed tube for 2 hours. The resulting mixed anhydride was cooled to room temperature and was added dropwise to a stirred solution of 2-alkenyl aniline (2 mmol, 1.0 equiv.) in anhydrous THF (16 mL). The solution was stirred at room temperature for 30 min. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) and then the organic layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with aqueous solution of $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was utilized in the subsequent step without further purification.

Step 4.

The crude formamide was mixed with anhydrous THF (16 mL) in a dry reaction flask under nitrogen. Anhydrous triethylamine (12.0 equiv.) was added, and the mixture (solution or suspension) was cooled to 0 ℃. Then, neat $POCl_3$ (4.0 equiv.) was added dropwise while maintaining the reaction temperature at 0 ℃. The mixture was stirred at 0 ℃ for an additional 2 hours, and then quenched with saturated aqueous solution of $NaHCO_3$ (50 mL, Caution! Gas evolution) at 0 ℃. After the gas evolution subsided, the mixture was extracted with ethyl acetate (3 × 30 mL), washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding product (0.4 g, 74% yield in two steps).

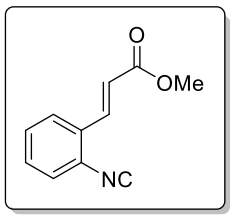
4.2. Substrates characterization

Ethyl (*E*)-3-(2-isocyanophenyl)acrylate (1aa)



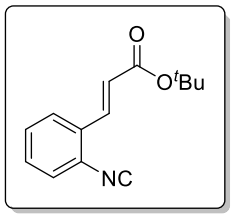
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.0 Hz, 1H), 7.70-7.64 (m, 1H), 7.47-7.39 (m, 3H), 6.54 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 166.1, 137.7, 130.9, 130.8, 129.7, 127.8, 127.0, 126.1, 122.5, 61.0, 14.4; **HRMS** (ESI) calcd for $C_{12}H_{12}NO_2$ $[M+H]^+$: 202.0863, found: 202.0852.

Methyl (*E*)-3-(2-isocyanophenyl)acrylate (1ab)



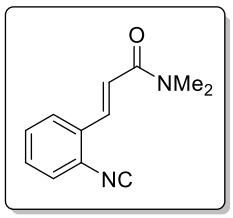
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.0 Hz, 1H), 7.70-7.65 (m, 1H), 7.48-7.39 (m, 3H), 6.55 (d, *J* = 16.1 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 166.5, 138.0, 130.9, 129.8, 127.9, 127.0, 126.1, 122.1, 52.2; **HRMS** (ESI) calcd for $C_{11}H_{10}NO_2$ $[M+H]^+$: 188.0706, found: 188.0701.

Tert-butyl (*E*)-3-(2-isocyanophenyl)acrylate (1ac)



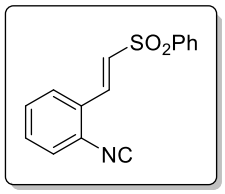
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.69-7.63 (m, 1H), 7.46-7.36 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 1.55 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 165.4, 136.8, 131.1, 130.5, 129.7, 127.8, 126.9, 126.0, 124.4, 81.3, 28.2; **HRMS** (ESI) calcd for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1176, found: 230.1170.

(*E*)-3-(2-isocyanophenyl)-*N*,*N*-dimethylacrylamide (1ad)



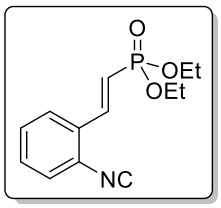
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 15.6 Hz, 1H), 7.65-7.59 (m, 1H), 7.46-7.34 (m, 3H), 7.06 (d, *J* = 15.6 Hz, 1H), 3.19 (s, 3H), 3.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 166.1, 135.8, 131.9, 129.9, 129.6, 128.0, 127.9, 125.5, 122.6, 37.7, 36.0; **HRMS** (ESI) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$: 201.1022, found: 201.1016.

(*E*)-1-isocyano-2-(2-(phenylsulfonyl)vinyl)benzene (1ae)



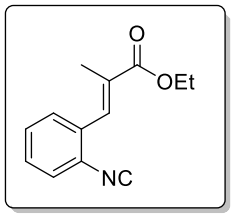
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.90 (m, 3H), 7.70-7.64 (m, 1H), 7.62-7.56 (m, 3H), 7.50-7.41 (m, 3H), 7.05 (d, *J* = 15.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 139.9, 135.8, 133.9, 131.8, 129.9, 129.6, 128.7, 128.08, 128.06, 127.8, 126.3; **HRMS** (ESI) calcd for $C_{15}H_{11}NO_2SNa$ $[M+Na]^+$: 292.0403, found: 292.0397.

(*E*)-1-isocyano-2-(2-(phenylsulfonyl)vinyl)benzene (1af)



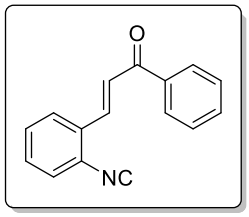
The title compound was prepared according to procedure **A** and purified by column chromatography to give a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.62 (m, 2H), 7.49-7.38 (m, 3H), 6.45 (t, *J* = 17.3 Hz, 1H), 4.25-4.14 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 141.2 (d, $J_{C\text{-}P}$ = 7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 24 Hz), 130.8, 129.8, 127.8 (d, $J_{C\text{-}P}$ = 1 Hz), 126.9 (d, $J_{C\text{-}P}$ = 1 Hz), 125.8, 119.5 (d, $J_{C\text{-}P}$ = 191 Hz), 62.4 (d, $J_{C\text{-}P}$ = 6 Hz), 16.5 (d, $J_{C\text{-}P}$ = 6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.1; **HRMS** (ESI) calcd for $C_{13}H_{16}NO_3PNa$ $[M+Na]^+$: 288.0760, found: 288.0758.

Ethyl (*E*)-3-(2-isocyanophenyl)-2-methylacrylate (1ag)



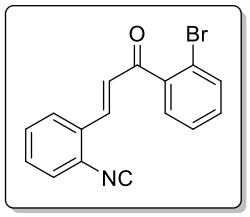
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.7 Hz, 1H), 7.48-7.34 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.03 (d, *J* = 1.6 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 167.5, 133.1, 133.0, 132.8, 130.0, 129.2, 129.1, 127.3, 126.0, 61.3, 14.5, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{14}NO_2$ $[M+H]^+$: 216.1019, found: 216.1013.

(*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one (1ah)



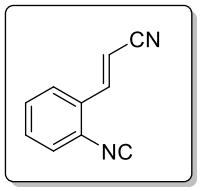
The title compound was prepared according to procedure **C** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.01 (m, 3H), 7.82-7.76 (m, 1H), 7.67-7.59 (m, 2H), 7.56 -7.42 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 169.1, 138.1, 137.7, 133.3, 131.4, 130.9, 129.8, 128.9, 128.8, 128.1, 127.7, 126.2; **HRMS** (ESI) calcd for $C_{16}H_{11}NONa$ $[M+Na]^+$: 256.0733, found: 256.0725.

(*E*)-1-(2-bromophenyl)-3-(2-isocyanophenyl)prop-2-en-1-one (1ai)



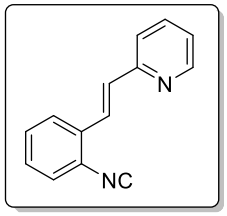
The title compound was prepared according to procedure **C** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.70 (m, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51-7.40 (m, 5H), 7.36 (td, *J* = 7.6, 2.1 Hz, 1H), 7.18 (d, *J* = 16.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 169.2, 140.5, 139.3, 133.6, 132.0, 131.3, 130.9, 129.8, 129.5, 127.8, 127.6, 127.2, 126.5, 119.6; **HRMS** (ESI) calcd for $C_{16}H_{10}BrNONa$ $[M+Na]^+$: 333.9838, found: 333.9830.

(*E*)-3-(2-isocyanophenyl)acrylonitrile (1aj)



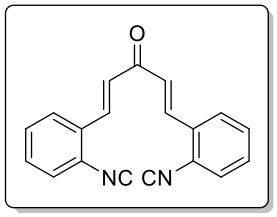
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.6 Hz, 1H), 7.65-7.59 (m, 1H), 7.54-7.45 (m, 3H), 6.05 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 144.1, 131.9, 130.0, 129.7, 128.0, 126.2, 125.7, 117.3, 100.7; **HRMS** (ESI) calcd for $C_{10}H_7N_2$ $[M+H]^+$: 155.0609, found: 155.0592.

(*E*)-2-(2-isocyanostyryl)pyridine (1ak)



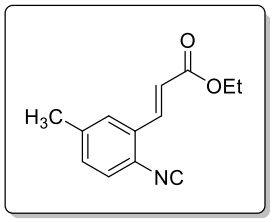
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.87 (d, *J* = 16.1 Hz, 1H), 7.79-7.74 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44-7.37 (m, 2H), 7.33-7.25 (m, 2H), 7.19 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) 167.5, 154.8, 149.8, 136.6, 133.0, 132.3, 129.5, 128.7, 127.5, 126.2, 126.1, 125.2, 122.8, 122.1; **HRMS** (ESI) calcd for $C_{14}H_{10}N_2Na$ $[M+Na]^+$: 229.0736, found: 229.0732.

(1*E*,4*E*)-1,5-bis(2-isocyanophenyl)penta-1,4-dien-3-one (1al)



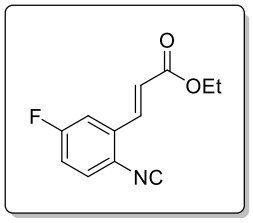
The title compound was prepared according to procedure **D** and purified by column chromatography to give a green solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 16.1 Hz, 2H), 7.82-7.75 (m, 2H), 7.53-7.45 (m, 6H), 7.21 (d, *J* = 16.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.1, 169.1, 137.1, 131.2, 131.0, 129.9, 128.5, 128.0, 127.3, 126.5; **HRMS** (ESI) calcd for $C_{19}H_{12}N_2ONa$ $[M+Na]^+$: 307.0842, found: 307.0840.

Ethyl (*E*)-3-(2-isocyano-5-methylphenyl)acrylate (1ba)



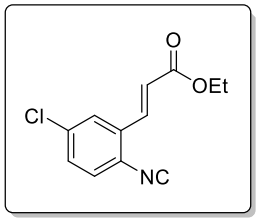
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.1 Hz, 1H), 7.46 (s, 1H), 7.34-7.29 (m, 1H), 7.24-7.17 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 166.2, 140.1, 137.9, 131.6, 130.6, 127.6, 127.4, 123.7, 122.2, 61.0, 21.5, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{14}NO_2$ $[M+H]^+$: 216.1019, found: 216.1013.

Ethyl (*E*)-3-(5-fluoro-2-isocyanophenyl)acrylate (1ca)



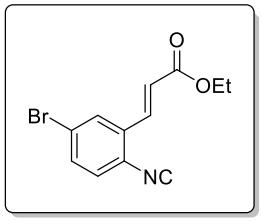
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 16.0, 1.4 Hz, 1H), 7.45 (dd, *J* = 8.8, 5.0 Hz, 1H), 7.35 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.13 (ddd, *J* = 8.8, 7.4, 2.8 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 165.7, 162.3 (d, $J_{C\text{-}F}$ = 252 Hz), 136.7 (d, $J_{C\text{-}F}$ = 2 Hz), 133.4 (d, $J_{C\text{-}F}$ = 9 Hz), 129.8 (d, $J_{C\text{-}F}$ = 9 Hz), 123.8, 122.4, 118.1 (d, $J_{C\text{-}F}$ = 24 Hz), 113.7 (d, $J_{C\text{-}F}$ = 24 Hz), 61.2, 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.8; **HRMS** (ESI) calcd for $C_{12}H_{10}FNO_2Na$ $[M+Na]^+$: 242.0588, found: 242.0579.

Ethyl (*E*)-3-(5-chloro-2-isocyanophenyl)acrylate (1da)



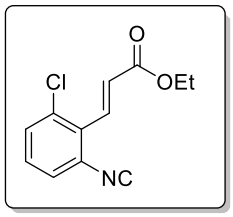
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.64 (s, 1H), 7.39 (s, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 165.7, 136.5, 135.9, 132.6, 130.8, 129.0, 127.1, 124.4, 123.9, 61.2, 14.4; **HRMS** (ESI) calcd for $C_{12}H_{10}ClNO_2Na$ $[M+Na]^+$: 258.0292, found: 258.0281.

Ethyl (*E*)-3-(5-bromo-2-isocyanophenyl)acrylate (1ea)



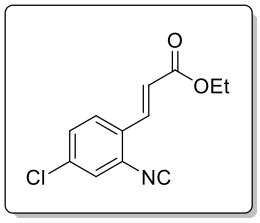
The title compound was prepared according to procedure **B** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.80 (d, *J* = 2.1 Hz, 1H), 7.54 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 165.7, 136.4, 133.7, 132.8, 130.0, 129.1, 124.9, 123.9, 123.8, 61.2, 14.4; **HRMS** (ESI) calcd for $C_{12}H_{11}BrNO_2$ $[M+H]^+$: 279.9968, found: 279.9953.

Ethyl (*E*)-3-(2-chloro-6-isocyanophenyl)acrylate (1fa)



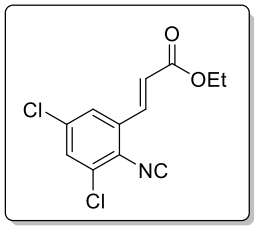
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.4 Hz, 1H), 7.50 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 16.4 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 166.0, 135.8, 135.4, 131.3, 130.1, 130.1, 127.7, 126.9, 126.1, 61.2, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{11}ClNO_2$ $[M+H]^+$: 236.0473, found: 236.0460.

Ethyl (*E*)-3-(4-chloro-2-isocyanophenyl)acrylate (1ga)



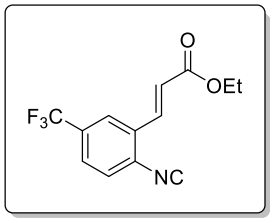
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.48-7.39 (m, 2H), 6.52 (d, *J* = 16.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 165.9, 136.6, 136.4, 130.3, 129.6, 128.1, 127.8, 126.7, 123.0, 61.2, 14.4; **HRMS** (ESI) calcd for $C_{12}H_{11}ClNO_2$ $[M+H]^+$: 236.0473, found: 236.0461.

Ethyl (*E*)-3-(3,5-dichloro-2-isocyanophenyl)acrylate (1ha)



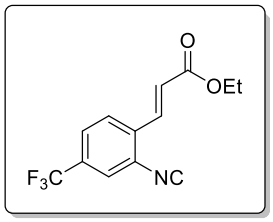
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.63-7.48 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 165.4, 136.2, 135.8, 134.1, 133.1, 130.8, 125.4, 125.0, 123.5, 61.4, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{10}Cl_2NO_2$ $[M+H]^+$: 270.0083, found: 270.0073.

Ethyl (*E*)-3-(2-isocyano-5-(trifluoromethyl)phenyl)acrylate (1ia)



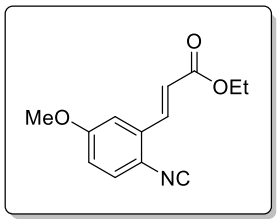
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.90 (m, 2H), 7.68 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 165.6, 136.3, 131.98 (q, J_{C-F} = 34 Hz), 131.96, 128.5, 127.4 (q, J_{C-F} = 3 Hz), 124.5, 124.3 (q, J_{C-F} = 4 Hz), 123.0 (q, J_{C-F} = 273 Hz), 61.3, 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.1; **HRMS** (ESI) calcd for $C_{13}H_{11}F_3NO_2$ $[M+H]^+$: 270.0736, found: 270.0725.

Ethyl (*E*)-3-(2-isocyano-4-(trifluoromethyl)phenyl)acrylate (1ja)



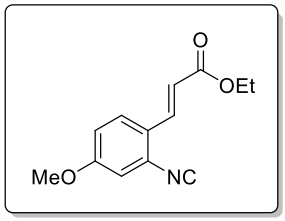
The title compound was prepared according to procedure **A** and purified by column chromatography to give a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.0 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.73-7.66 (m, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 165.5, 136.3, 134.4, 132.8 (q, $J_{C\text{-}F}$ = 34 Hz), 127.9, 126.4 (q, $J_{C\text{-}F}$ = 4 Hz), 126.3, 125.05, 125.01 (q, $J_{C\text{-}F}$ = 4 Hz), 122.8 (d, $J_{C\text{-}F}$ = 273 Hz), 61.4, 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.2; **HRMS** (ESI) calcd for $C_{13}H_{11}F_3NO_2$ $[M+H]^+$: 270.0736, found: 270.0728.

Ethyl (*E*)-3-(2-isocyano-5-methoxyphenyl)acrylate (1ka)



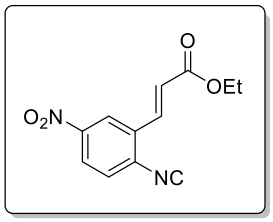
The title compound was prepared according to procedure **B** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.0 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 166.1, 160.0, 137.9, 132.2, 129.1, 122.6, 119.3, 116.7, 111.4, 61.0, 55.8, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{14}NO_3$ $[M+H]^+$: 232.0968, found: 232.0960.

Ethyl (*E*)-3-(2-isocyano-4-methoxyphenyl)acrylate (1la)



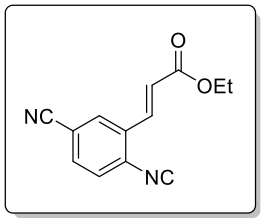
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 15.9 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 6.97 (ddd, *J* = 8.9, 2.6, 0.6 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 166.5, 161.3, 137.5, 128.2, 127.2, 123.4, 120.0, 116.7, 112.4, 60.8, 55.9, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{14}NO_3$ $[M+H]^+$: 232.0968, found: 232.0957.

Ethyl (*E*)-3-(2-isocyano-5-nitrophenyl)acrylate (1ma)



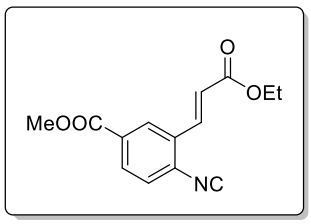
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.5 Hz, 1H), 8.29 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.96 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 165.3, 147.8, 135.5, 132.8, 130.1, 129.1, 125.5, 125.2, 122.3, 61.5, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{10}N_2O_4Na$ $[M+Na]^+$: 269.0533, found: 269.0525.

Ethyl (*E*)-3-(5-cyano-2-isocyanophenyl)acrylate (1na)



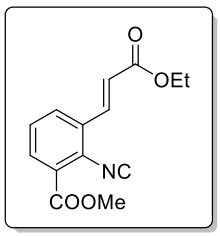
The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.71 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 165.3, 135.5, 133.6, 132.5, 131.1, 128.8, 125.1, 116.9, 114.1, 61.4, 14.3; **HRMS** (ESI) calcd for $C_{13}H_{10}N_2O_2Na$ $[M+Na]^+$: 249.0634, found: 249.0626.

Methyl (*E*)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-isocyanobenzoate (1oa)



The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.8 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.97 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 165.8, 165.2, 136.8, 131.5, 131.4, 131.3, 129.1, 128.4, 128.0, 123.8, 61.2, 52.9, 14.4; **HRMS** (ESI) calcd for $C_{14}H_{14}NO_4$ $[M+H]^+$: 260.0917, found: 260.0905.

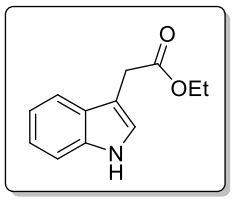
Methyl (*E*)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-isocyanobenzoate (1pa)



The title compound was prepared according to procedure **A** and purified by column chromatography to give a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 16.0 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 165.8, 164.5, 137.4, 132.9, 132.4, 130.4, 129.2, 128.6, 124.6, 123.8, 61.2, 53.0, 14.4; **HRMS** (ESI) calcd for $C_{14}H_{13}NO_4Na$ $[M+Na]^+$: 282.0737, found: 282.0729.

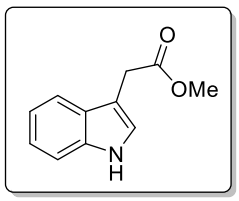
4.3 Products Characterization

Ethyl 2-(1*H*-indol-3-yl)acetate (2aa)



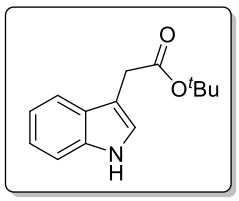
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 80 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.61 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.28 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.21-7.09 (m, 2H), 7.05 (d, *J* = 2.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 1.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 136.2, 127.3, 123.3, 122.2, 119.7, 118.9, 111.3, 108.4, 60.9, 31.5, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{13}NO_2Na$ $[M+Na]^+$: 226.0838, found: 226.0833.

Methyl 2-(1*H*-indol-3-yl)acetate (2ab)



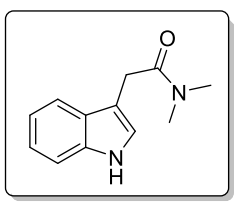
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 67 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.61 (dd, *J* = 7.8 Hz, 0.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.22-7.11 (m, 2H), 7.09 (d, *J* = 2.3 Hz, 1H), 3.78 (d, *J* = 0.9 Hz, 2H), 3.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 136.2, 127.3, 123.2, 122.3, 119.8, 118.9, 111.3, 108.4, 52.1, 31.3; **HRMS** (ESI) calcd for $C_{11}H_{11}NO_2Na$ $[M+Na]^+$: 212.0682, found: 212.0680.

Tert-butyl 2-(1*H*-indol-3-yl)acetate (2ac)



The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 84 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.31 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.21-7.06 (m, 3H), 3.68 (d, *J* = 0.8 Hz, 2H), 1.46 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 136.2, 127.4, 123.1, 122.1, 119.6, 119.1, 111.3, 109.1, 80.8, 32.8, 28.2; **HRMS** (ESI) calcd for $C_{14}H_{17}NO_2Na$ $[M+Na]^+$: 254.1151, found: 254.1149.

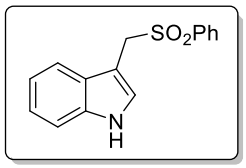
2-(1*H*-indol-3-yl)-*N*,*N*-dimethylacetamide (2ad)



The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 70 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.29 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.18-7.06 (m, 2H), 6.97-6.91 (m, 1H), 3.81 (d, *J* = 1.0 Hz, 2H), 2.99 (s, 3H), 2.97 (s, 3H); **^{13}C NMR** (100

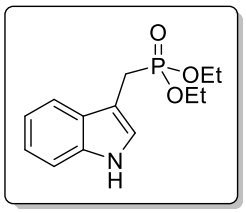
MHz, $CDCl_3$) δ 171.9, 136.3, 127.2, 122.9, 122.0, 119.4, 118.7, 111.4, 108.8, 37.9, 35.8, 31.4; **HRMS** (ESI) calcd for $C_{12}H_{14}N_2ONa$ $[M+Na]^+$:225.0998, found: 225.0992.

3-((phenylsulfonyl)methyl)-1*H*-indole (2ae)



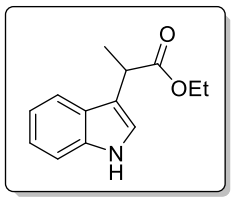
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 65 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.70-7.66 (m, 2H), 7.53 (ddt, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.42-7.30 (m, 3H), 7.27-7.23 (m, 1H), 7.15 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 7.01 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 4.54 (d, *J* = 0.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.4, 135.9, 133.6, 129.0, 128.7, 127.1, 126.0, 122.6, 120.5, 118.6, 111.4, 103.0, 54.6; **HRMS** (ESI) calcd for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$: 294.0559, found: 294.0560.

3-((phenylsulfonyl)methyl)-1*H*-indole (2af)



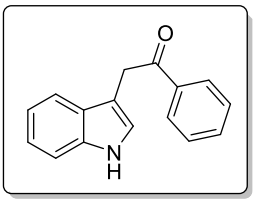
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 85 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19-7.06 (m, 3H), 4.10-3.90 (m, 4H), 3.30 (d, *J* = 20.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.2, 127.5 (d, $J_{C\text{-}P}$ = 6 Hz), 124.0 (d, $J_{C\text{-}P}$ = 8 Hz), 122.0, 119.4, 118.8, 111.5, 104.5 (d, $J_{C\text{-}P}$ = 9 Hz), 62.2 (d, $J_{C\text{-}P}$ = 7 Hz), 23.1 (d, $J_{C\text{-}P}$ = 144 Hz), 16.5 (d, $J_{C\text{-}P}$ = 6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.9; **HRMS** (ESI) calcd for $C_{13}H_{18}NO_3PNa$ $[M+Na]^+$: 290.0917, found: 290.0912.

Ethyl 2-(1*H*-indol-3-yl)propanoate (2ag)



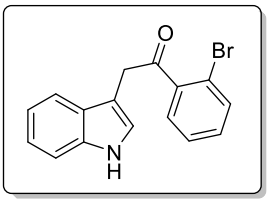
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown oil, 62 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.72-7.67 (m, 1H), 7.33 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.15-7.08 (m, 2H), 4.21-4.06 (m, 2H), 4.02 (qd, *J* = 7.2, 0.8 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 136.4, 126.6, 122.3, 121.7, 119.6, 119.4, 115.7, 111.3, 60.8, 37.2, 18.0, 14.3; **HRMS** (ESI) calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.0995, found: 240.0990.

2-(1*H*-indol-3-yl)-1-phenylethan-1-one (2ah)



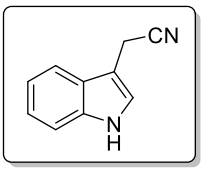
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 88 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.09-8.03 (m, 2H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.57-7.51 (m, 1H), 7.48-7.40 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22-7.10 (m, 2H), 7.07 (s, 1H), 4.41 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.1, 136.7, 136.2, 133.2, 128.7, 127.4, 123.3, 122.3, 119.8, 118.9, 111.4, 109.0, 35.7; **HRMS** (ESI) calcd for $C_{16}H_{13}NONa$ $[M+Na]^+$: 258.0889, found: 258.0888.

1-(2-bromophenyl)-2-(1*H*-indol-3-yl)ethan-1-one (2ai)



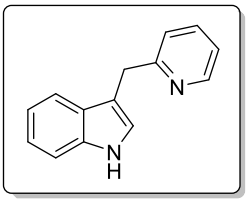
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 123 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.60-7.52 (m, 2H), 7.32-7.24 (m, 3H), 7.24-7.20 (m, 1H), 7.17 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13-7.07 (m, 2H), 4.36 (d, *J* = 0.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 141.7, 136.2, 133.6, 131.5, 128.8, 127.4, 123.7, 122.3, 119.8, 118.9, 118.7, 111.4, 107.8, 39.6; **HRMS** (ESI) calcd for $C_{16}H_{12}BrNONa$ $[M+Na]^+$: 335.9995, found: 335.9988.

2-(1*H*-indol-3-yl)acetonitrile (2aj)



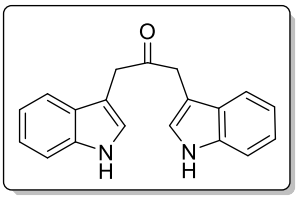
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown oil, 56 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.28-7.21 (m, 1H), 7.21-7.14 (m, 2H), 3.82 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.3, 126.1, 123.0, 122.9, 120.3, 118.4, 118.2, 111.7, 104.7, 14.5; **HRMS** (ESI) calcd for $C_{10}H_9N_2$ $[M+H]^+$: 157.0760, found: 157.0758.

3-(pyridin-2-ylmethyl)-1*H*-indole (2ak)



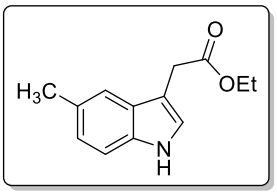
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 60 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 5.1, 1.8 Hz, 1H), 8.31 (s, 1H), 7.57-7.48 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.12-7.03 (m, 3H), 4.31 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 149.2, 136.7, 136.6, 127.5, 122.93, 122.86, 122.1, 121.2, 119.5, 119.3, 113.9, 111.3, 34.6; **HRMS** (ESI) calcd for $C_{14}H_{12}N_2Na$ $[M+Na]^+$: 231.0893, found: 231.0890.

1,3-di(1*H*-indol-3-yl)propan-2-one (2al)



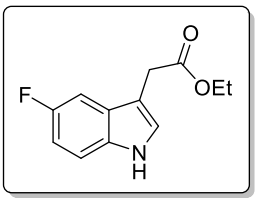
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 30 mg, 35% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.19-7.13 (m, 2H), 7.11-7.04 (m, 2H), 6.93 (d, *J* = 2.6 Hz, 2H), 3.87 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.8, 136.2, 127.4, 123.5, 122.3, 119.8, 118.8, 111.4, 108.6, 38.7; **HRMS** (ESI) calcd for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$: 311.1155, found: 311.1150.

Ethyl 2-(5-methyl-1*H*-indol-3-yl)acetate (2ba)



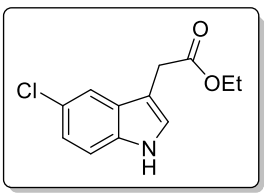
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 82 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.42-7.38 (m, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.09-7.06 (m, 1H), 7.01 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 0.9 Hz, 2H), 2.45 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 134.5, 129.0, 127.6, 123.9, 123.3, 118.6, 111.0, 108.1, 60.9, 31.5, 21.6, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.0995, found: 240.0988.

Ethyl 2-(5-fluoro-1*H*-indol-3-yl)acetate (2ca)



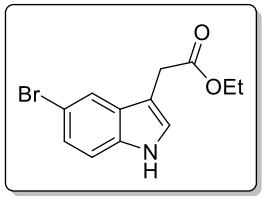
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 98 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.29-7.20 (m, 2H), 7.15 (d, *J* = 2.5 Hz, 1H), 6.93 (td, *J* = 9.0, 2.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.72 (d, *J* = 0.9 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 158.0 (d, $J_{C\text{-}F}$ = 235 Hz), 132.7, 127.7 (d, $J_{C\text{-}F}$ = 10 Hz), 125.0, 112.0 (d, $J_{C\text{-}F}$ = 10 Hz), 110.7 (d, $J_{C\text{-}F}$ = 26 Hz), 108.8 (d, $J_{C\text{-}F}$ = 5 Hz), 104.0 (d, $J_{C\text{-}F}$ = 24 Hz), 61.1, 31.5, 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.4; **HRMS** (ESI) calcd for $C_{12}H_{12}FNO_2Na$ $[M+Na]^+$: 244.0744, found: 244.0736.

Ethyl 2-(5-chloro-1*H*-indol-3-yl)acetate (2da)



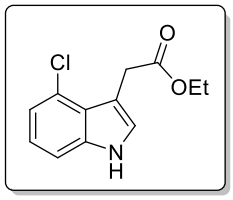
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 90 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.21 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.9 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.72 (d, *J* = 0.9 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 134.5, 128.4, 125.5, 124.7, 122.6, 118.6, 112.3, 108.3, 61.1, 31.3, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{12}ClNO_2Na$ $[M+Na]^+$: 260.0449, found: 260.0444.

Ethyl 2-(5-bromo-1*H*-indol-3-yl)acetate (2ea)



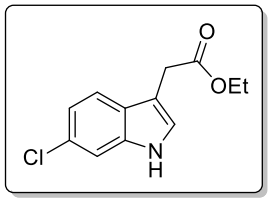
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 98 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.25 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 134.8, 129.1, 125.1, 124.5, 121.7, 113.0, 112.8, 108.3, 61.1, 31.3, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{12}BrNO_2Na$ $[M+Na]^+$: 303.9944, found: 303.9939.

Ethyl 2-(4-chloro-1*H*-indol-3-yl)acetate (2fa)



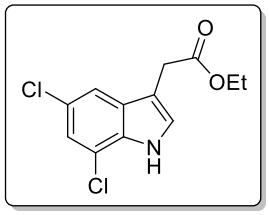
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 101 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.05-6.96 (m, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 0.8 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 137.8, 126.0, 125.2, 124.1, 122.6, 120.4, 110.3, 108.3, 61.1, 32.3, 14.4; **HRMS** (ESI) calcd for $C_{12}H_{12}ClNO_2Na$ $[M+Na]^+$: 260.0449, found: 260.0445.

Ethyl 2-(6-chloro-1*H*-indol-3-yl)acetate (2ga)



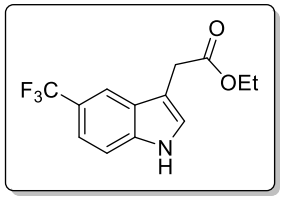
The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 103 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.11-7.04 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 0.9 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 136.5, 128.1, 125.9, 123.9, 120.4, 119.9, 111.2, 108.7, 61.1, 31.4, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{12}ClNO_2Na$ $[M+Na]^+$: 260.0449, found: 260.0448.

Ethyl 2-(5,7-dichloro-1*H*-indol-3-yl)acetate (2ha)



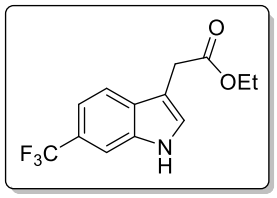
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 115 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.50 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.71 (d, *J* = 1.0 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 132.1, 129.2, 125.5, 125.2, 121.9, 117.6, 117.2, 109.7, 61.2, 31.4, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{12}Cl_2NO_2$ $[M+H]^+$: 272.0240, found: 272.0234.

Ethyl 2-(5-(trifluoromethyl)-1*H*-indol-3-yl)acetate (2ia)



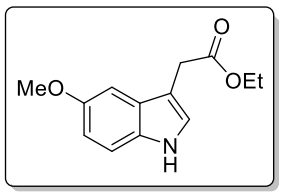
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 110 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.91 (s, 1H), 7.43-7.30 (m, 2H), 7.18 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 137.6, 126.7, 125.5 (q, $J_{C\text{-}F}$ = 270 Hz), 125.0, 122.2 (q, $J_{C\text{-}F}$ = 32 Hz), 119.0 (q, $J_{C\text{-}F}$ = 3 Hz), 116.9 (q, $J_{C\text{-}F}$ = 4 Hz), 111.6, 109.6, 61.2, 31.3, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.2; **HRMS** (ESI) calcd for $C_{13}H_{13}F_3NO_2$ $[M+H]^+$: 272.0893, found: 272.0892.

Ethyl 2-(6-(trifluoromethyl)-1*H*-indol-3-yl)acetate (2ja)



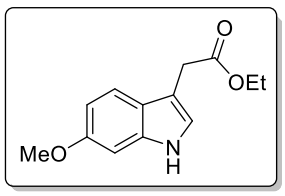
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 116 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.34 (dd, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 0.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 135.0, 129.5, 126.0, 125.3 (q, $J_{C\text{-}F}$ = 270 Hz), 124.3 (q, $J_{C\text{-}F}$ = 32 Hz), 119.4, 116.4 (q, $J_{C\text{-}F}$ = 4 Hz), 108.9 (q, $J_{C\text{-}F}$ = 4 Hz), 108.8, 61.2, 31.3, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.5; **HRMS** (ESI) calcd for $C_{13}H_{13}F_3NO_2$ $[M+H]^+$: 272.0893, found: 272.0881.

Ethyl 2-(5-methoxy-1*H*-indol-3-yl)acetate (2ka)



The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 101 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.12-7.04 (m, 2H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.73 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 154.2, 131.3, 127.7, 124.0, 112.6, 112.1, 108.3, 100.6, 60.9, 55.9, 31.6, 14.4; **HRMS** (ESI) calcd for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.0944, found: 256.0938.

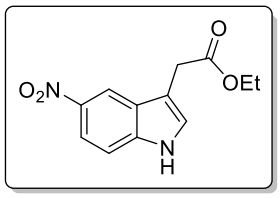
Ethyl 2-(6-methoxy-1*H*-indol-3-yl)acetate (2la)



The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 79 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.03 (s, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.83-6.75 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.72 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR**

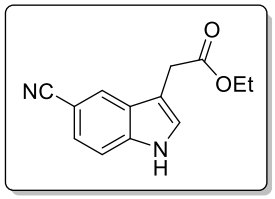
(100 MHz, $CDCl_3$) δ 172.4, 156.6, 137.0, 122.0, 121.7, 119.6, 109.7, 108.5, 94.7, 60.9, 55.7, 31.6, 14.3; **HRMS** (ESI) calcd for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.0944, found: 256.0943.

Ethyl 2-(5-nitro-1*H*-indol-3-yl)acetate (2ma)



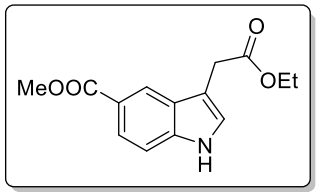
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 74 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.58 (d, *J* = 2.2 Hz, 1H), 8.05 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.81 (d, *J* = 1.0 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 141.7, 139.3, 126.8, 126.6, 117.9, 116.5, 111.4, 111.0, 61.4, 31.1, 14.3; **HRMS** (ESI) calcd for $C_{12}H_{12}N_2O_4Na$ $[M+Na]^+$: 271.0689, found: 271.0681.

Ethyl 2-(5-cyano-1*H*-indol-3-yl)acetate (2na)



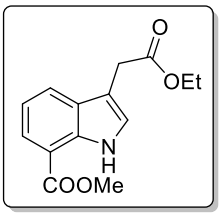
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 96 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.98-7.93 (m, 1H), 7.39-7.29 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 0.9 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 137.9, 127.1, 125.7, 124.9, 124.7, 121.0, 112.3, 109.2, 102.4, 61.3, 31.1, 14.3; **HRMS** (ESI) calcd for $C_{13}H_{13}N_2O_2$ $[M+H]^+$: 229.0972, found: 229.0967.

Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-5-carboxylate (2oa)



The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 82 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.39 (s, 1H), 7.88 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.15 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.79 (s, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 168.4, 138.9, 127.0, 124.7, 123.6, 122.1, 121.7, 111.1, 110.0, 61.1, 52.0, 31.3, 14.3; **HRMS** (ESI) calcd for $C_{14}H_{15}NO_4Na$ $[M+Na]^+$: 284.0893, found: 284.0891.

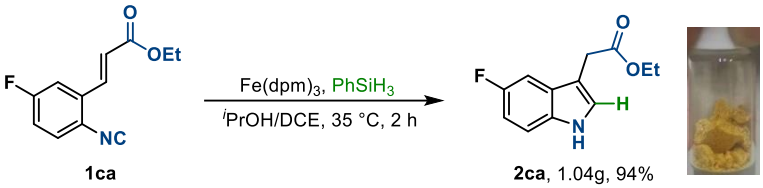
Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-7-carboxylate (2pa)



The title compound was prepared according to the general procedure and purified by column chromatography to give a brown solid, 82 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.89 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.85 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.29 (dd, *J* = 2.2 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.79 (d, *J* = 0.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 167.9, 136.1, 128.6, 124.8, 124.6, 124.2, 119.0, 112.6, 108.8, 61.0, 52.0, 31.4, 14.3; **HRMS** (ESI) calcd for $C_{14}H_{15}NO_4Na$ $[M+Na]^+$: 284.0893, found: 284.0894.

4.4. Procedure for gram-scale reaction and deuterium-labeling experiments

4.4.1. Gram-scale synthesis of product 2ca

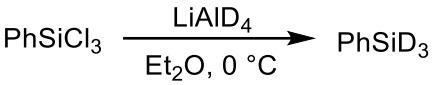


1ca **2ca**, 1.04g, 94%

Ethyl (*E*)-3-(5-fluoro-2-isocyanophenyl)acrylate **1ca** (1.12 g, 5.1 mmol), $Fe(dpm)_3$ (30 mg, 1 mol%), *i*-PrOH (10 mL), DCE (5 mL) and $PhSiH_3$ (810 mg, 7.5 mmol, 1.5 equiv.) were added to a 100 mL flame-dried Young-type tube. The reaction mixture was stirred at 35 ℃ for 2 hours, then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 5/1) to give the desired product **2ca** (1.04g) as a brown solid in 94% yield.

4.4.2. Deuterium-labeling experiments

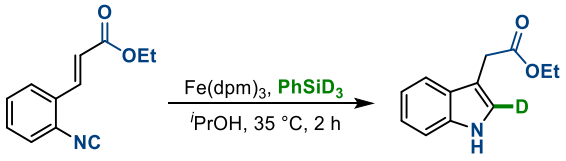
Synthesis of phenylsilane-*d*$_3$.



Following a modification of the method of Baran,[2] $LiAlD_4$ (262 mg, 6.24 mmol, 1 equiv.) was suspended in Et_2O (6.2 mL) under N_2 atmosphere and cooled to 0 ℃ with stirring. $PhSiCl_3$ (1.00 mL, 6.24 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was warmed to rt and then refluxed at 45 ℃ for 3.5 hours. The reaction mixture was then cooled to 0 ℃, where it was carefully quenched with ice cold H_2O. The organic layer was separated and held at 0 ℃ and the aqueous layer extracted with ice-cold Et_2O at 0 ℃. The organic layers were combined, washed with ice-cold brine at 0 ℃, dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 ℃ at 40 mbar [CAUTION: concentrating below 40 mbar (e.g., 11 mbar) can result in the total loss of product] to furnish pure $PhSiD_3$ as a colorless oil (0.56 g, 81 wt% solution in Et_2O, D: >95%, 65% yield).

Spectroscopic data was identical to that reported in the literature.

Deuteration study with $PhSiD_3$.

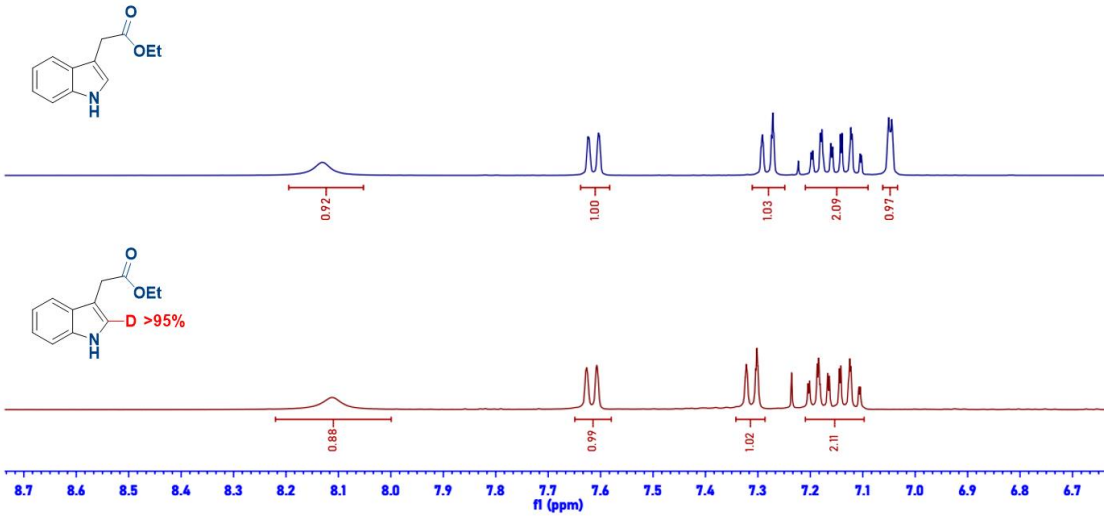


1aa **2aa-1**

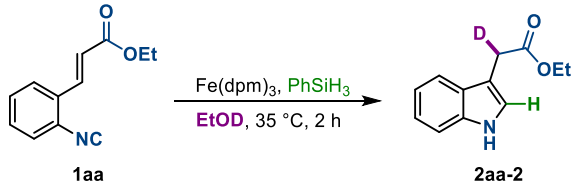
Ethyl (*E*)-3-(2-isocyanophenyl)acrylate **1aa** (100 mg, 0.50 mmol), $Fe(dpm)_3$ (15 mg, 5 mol%), *i*-PrOH (2 mL) and $PhSiD_3$ (137 mg, 81 wt% solution in Et_2O, 2.0 equiv.) were added to a 25 mL flame-dried Young-type tube. The reaction mixture was stirred at 35 ℃ for 2 hours,

then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 5/1) to give the deuterated product **2aa-1** (85 mg) as a brown solid in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.64-7.59 (m, 1H), 7.31 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.21-7.09 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). Deuterium incorporation was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aa-1



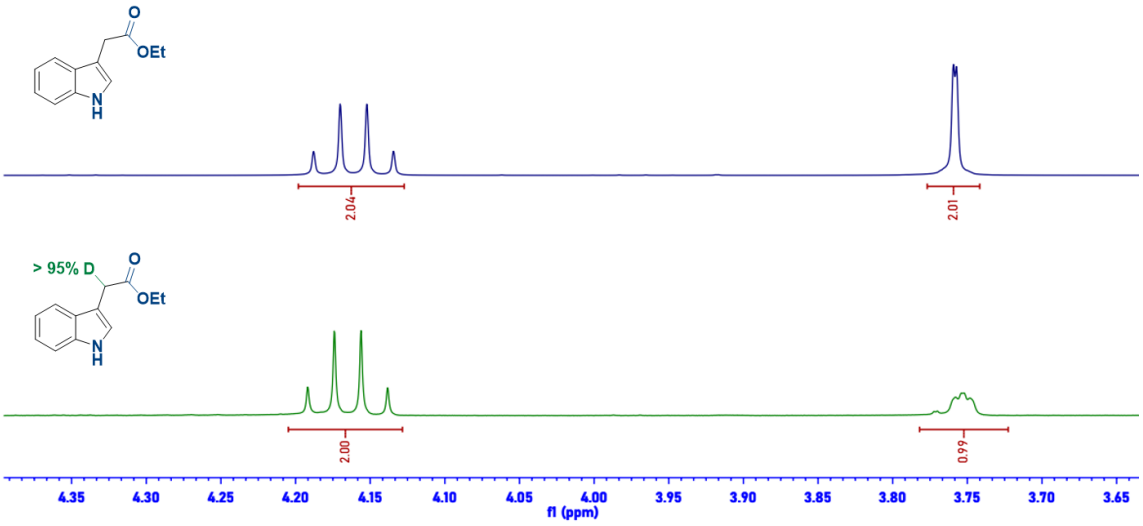
Deuteration study with EtOD.



1aa **2aa-2**

Ethyl (*E*)-3-(2-isocyanophenyl)acrylate **1aa** (100 mg, 0.50 mmol), $Fe(dpm)_3$ (15 mg, 5 mol%), EtOD (2 mL, D: 99%) and $PhSiH_3$ (108 mg, 2.0 equiv.) were added to a 25 mL flame-dried Young-type tube. The reaction mixture was stirred at 35 ℃ for 2 hours, then cooled to room temperature. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20/1 to 5/1) to give the desired product **2aa-2** (39 mg) as a brown solid in 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65-7.60 (m, 1H), 7.36 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.23-7.10 (m, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.78-3.73 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). Deuterium incorporation was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aa-2



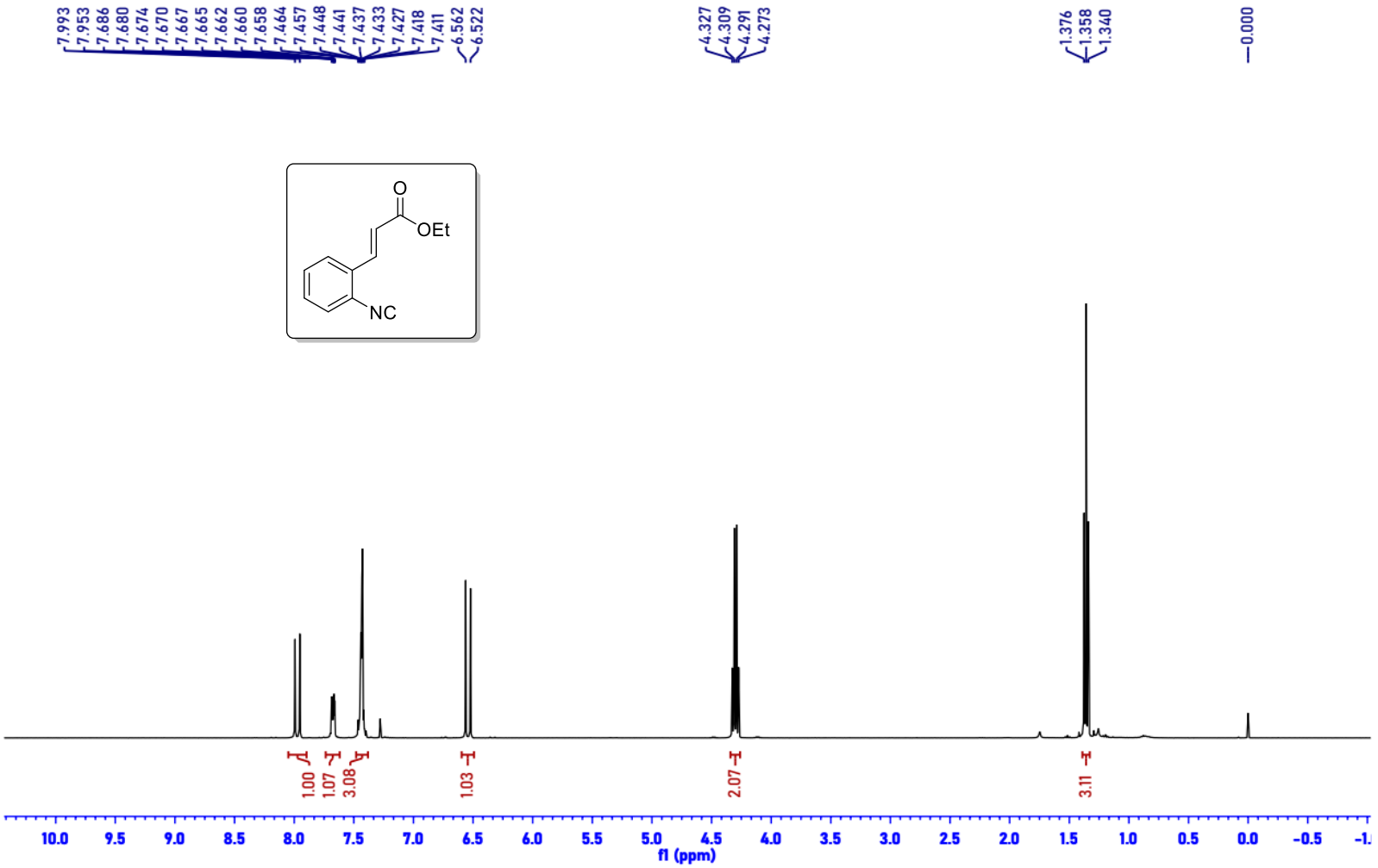
5. References

(1) A. Patti and S. Pedotti, *Tetrahedron*, 2010, **66**, 5607.

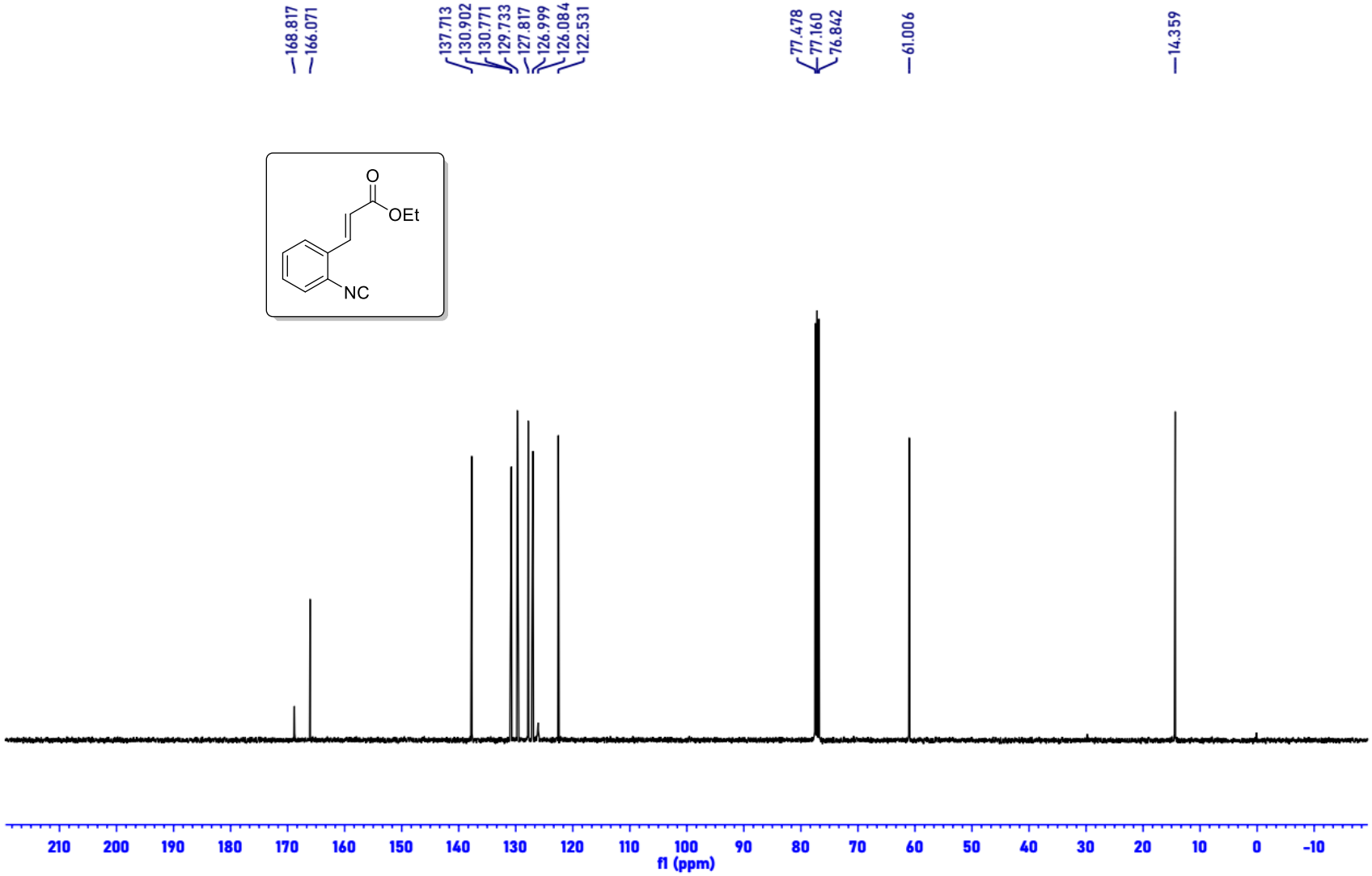
(2) J. C. Lo, D. Kim, C. Pan, J. T. Edwards, Y. Yabe, J. Gui, T. Qin, S. Gutierrez, J. Giacoboni, M. W. Smith, P. L. Holland and P. S. Baran, *J. Am. Chem. Soc.*, 2017, **139**, 2484.

6. NMR Spectra of Materials and Products

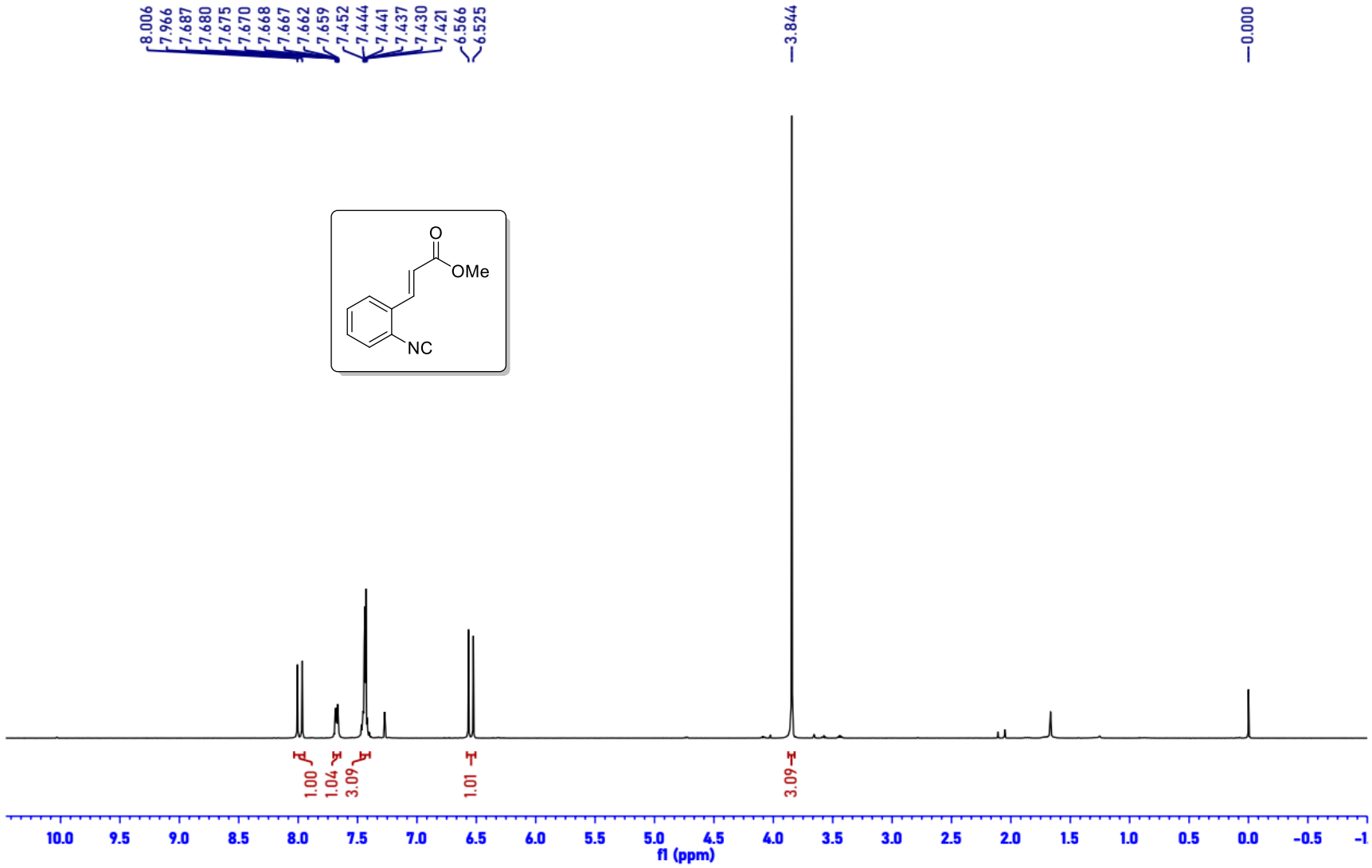
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1aa



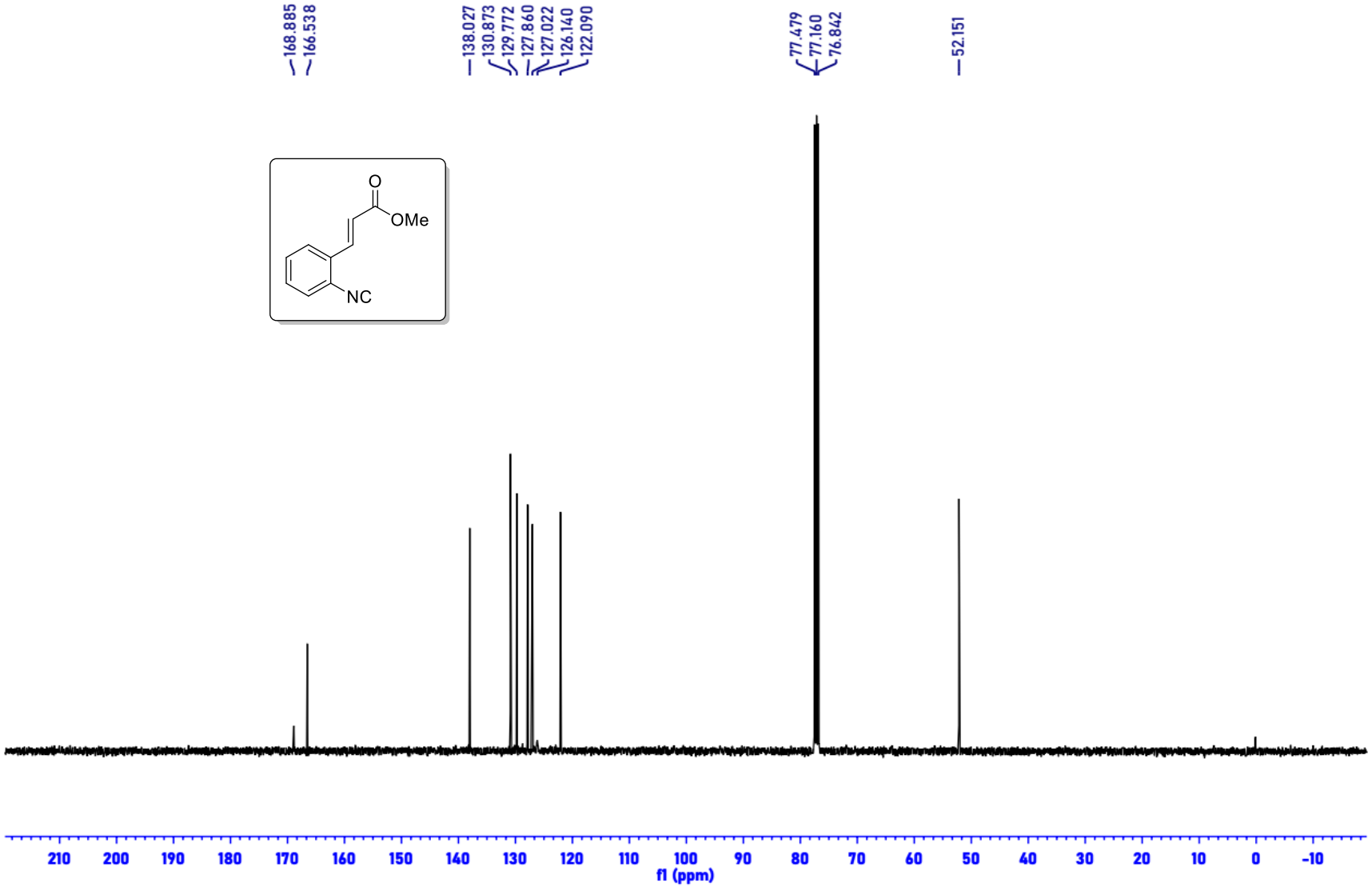
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1aa



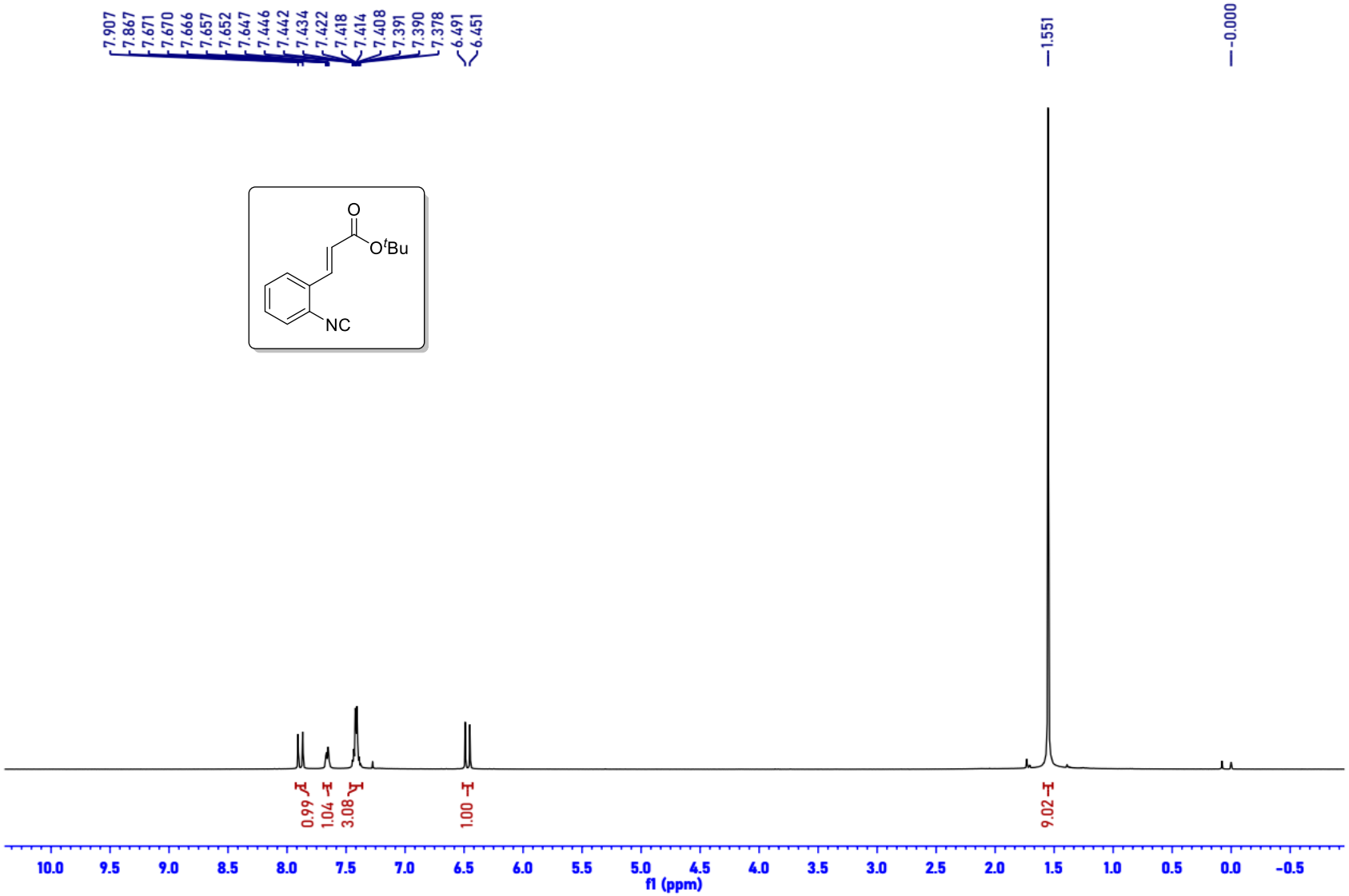
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ab



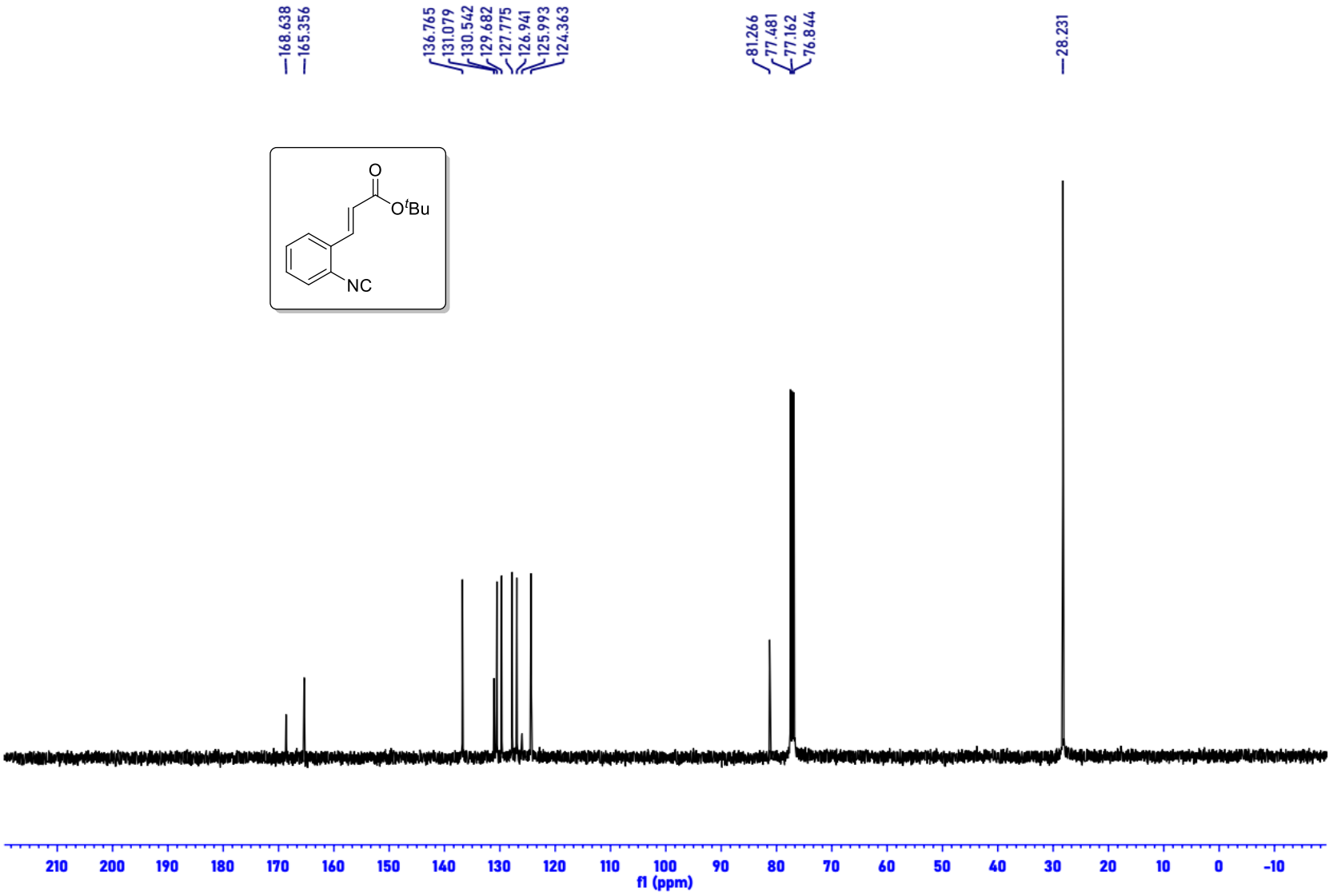
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ab



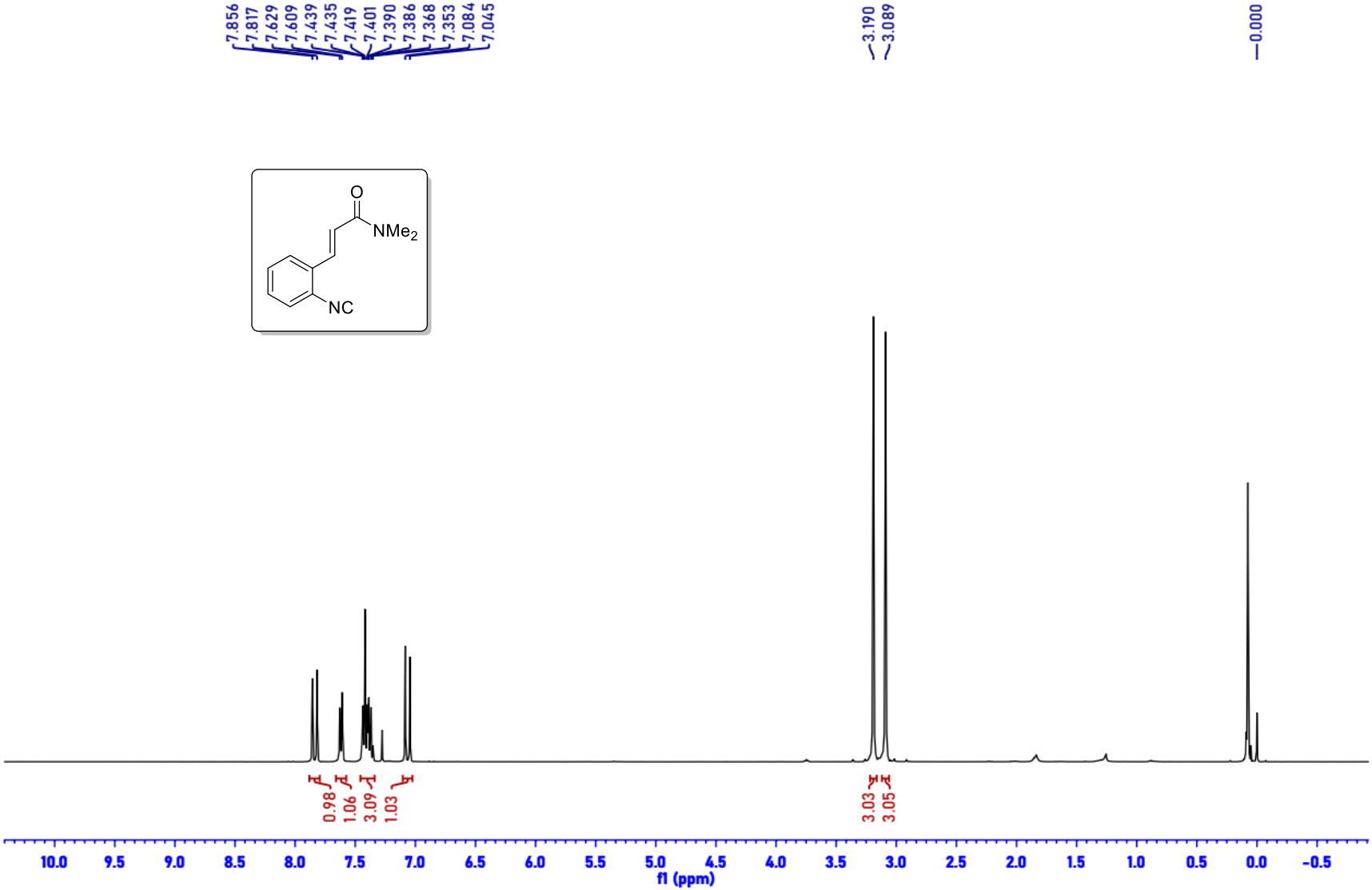
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ac



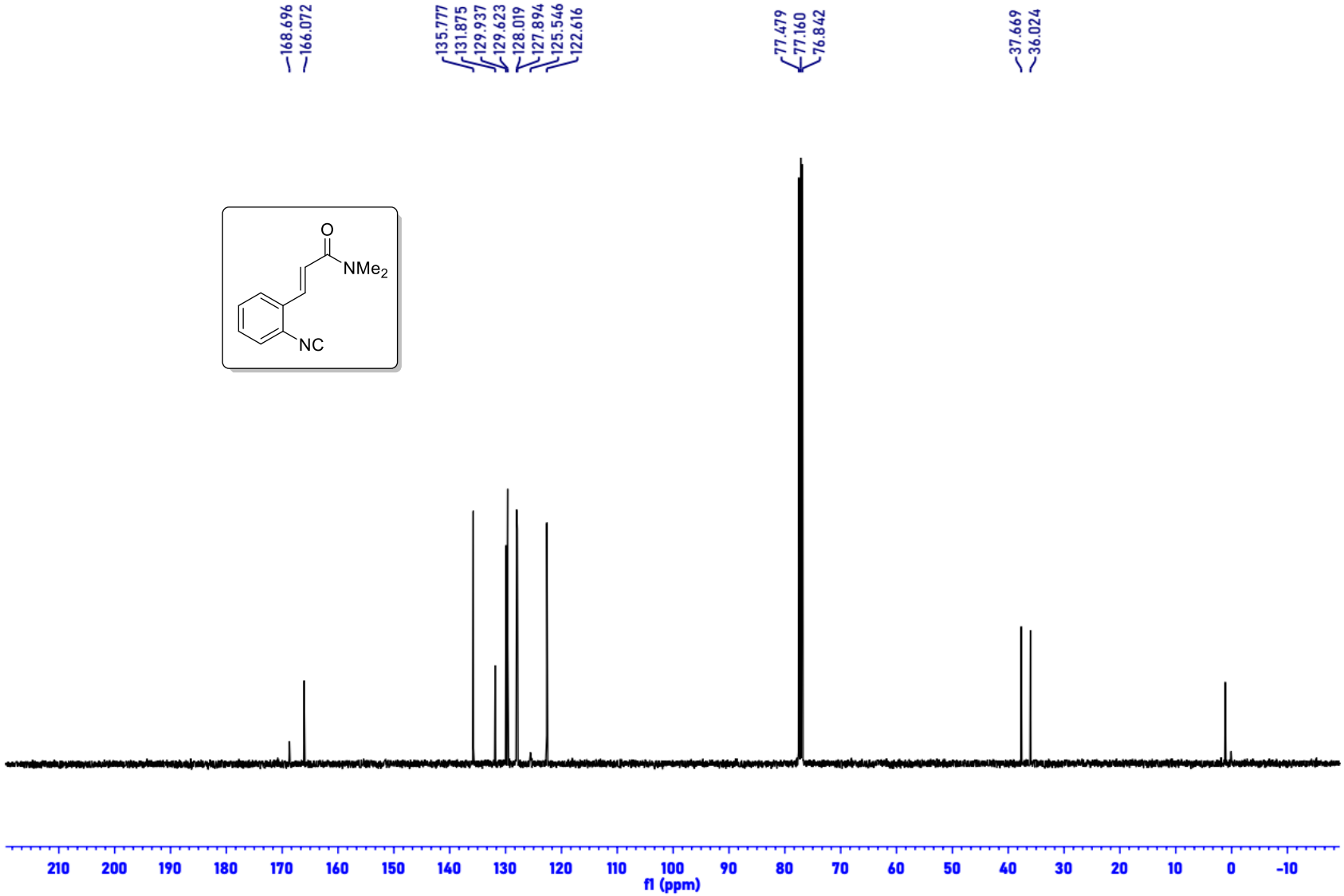
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ac



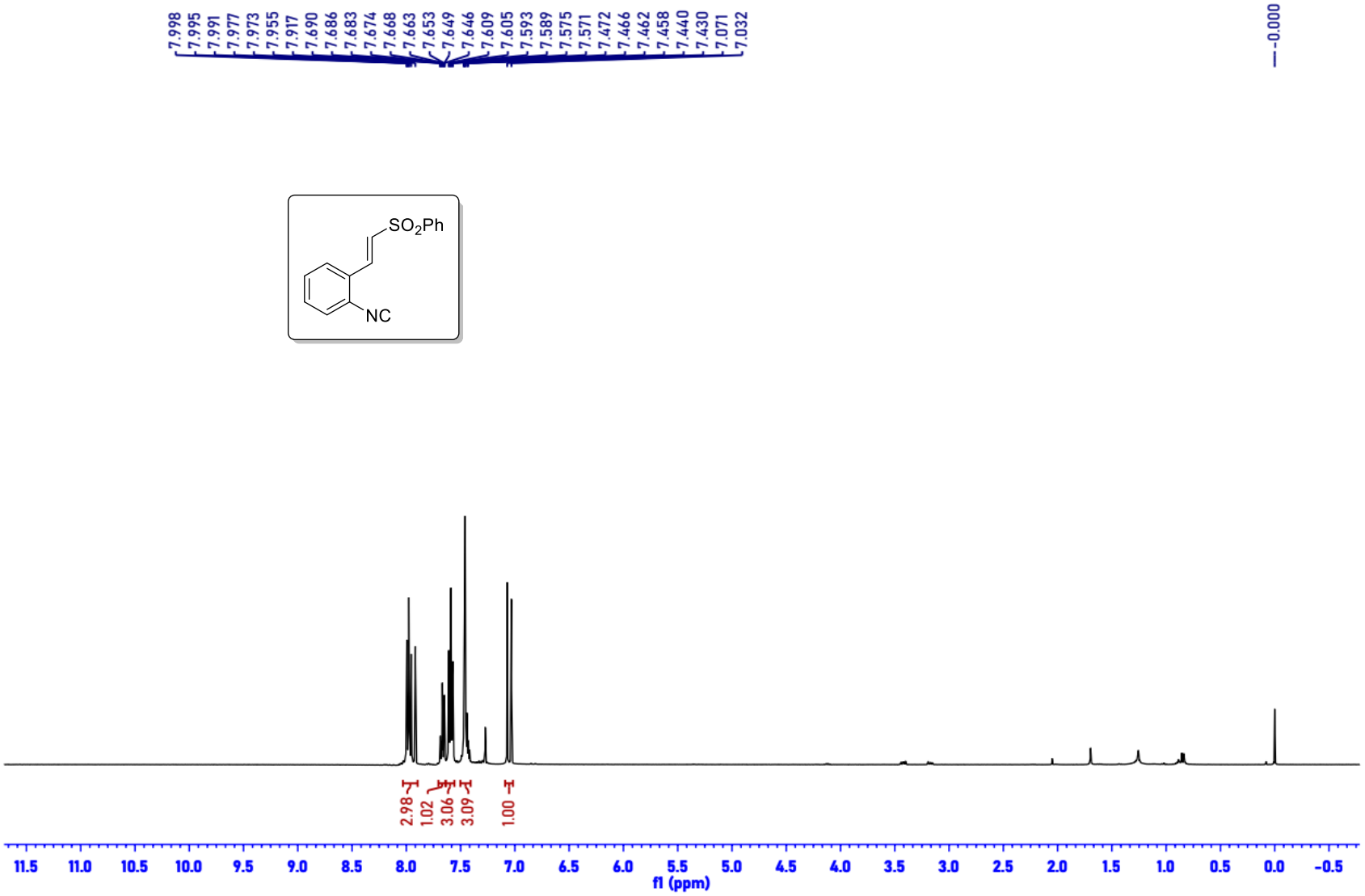
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ad



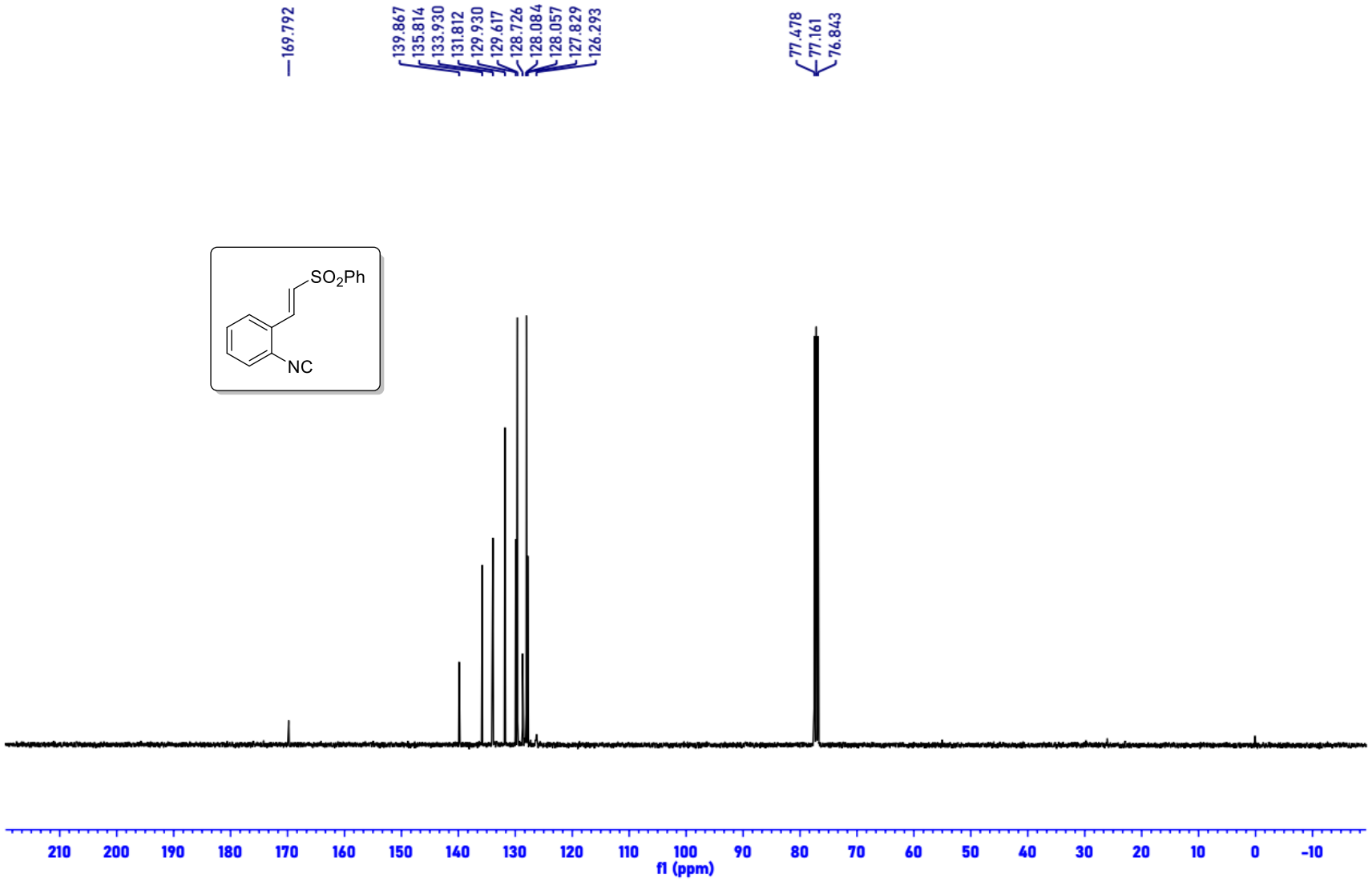
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ad



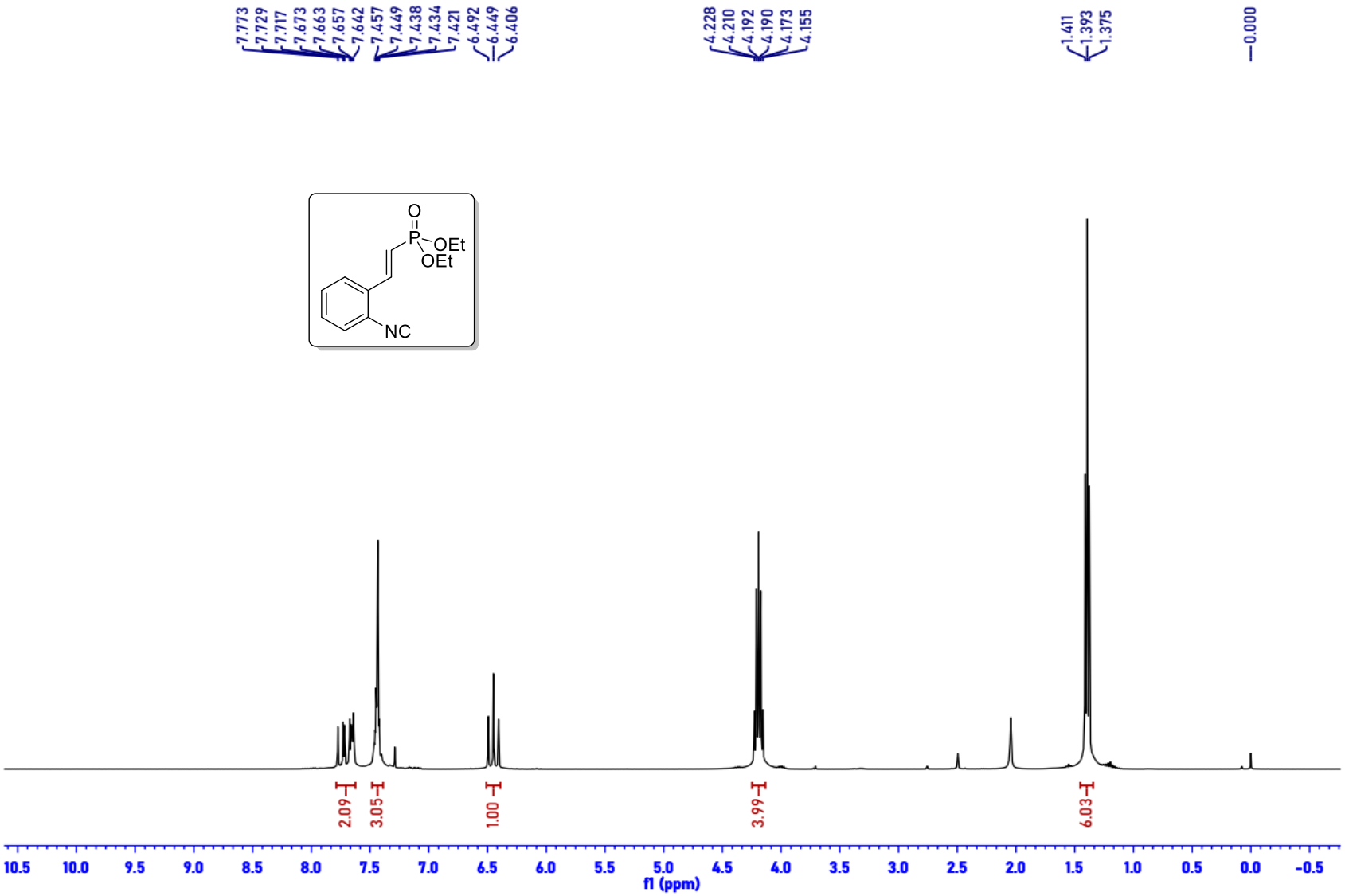
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ae



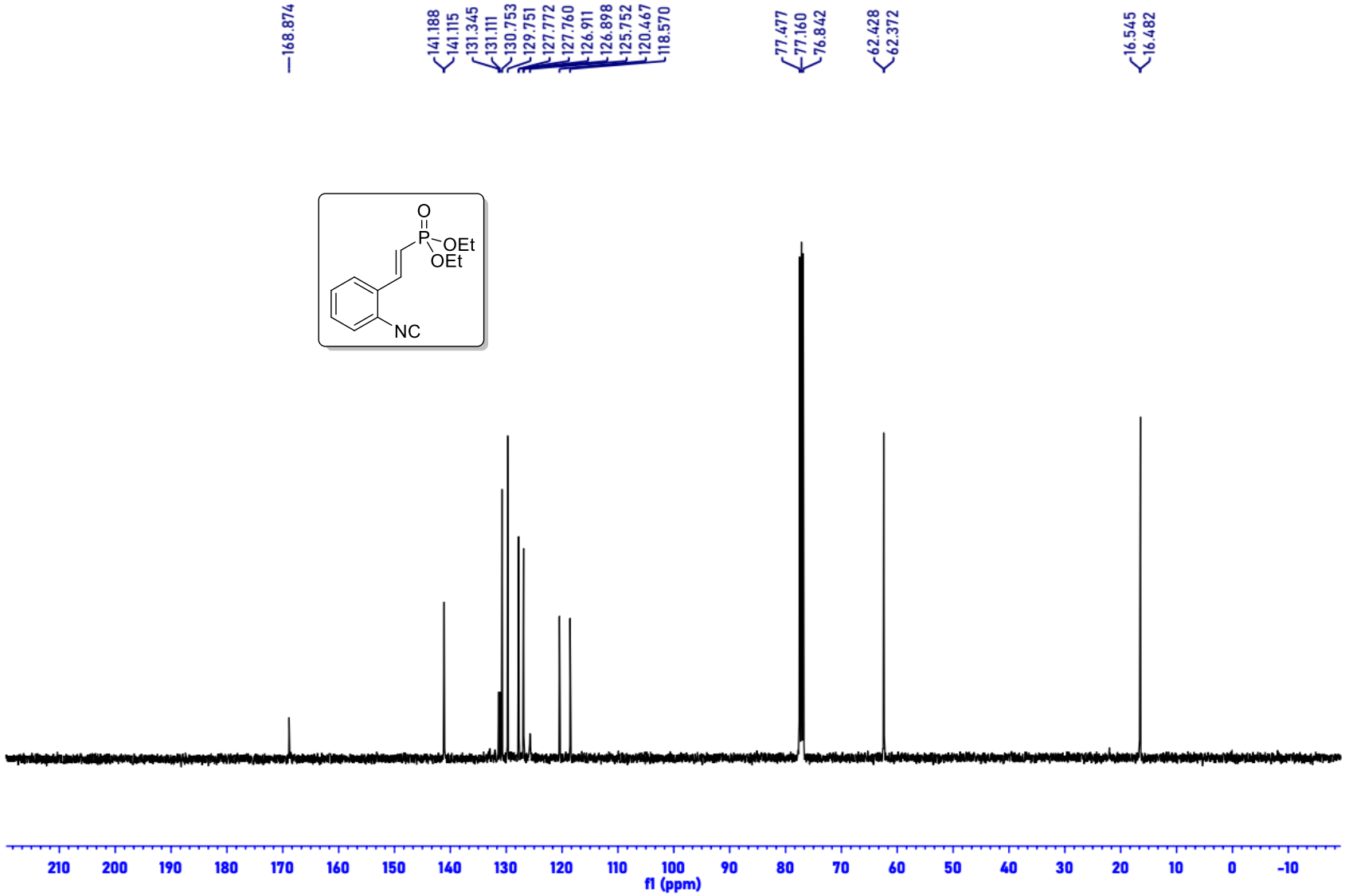
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ae



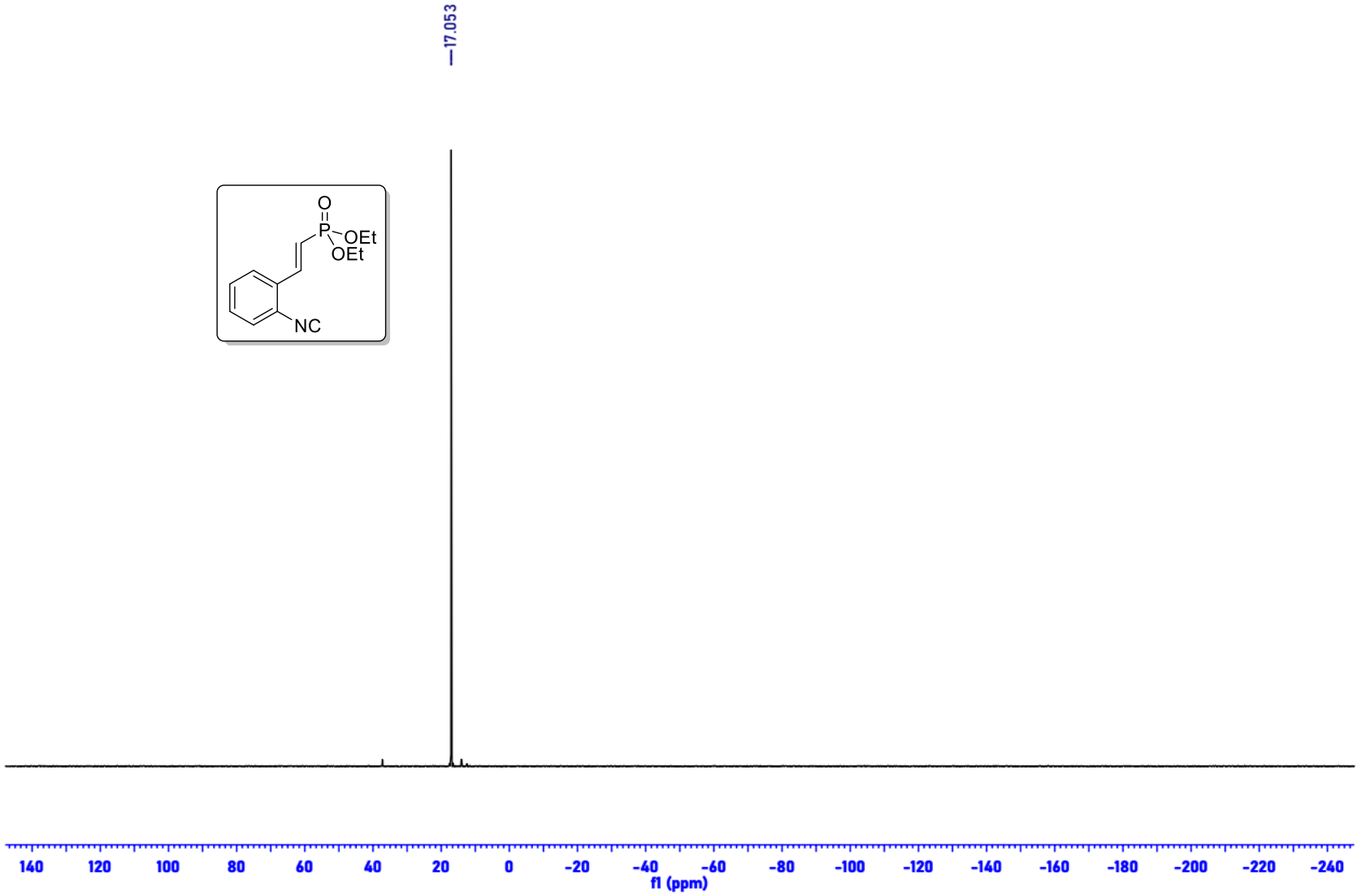
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1af



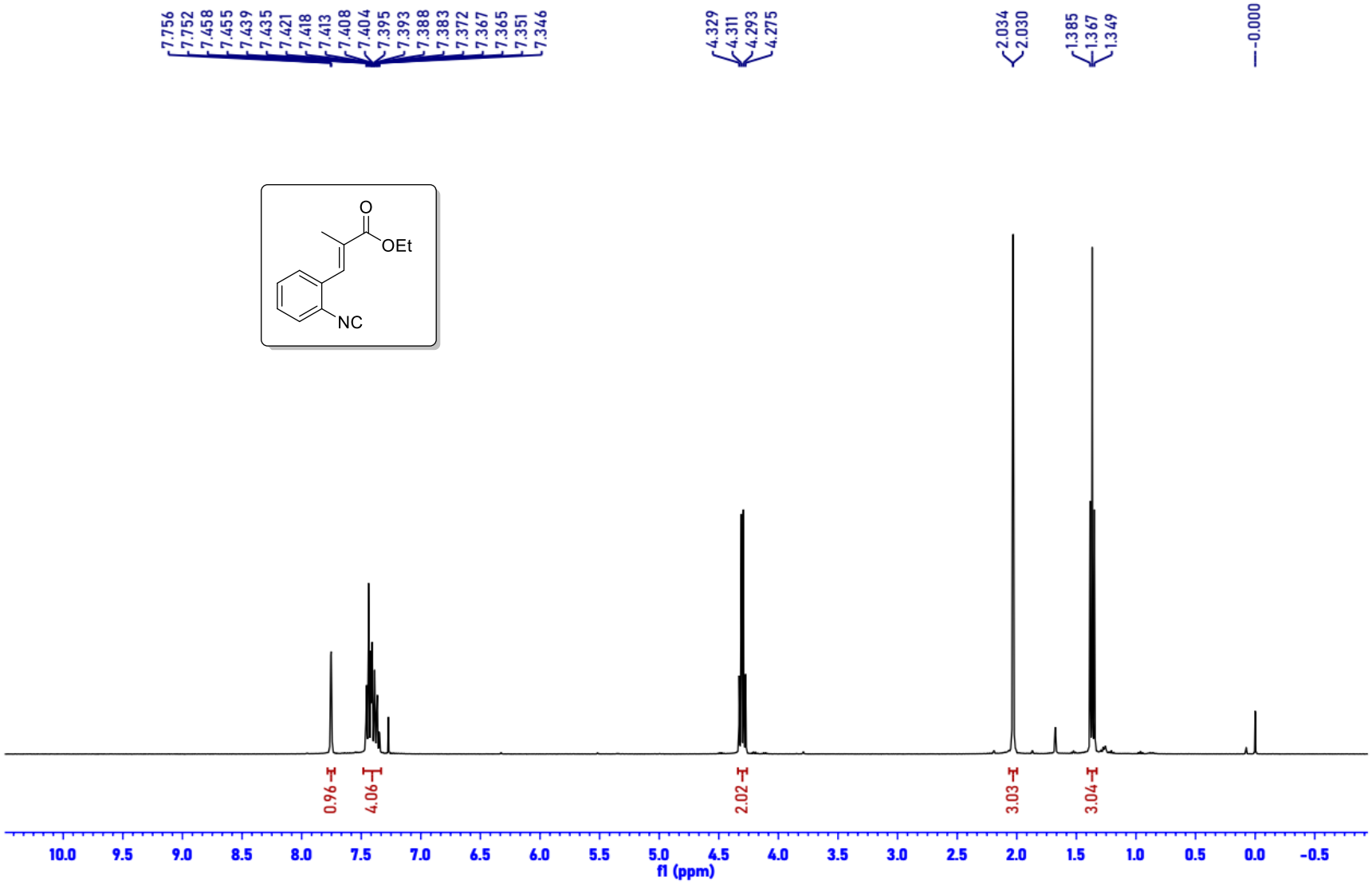
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1af



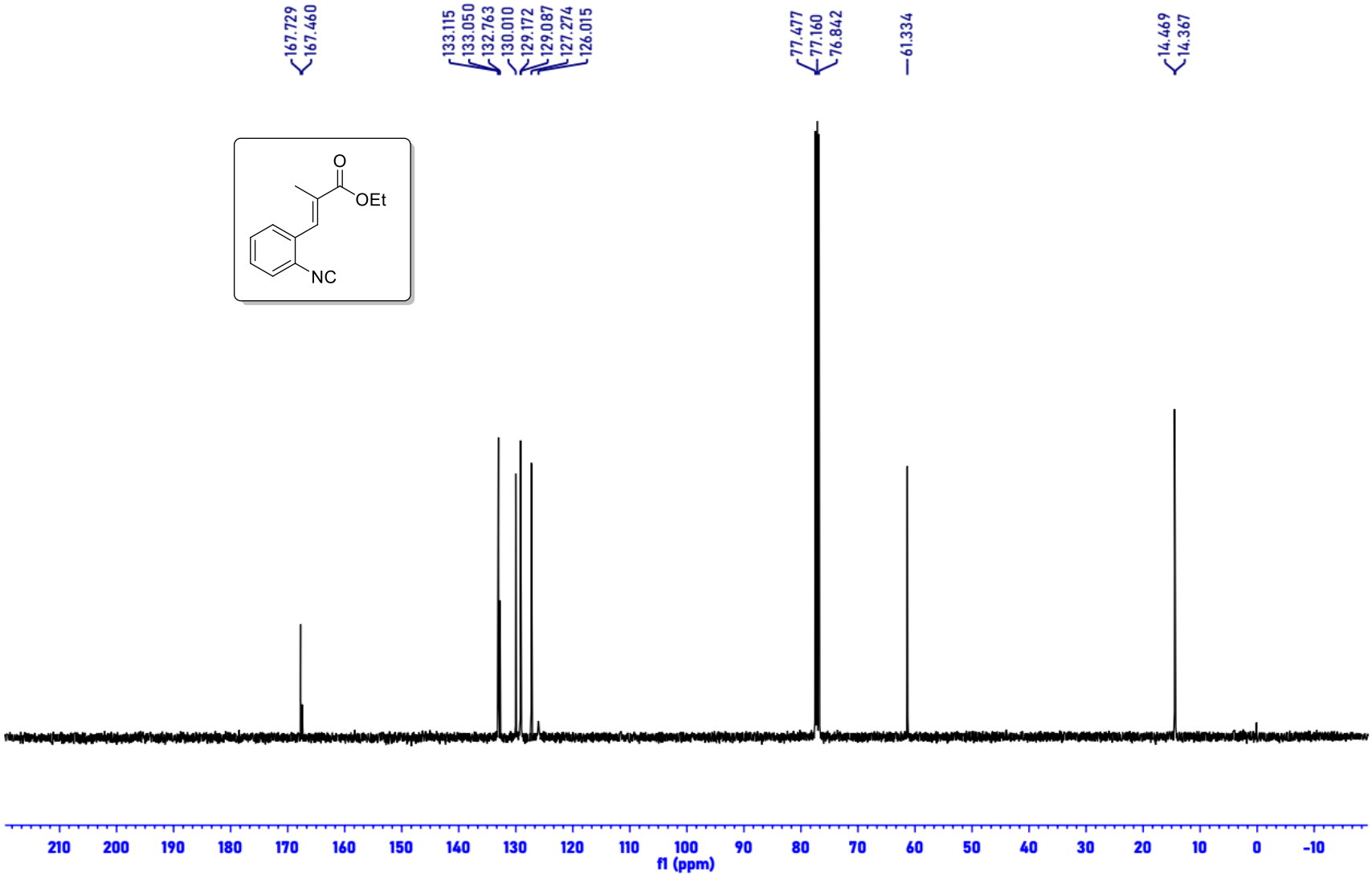
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 1af



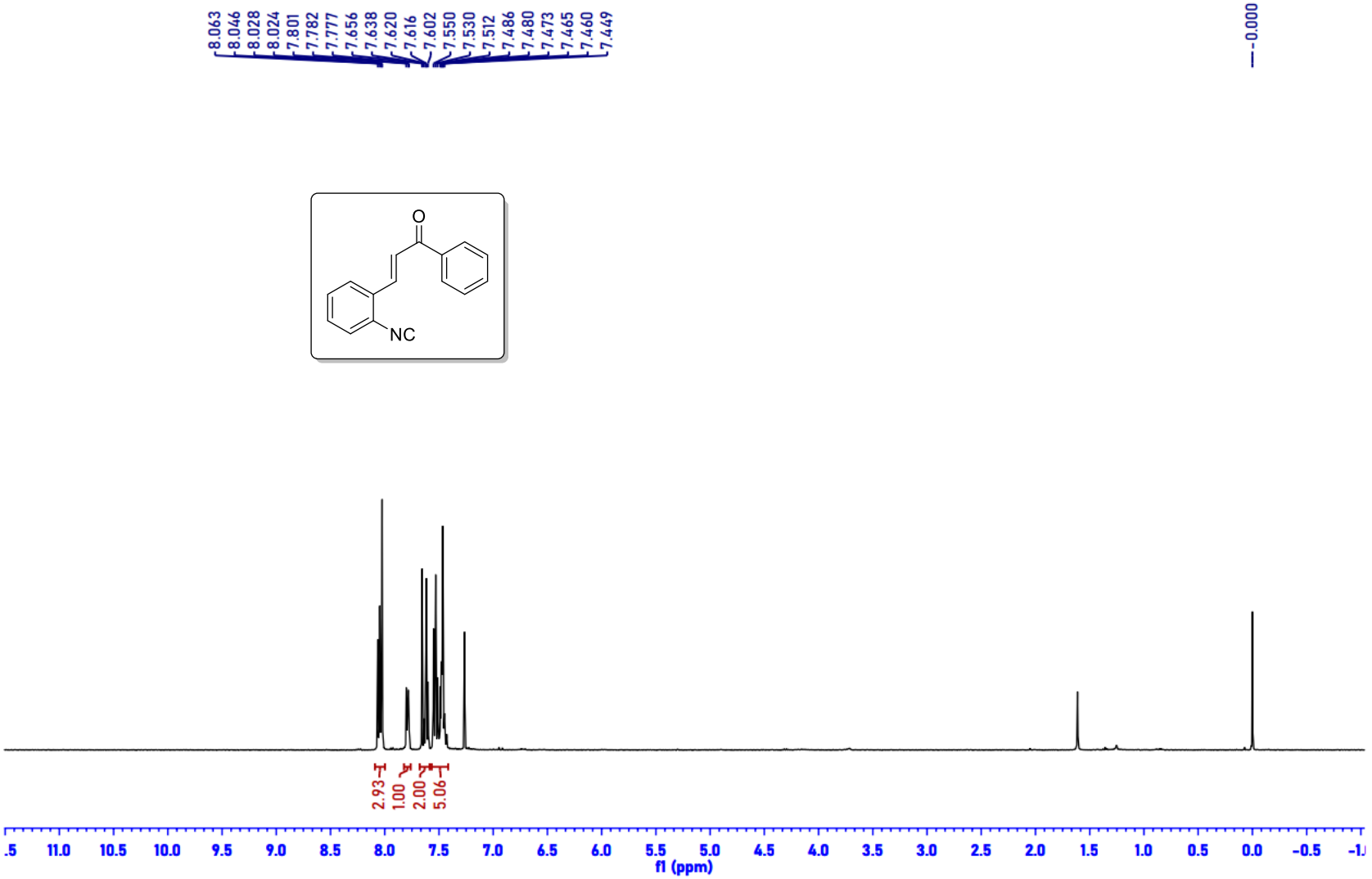
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ag



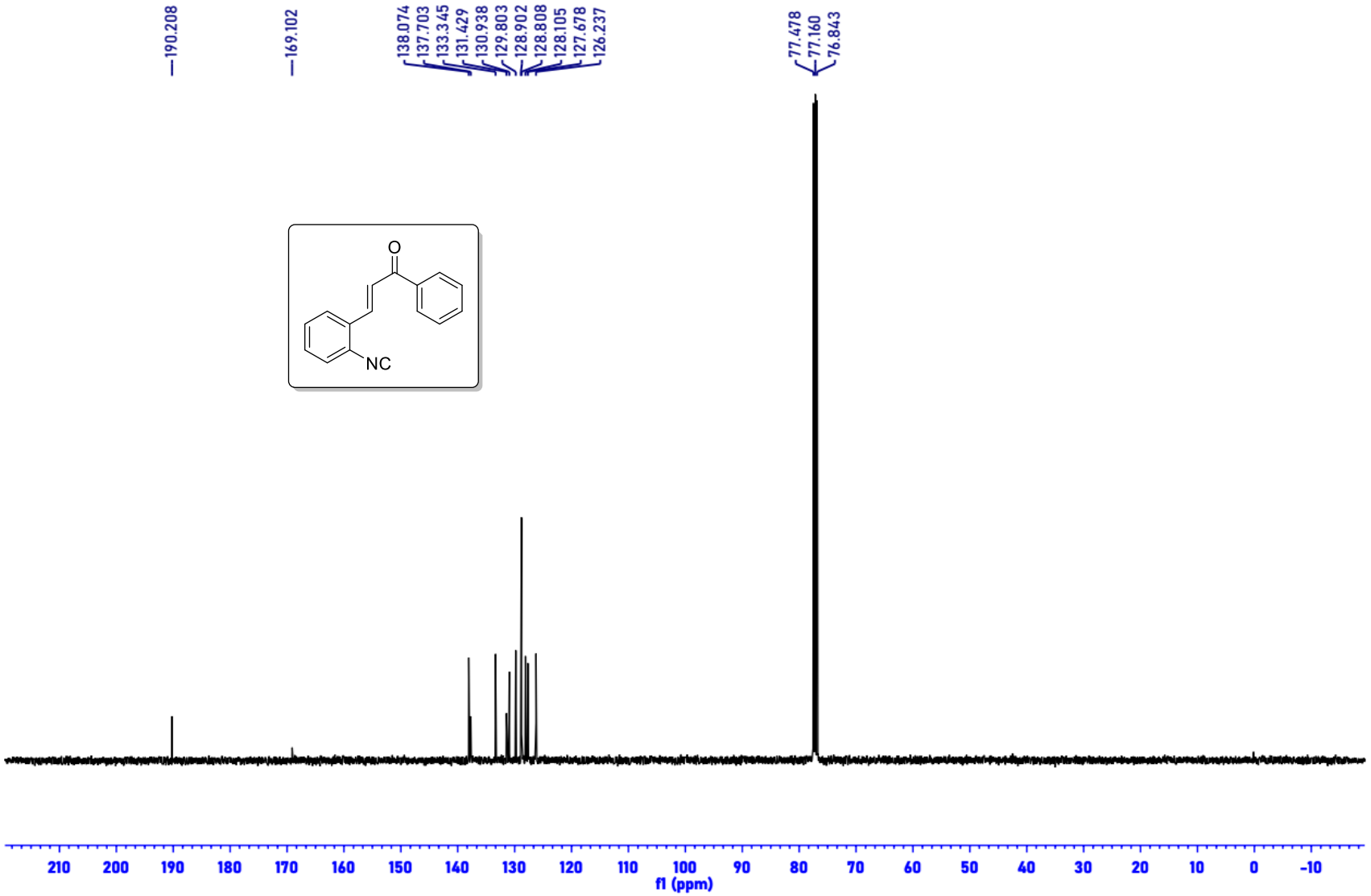
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ag



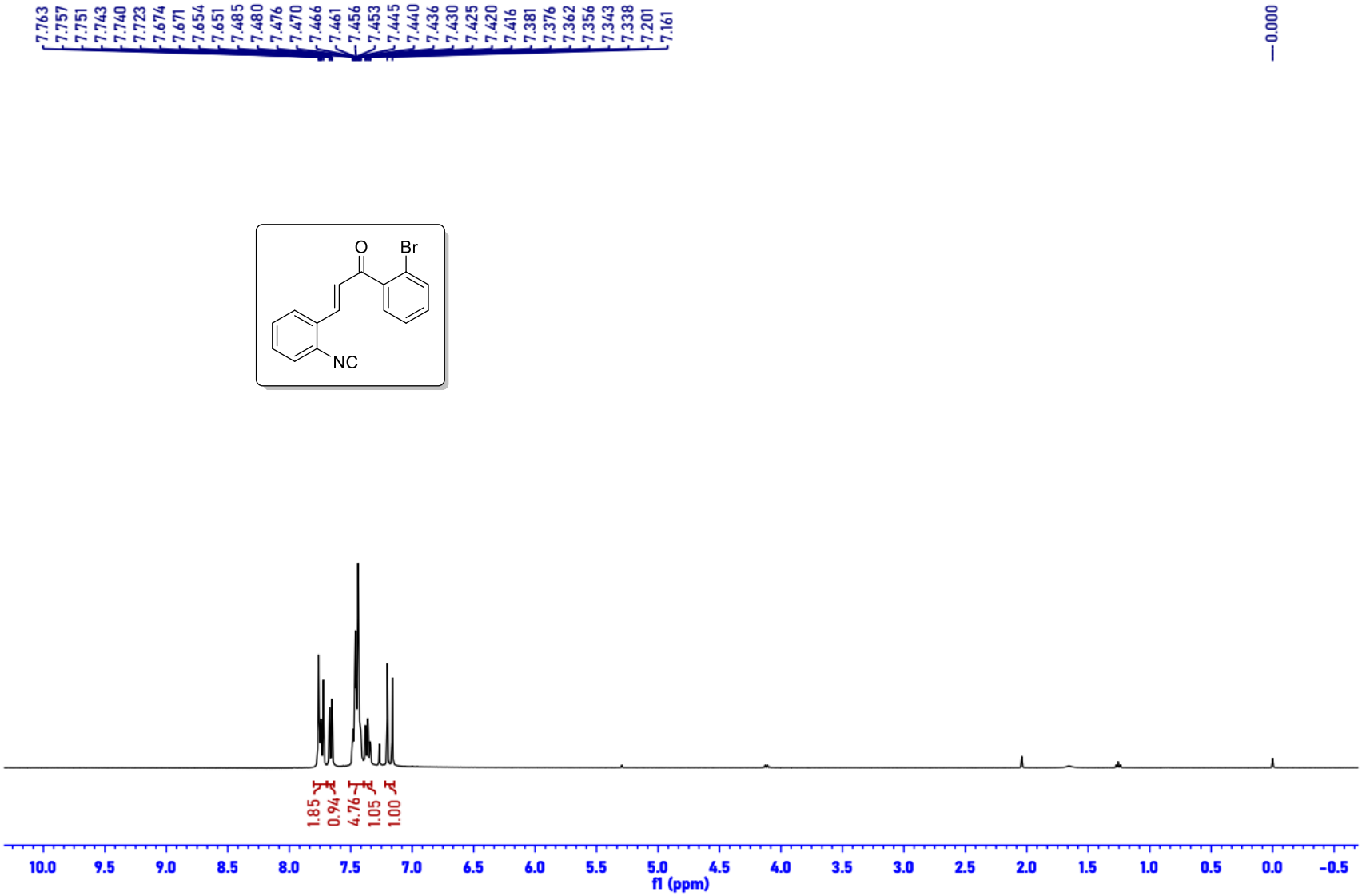
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ah



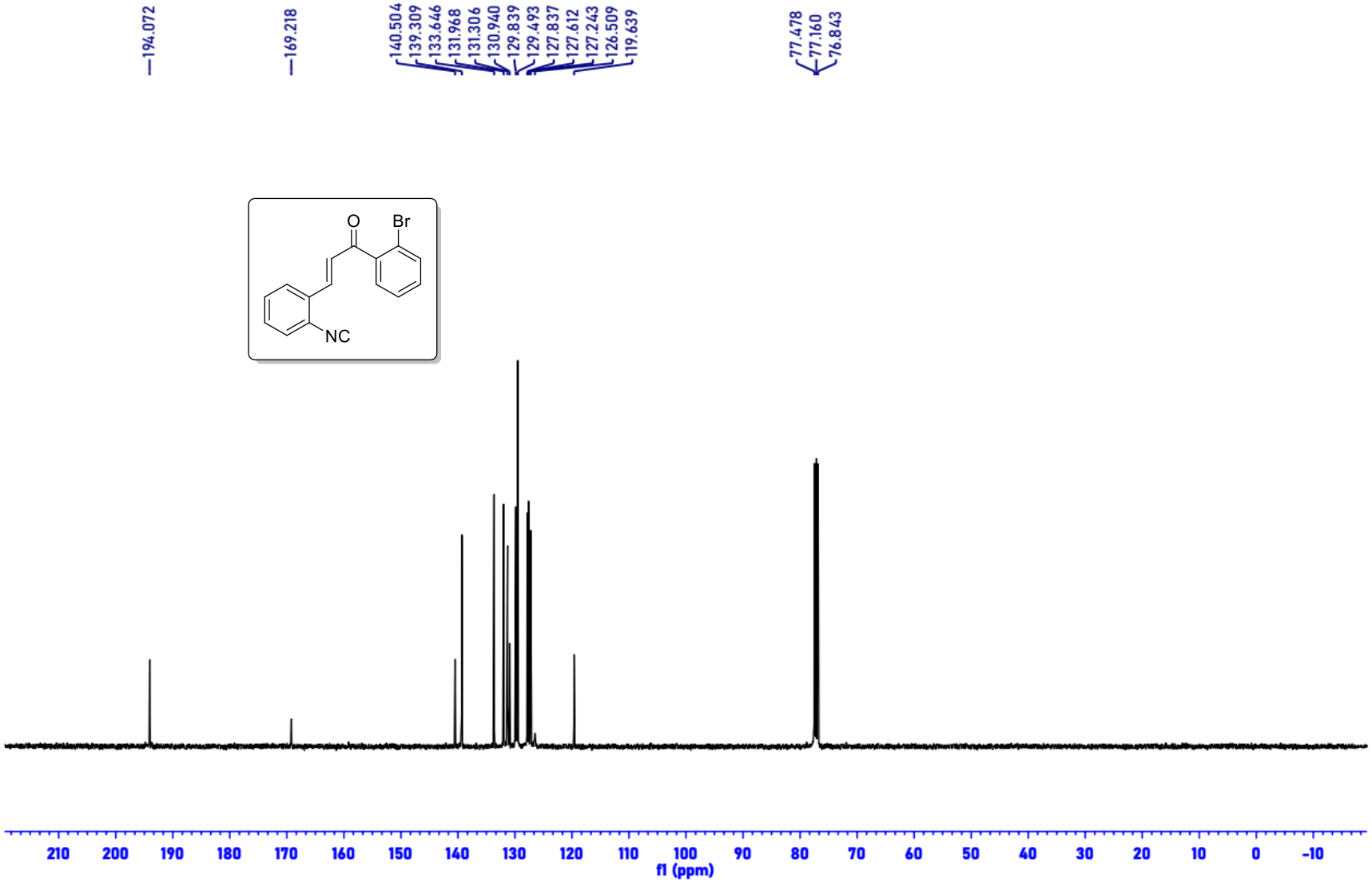
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ah



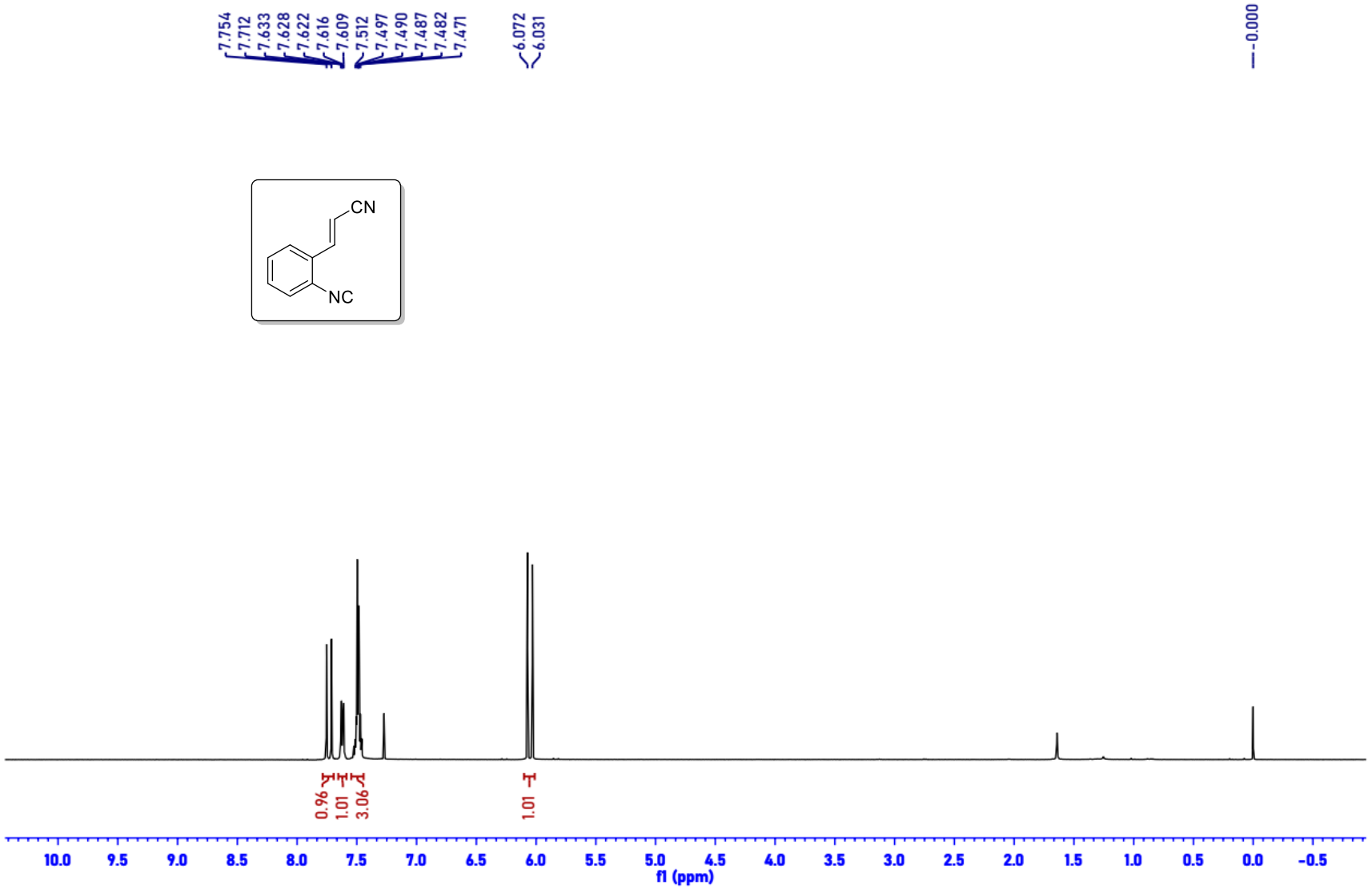
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ai



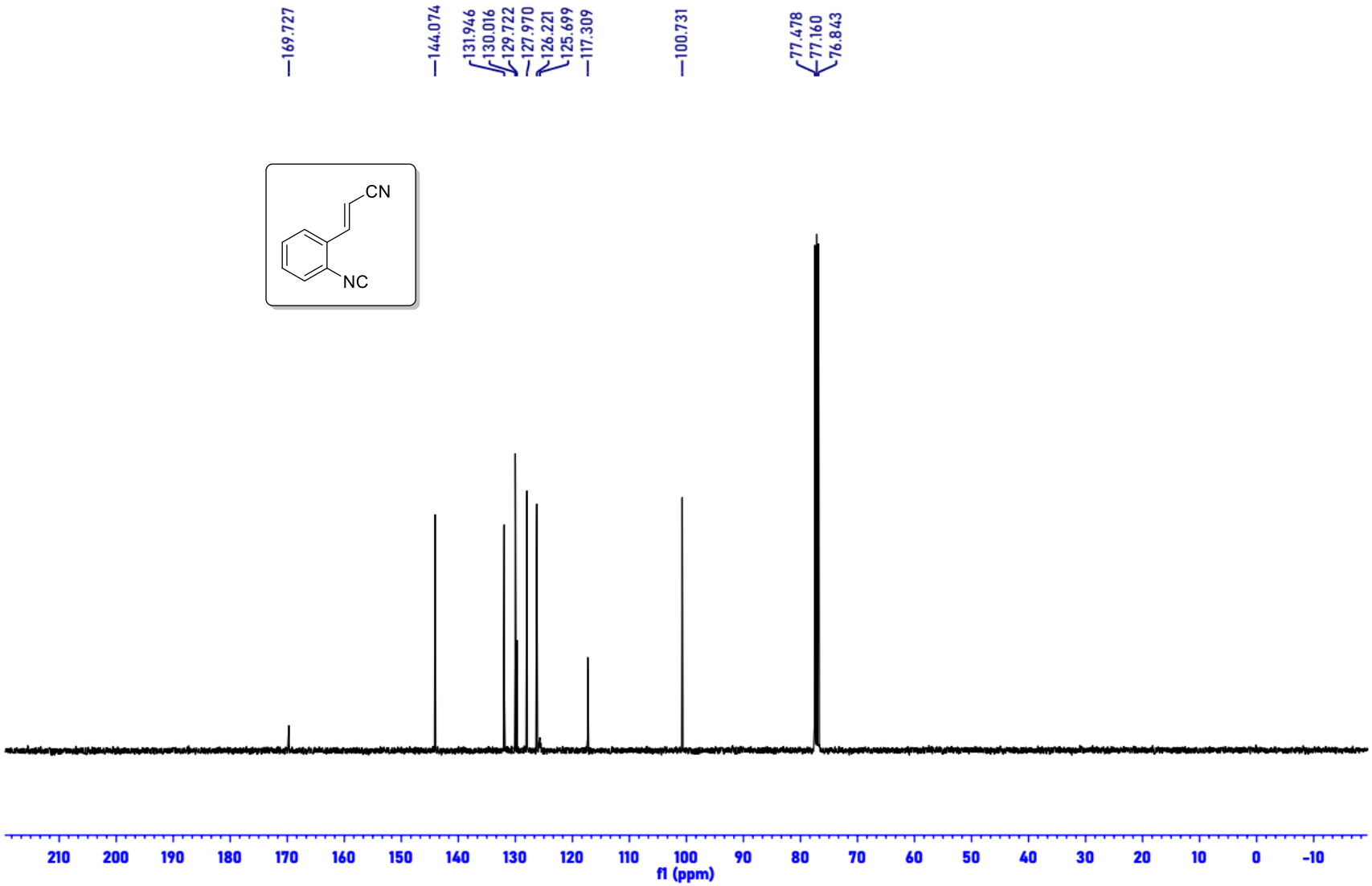
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ai



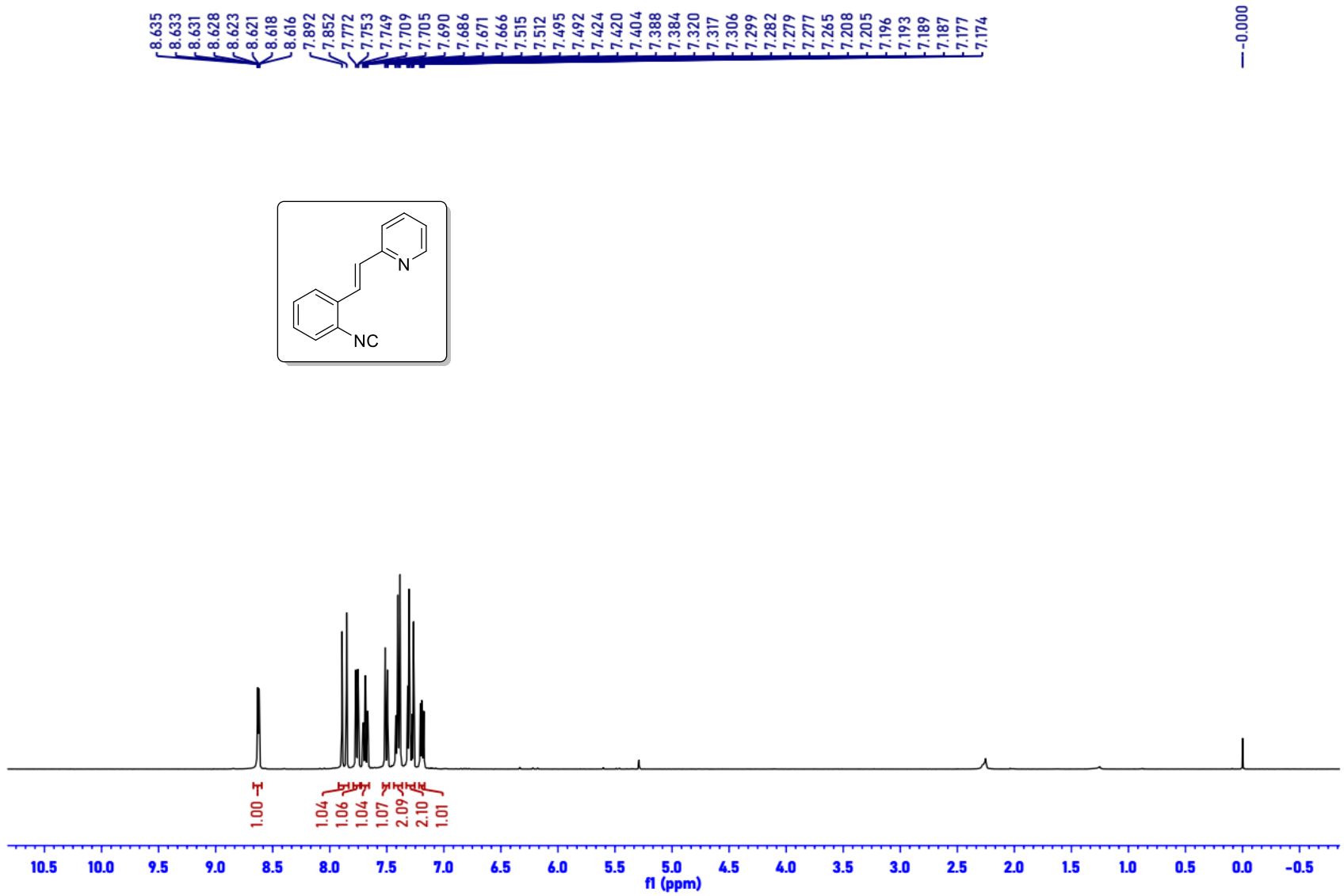
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1aj



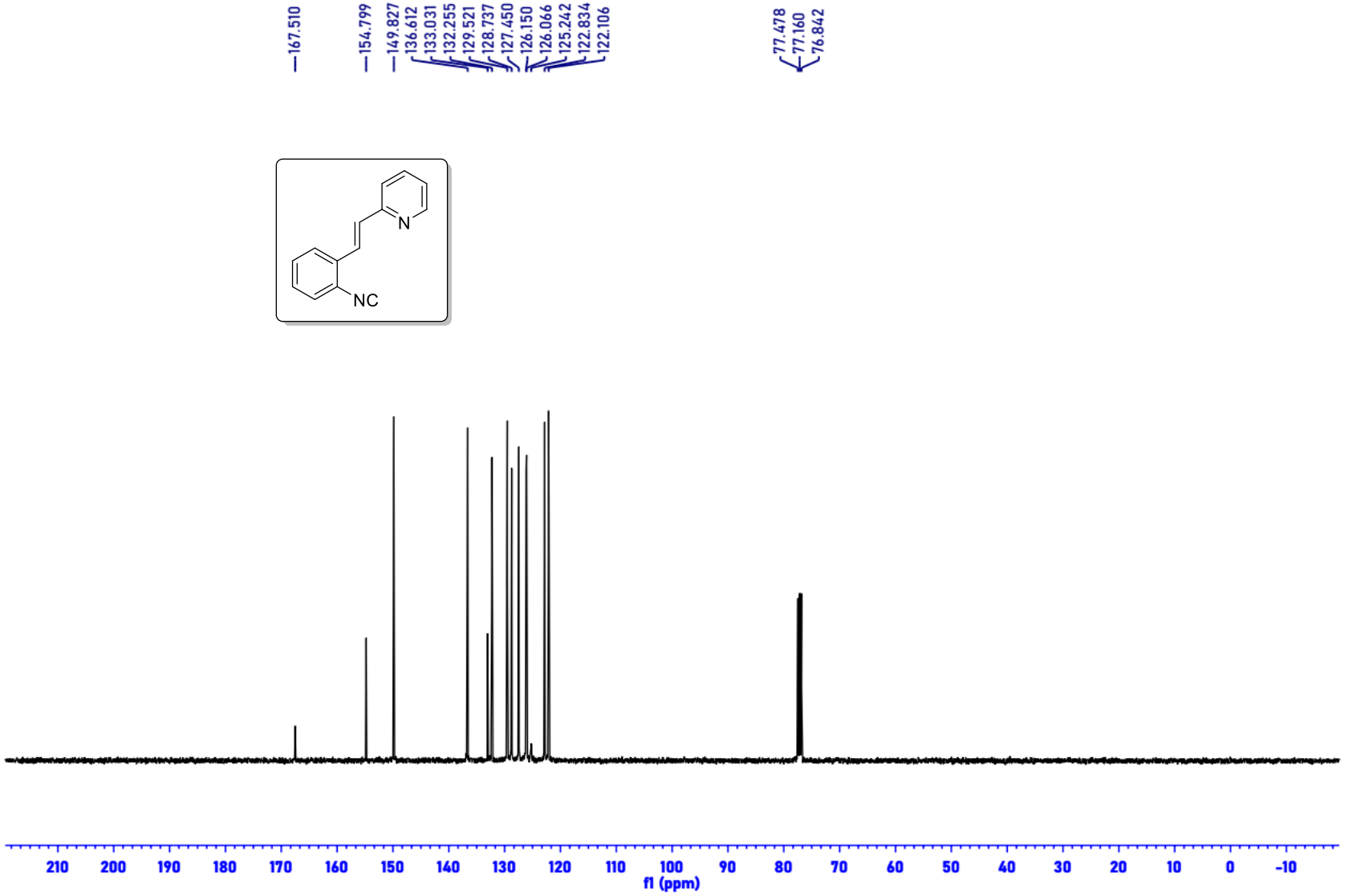
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1aj



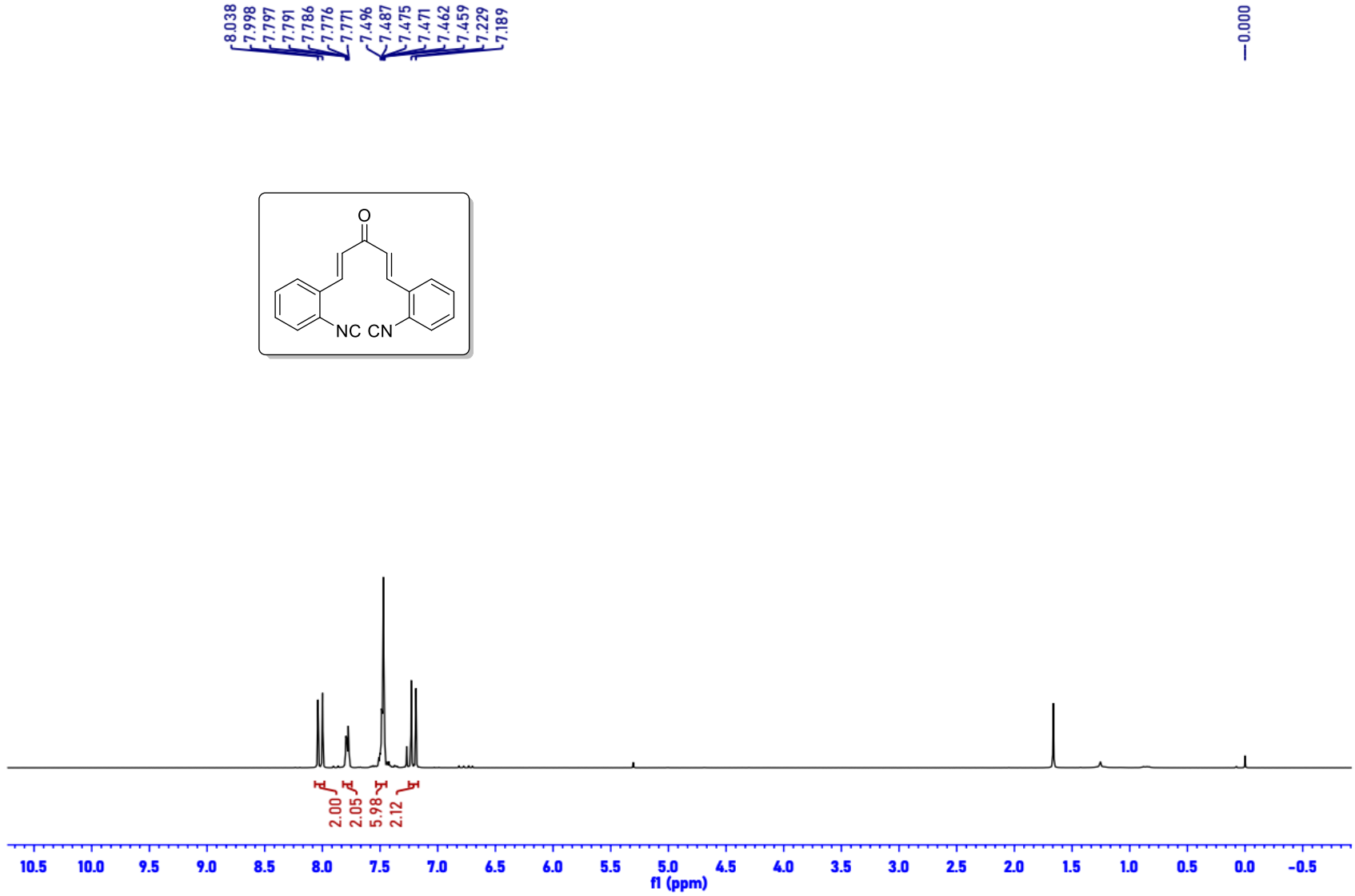
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ak



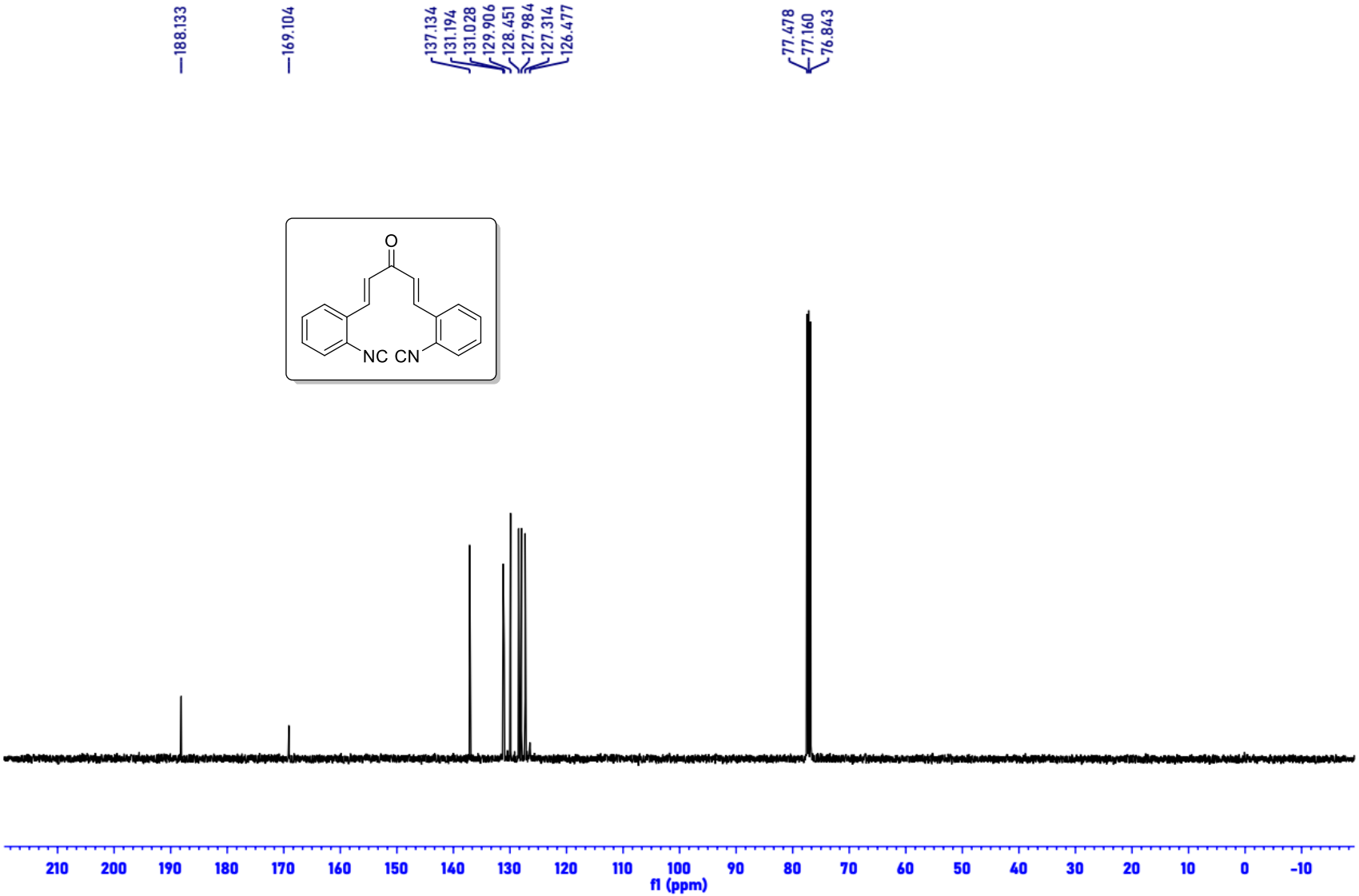
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ak



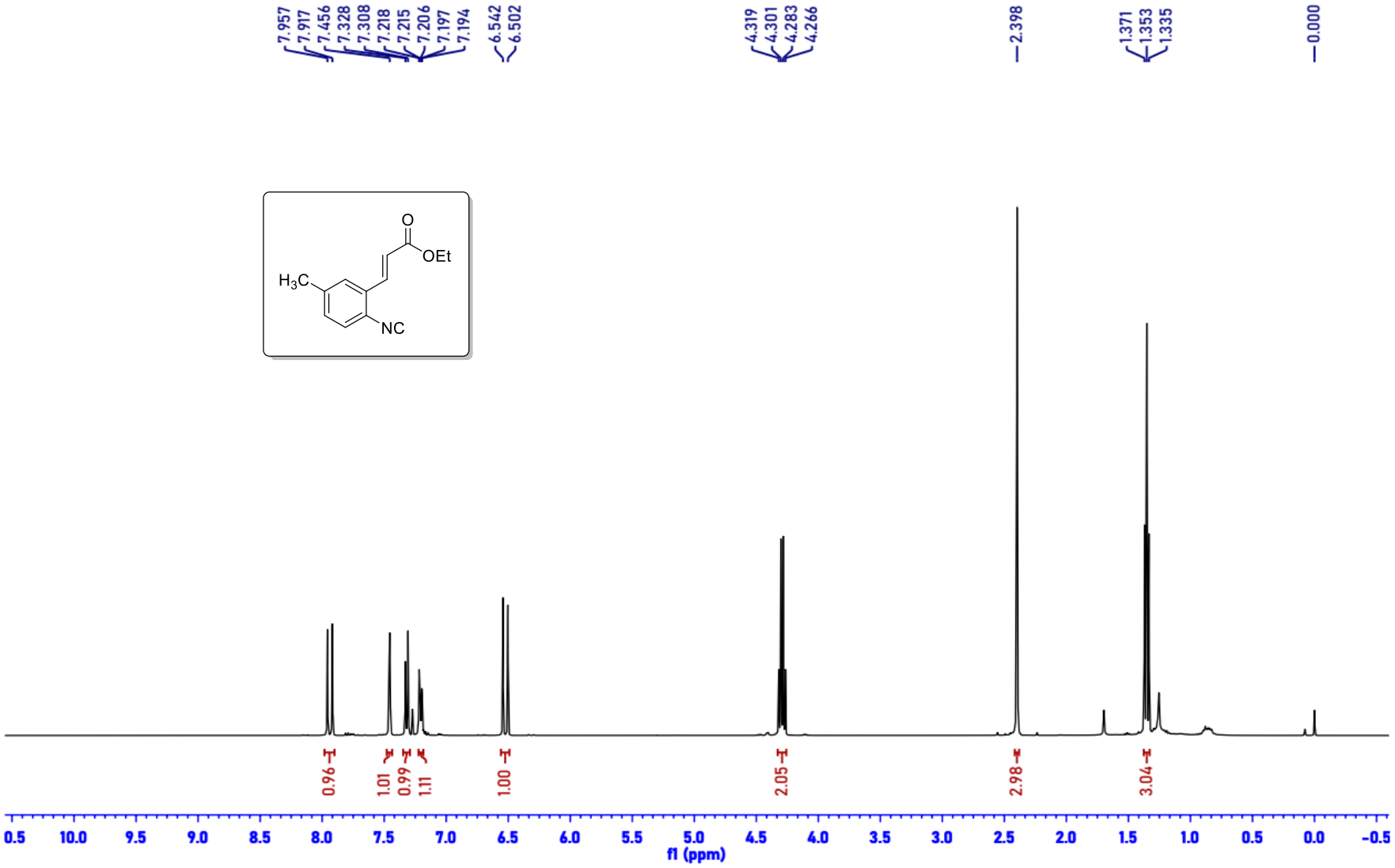
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1al



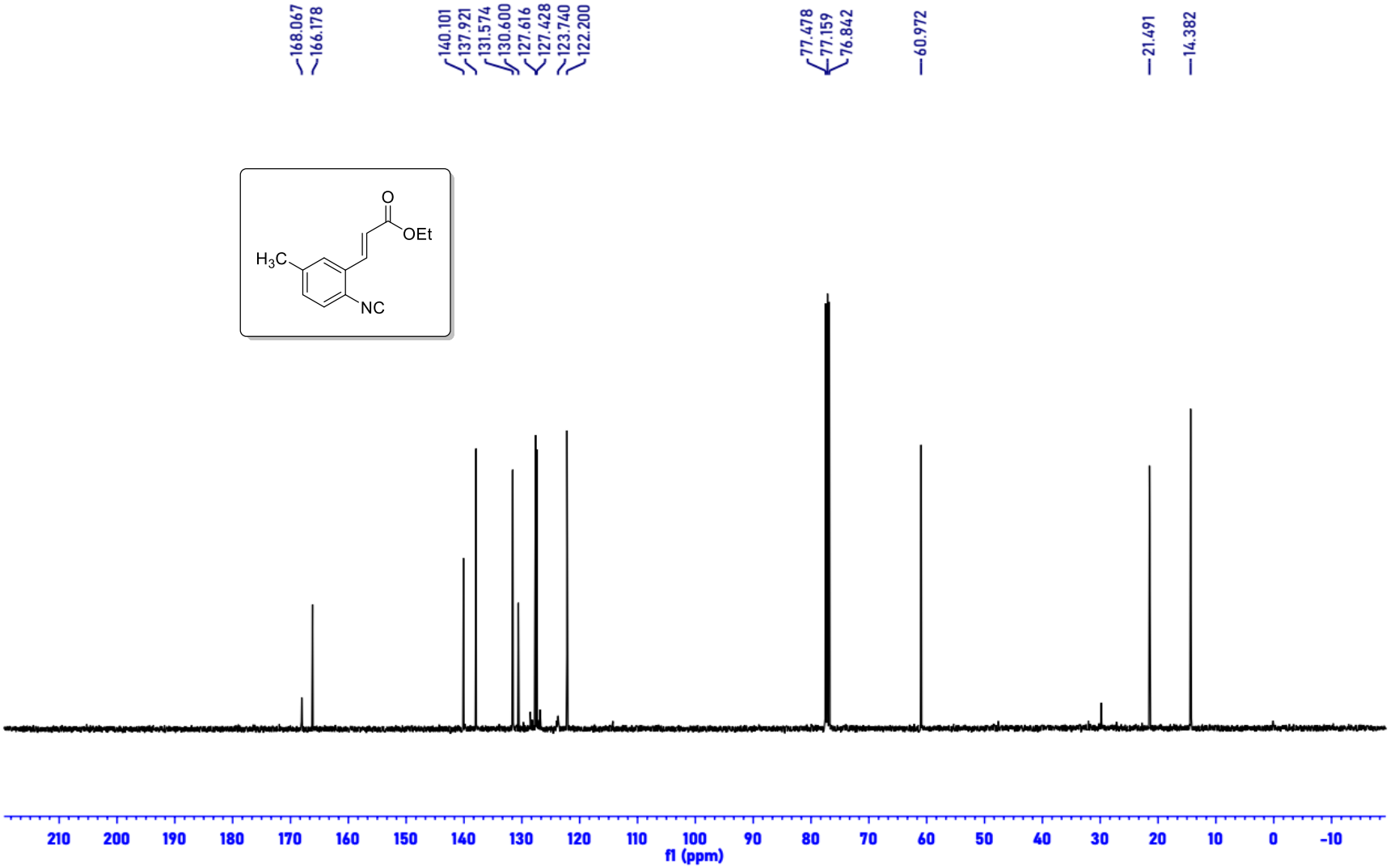
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1al



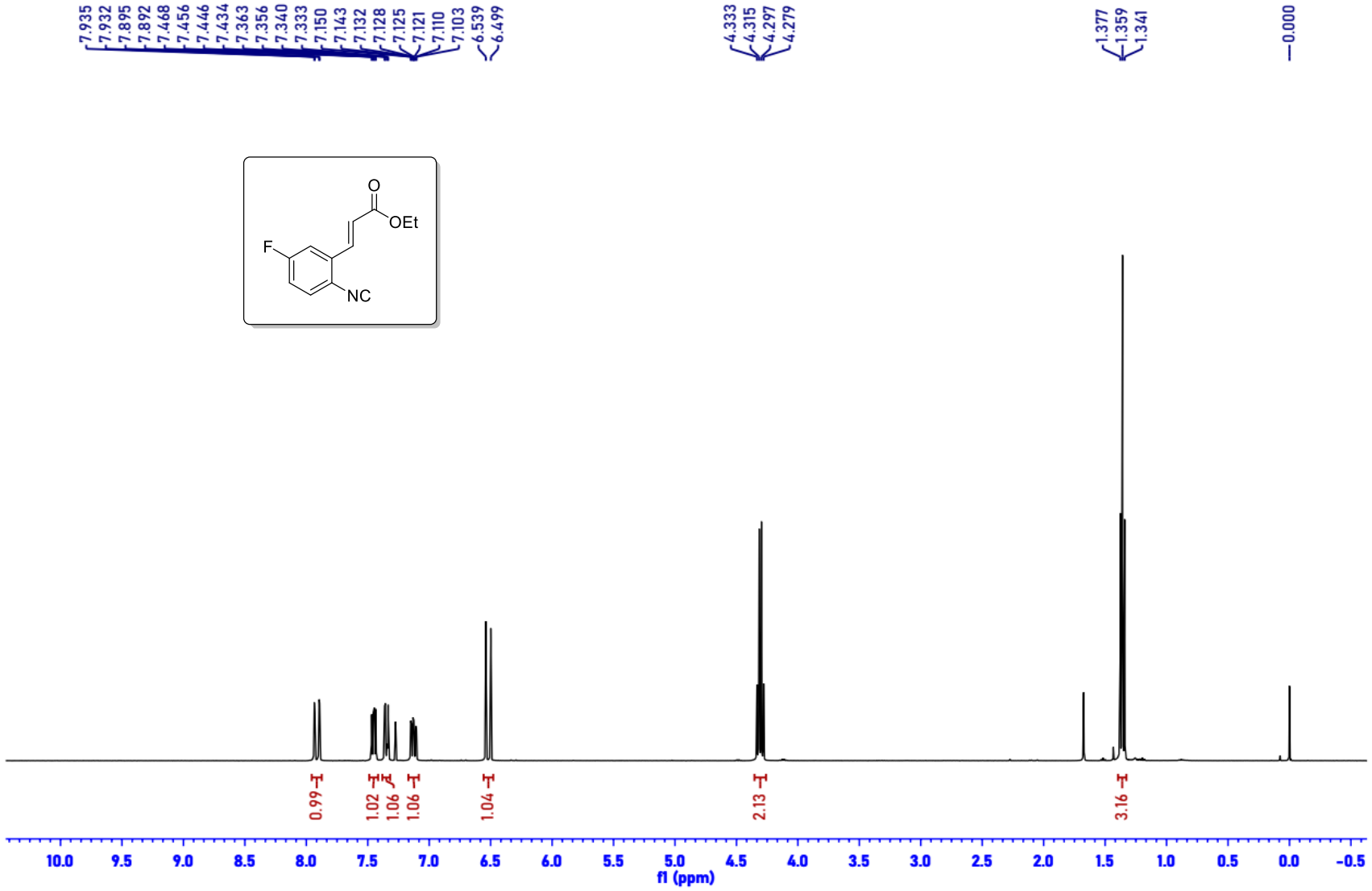
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ba



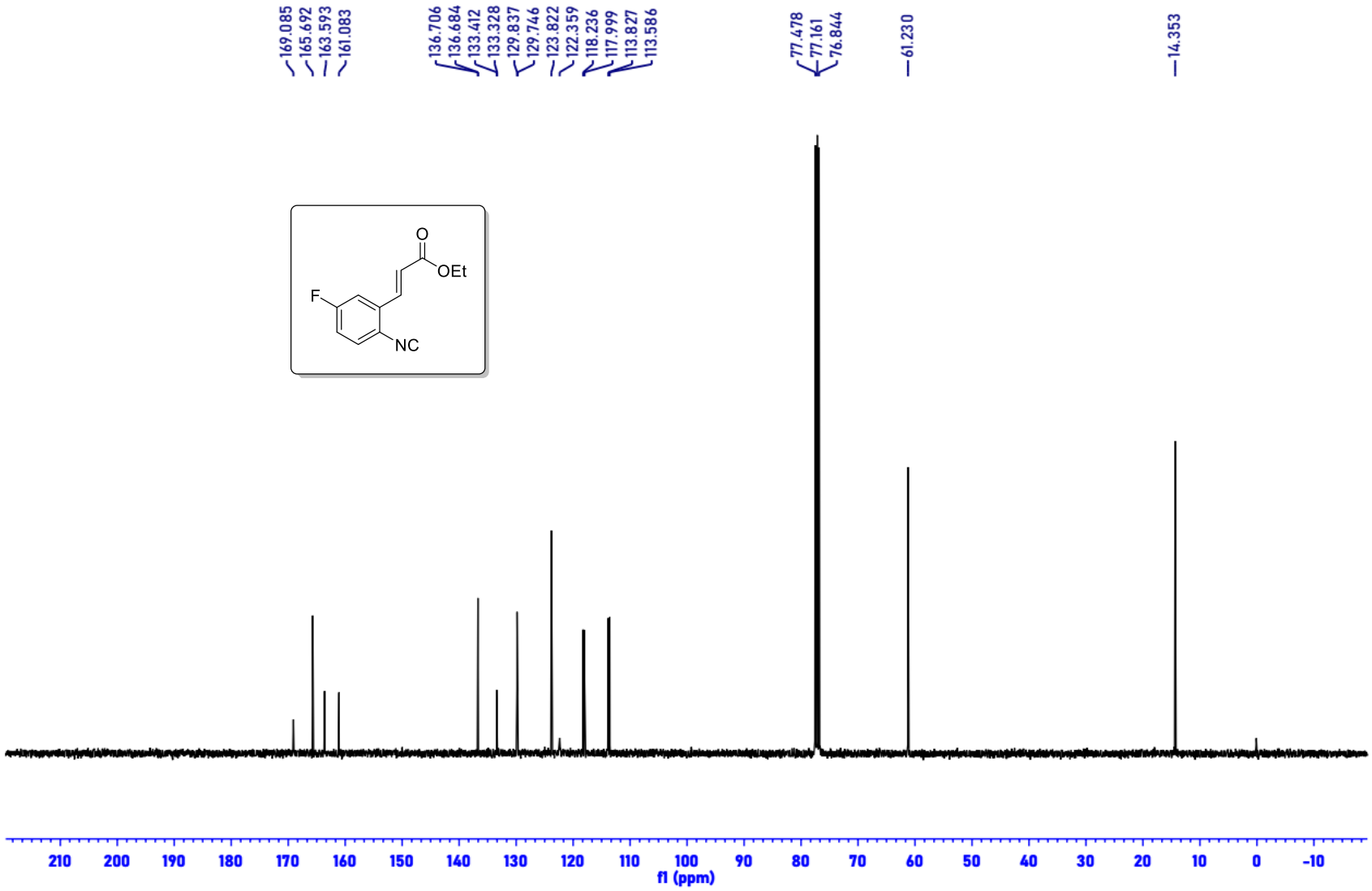
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ba



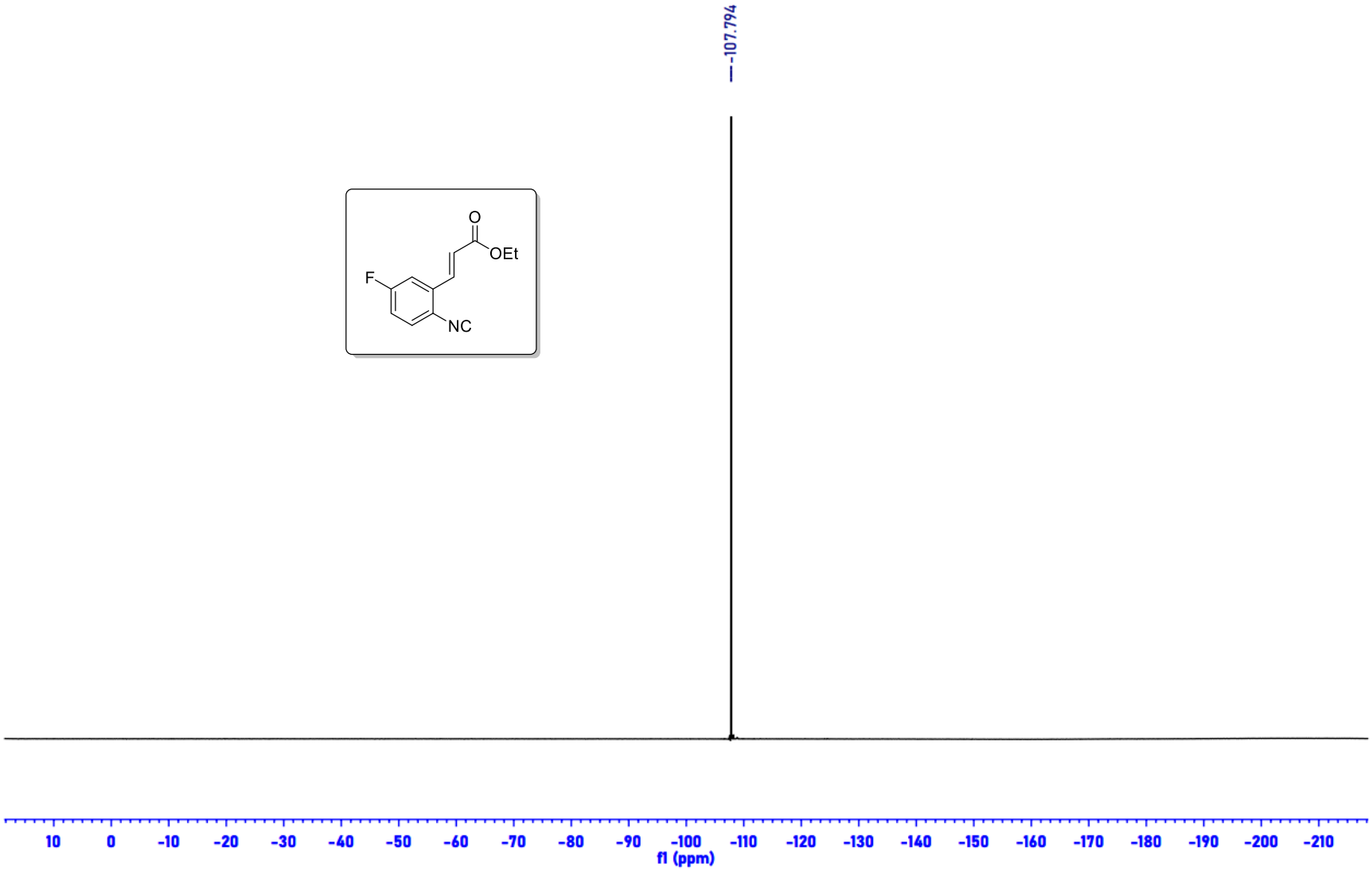
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ca



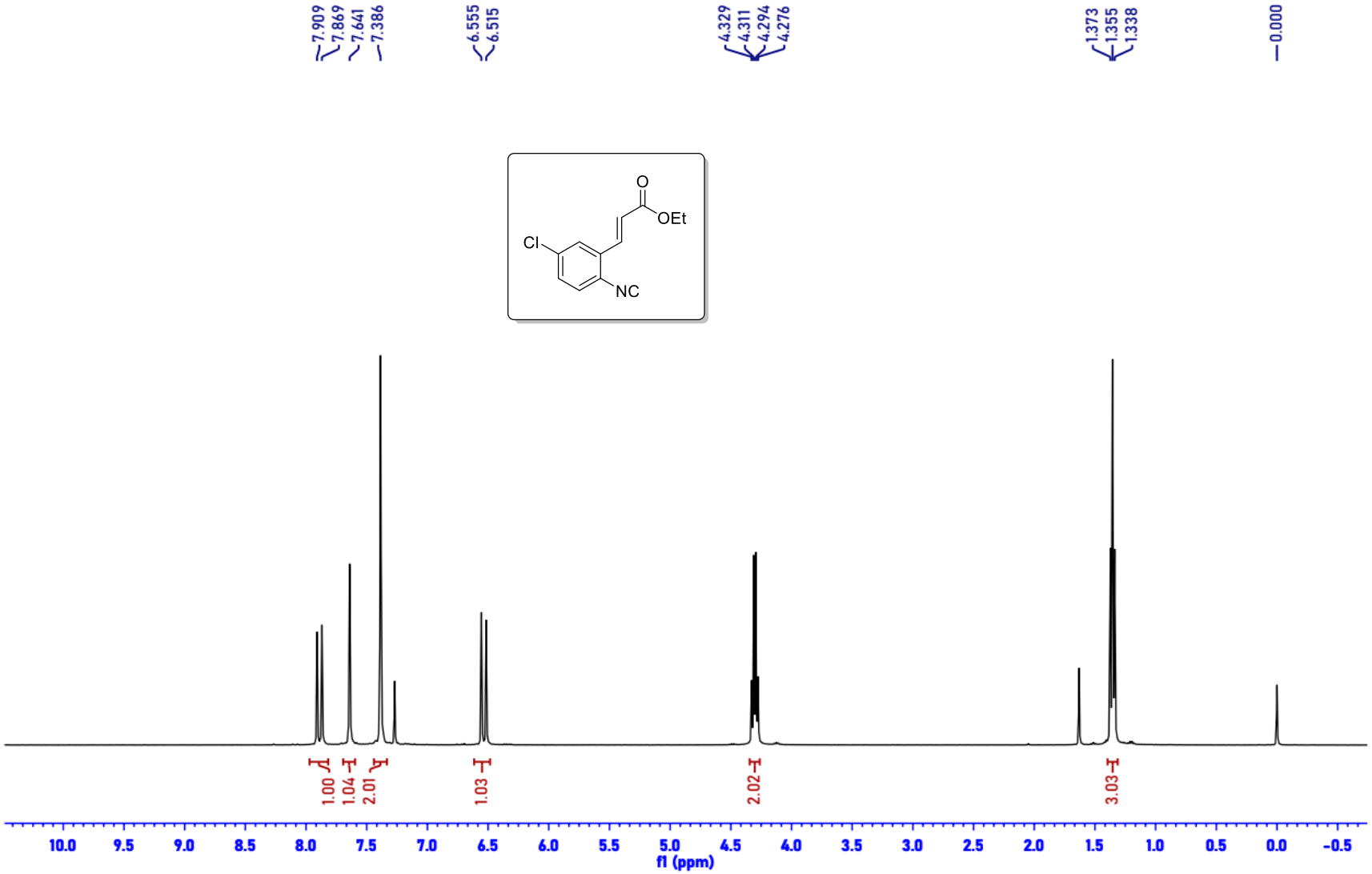
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ca



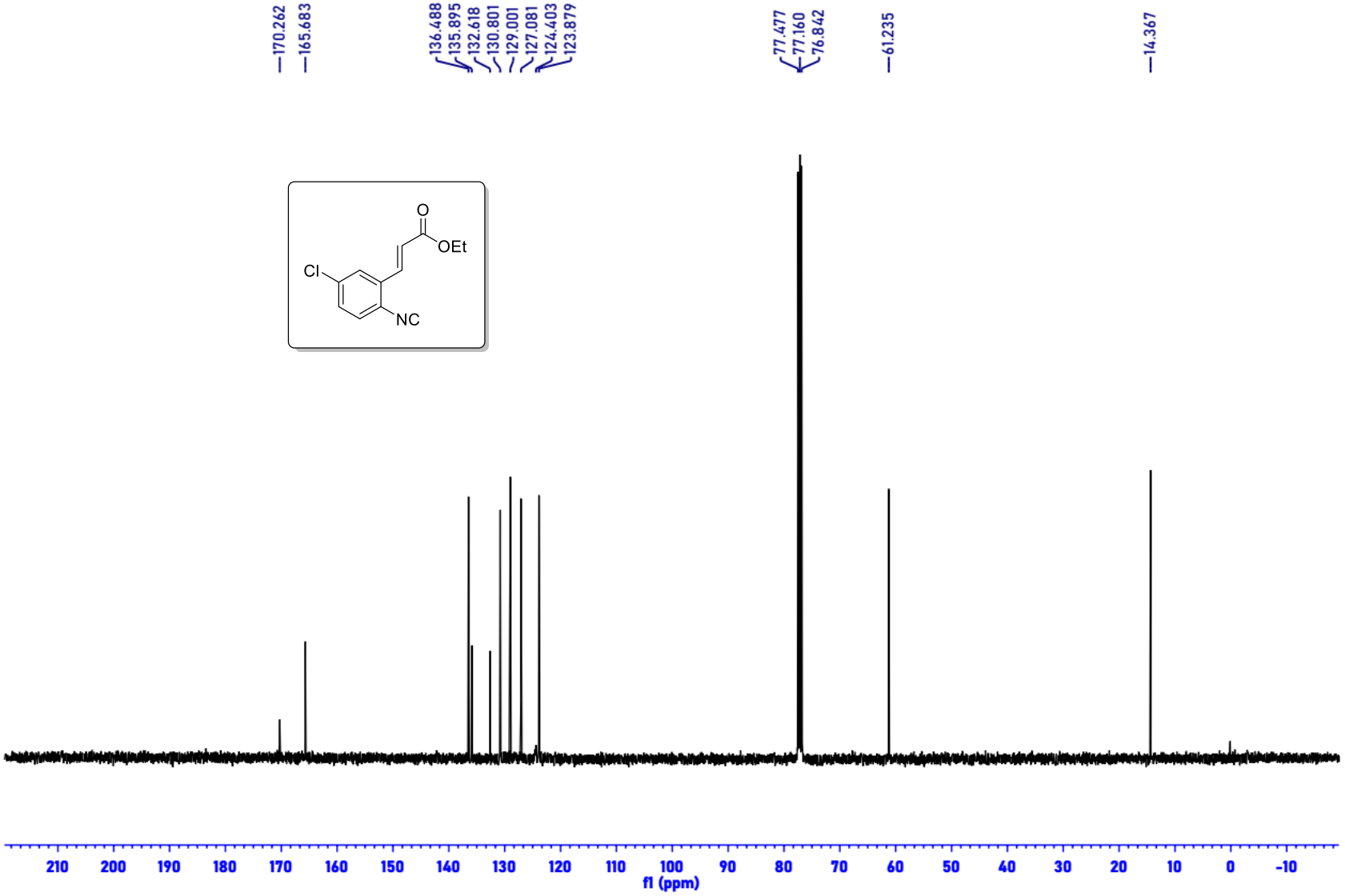
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1ca



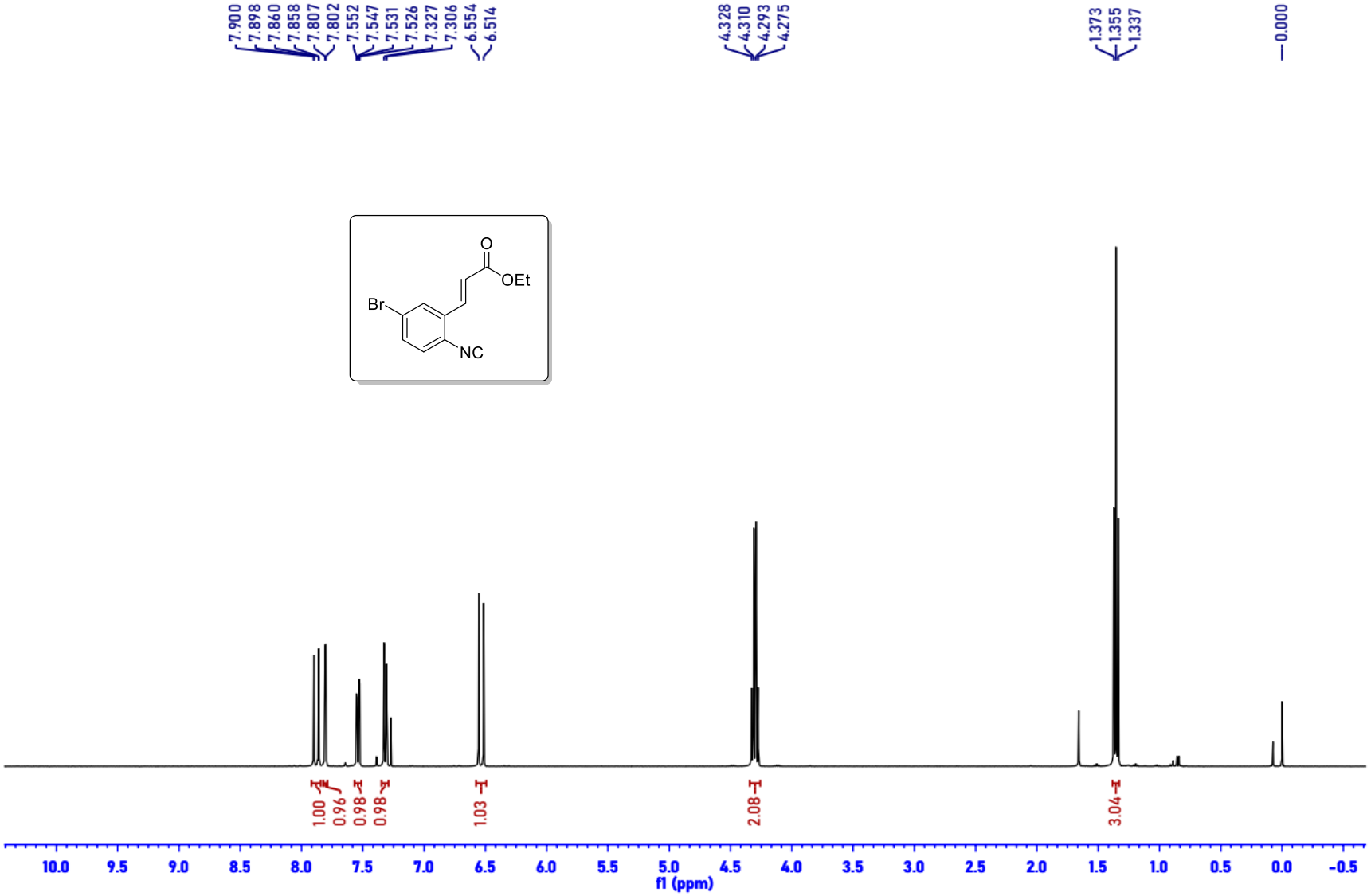
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1da



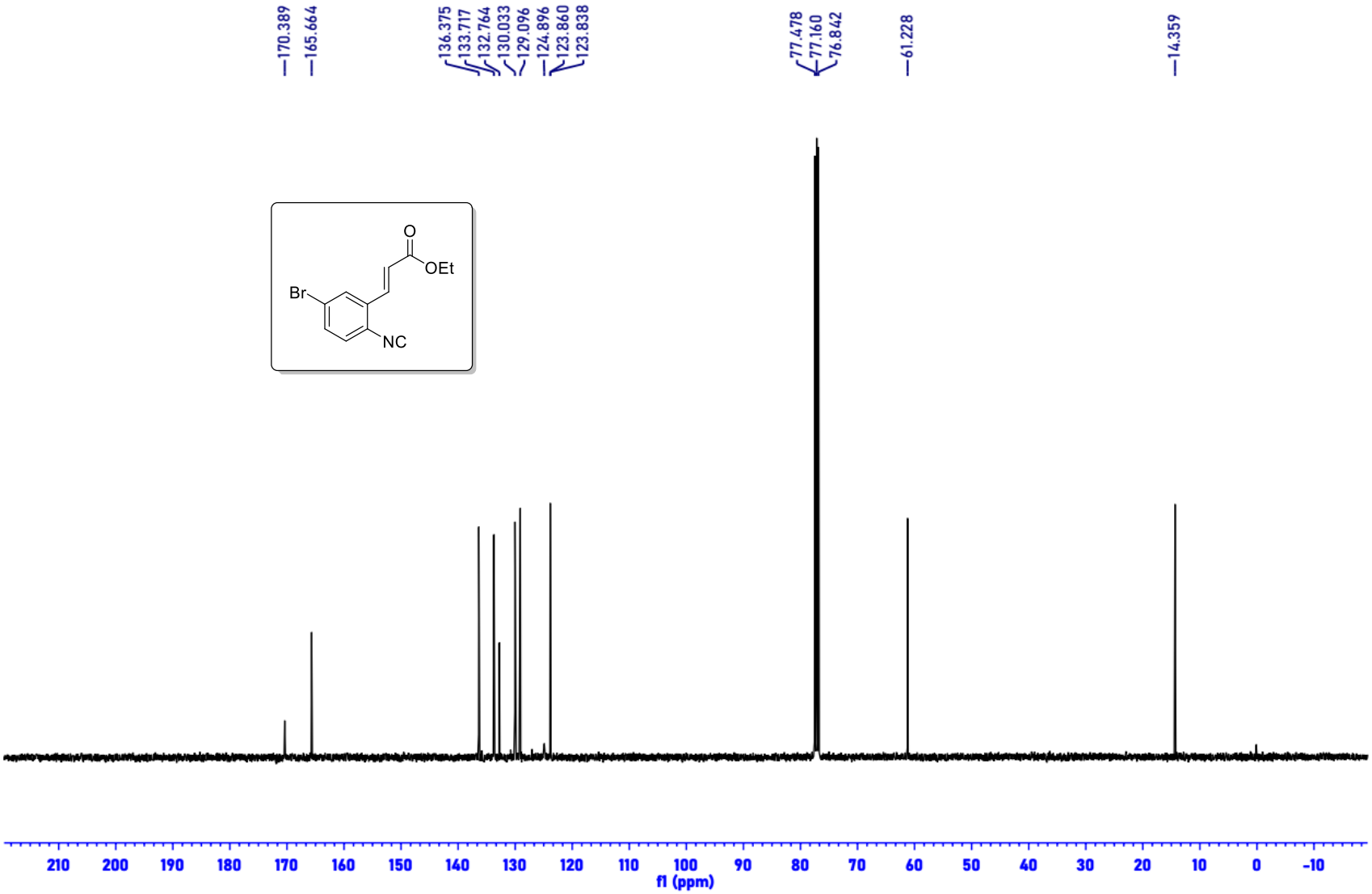
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1da



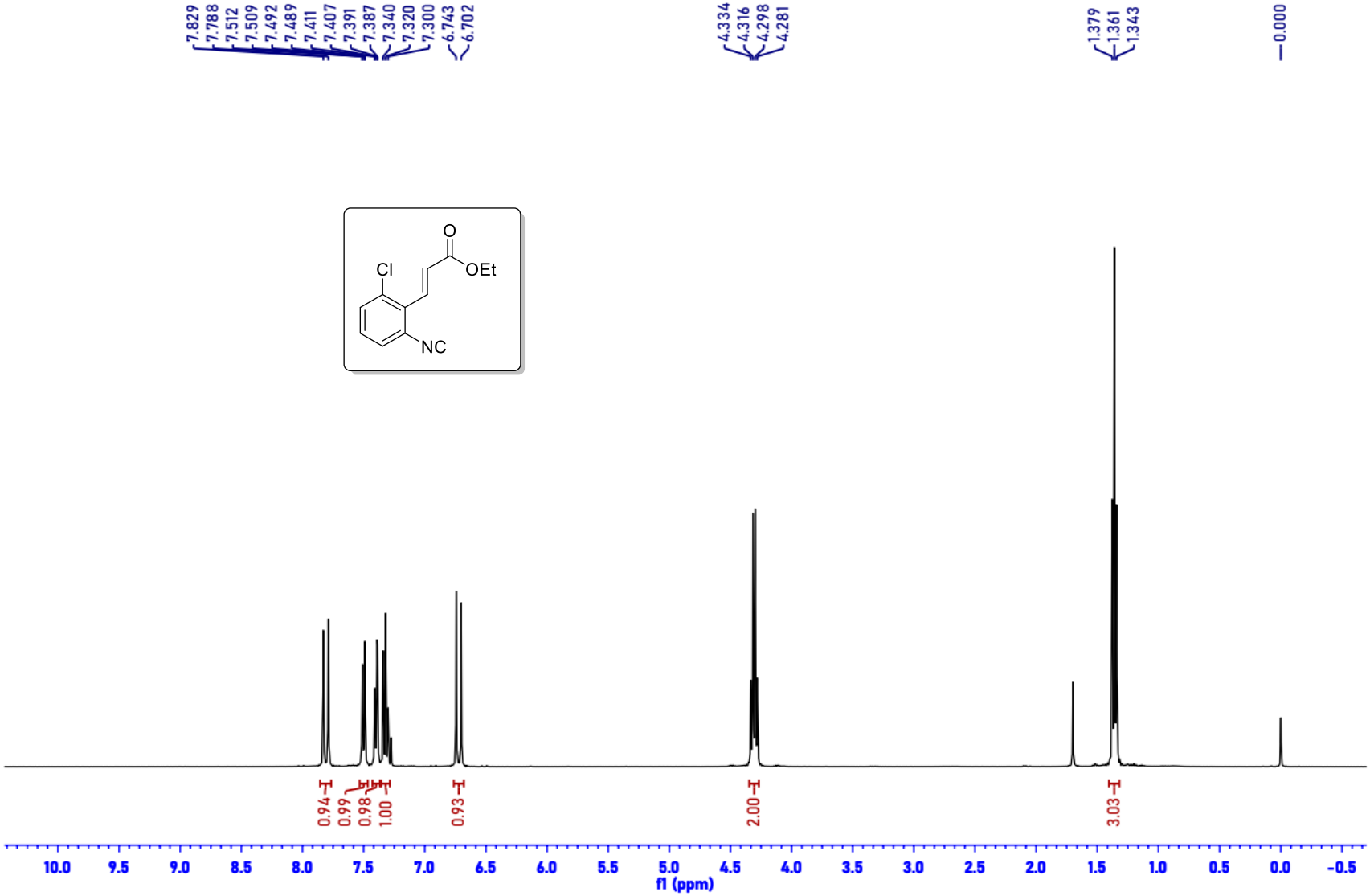
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ea



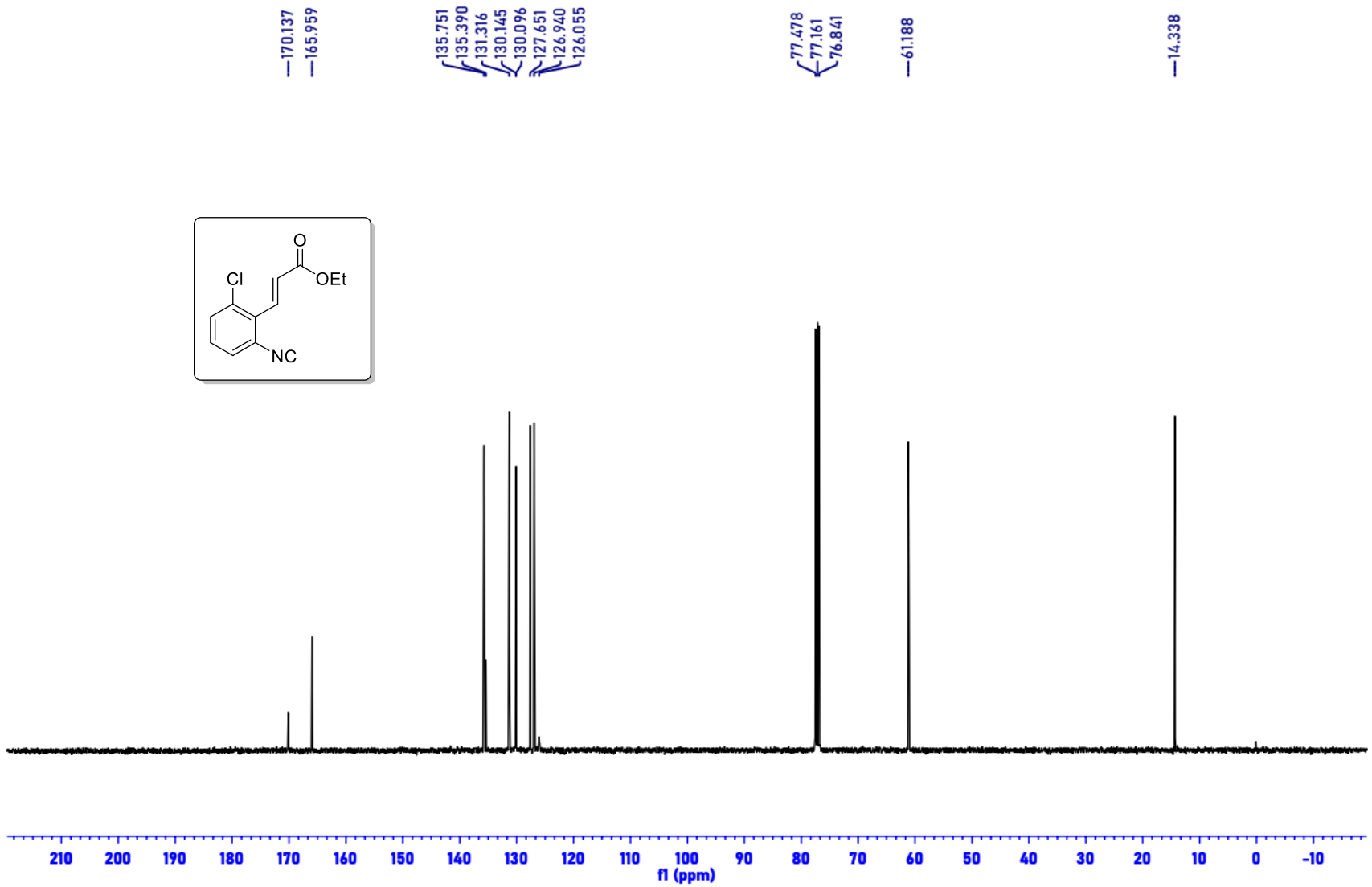
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ea



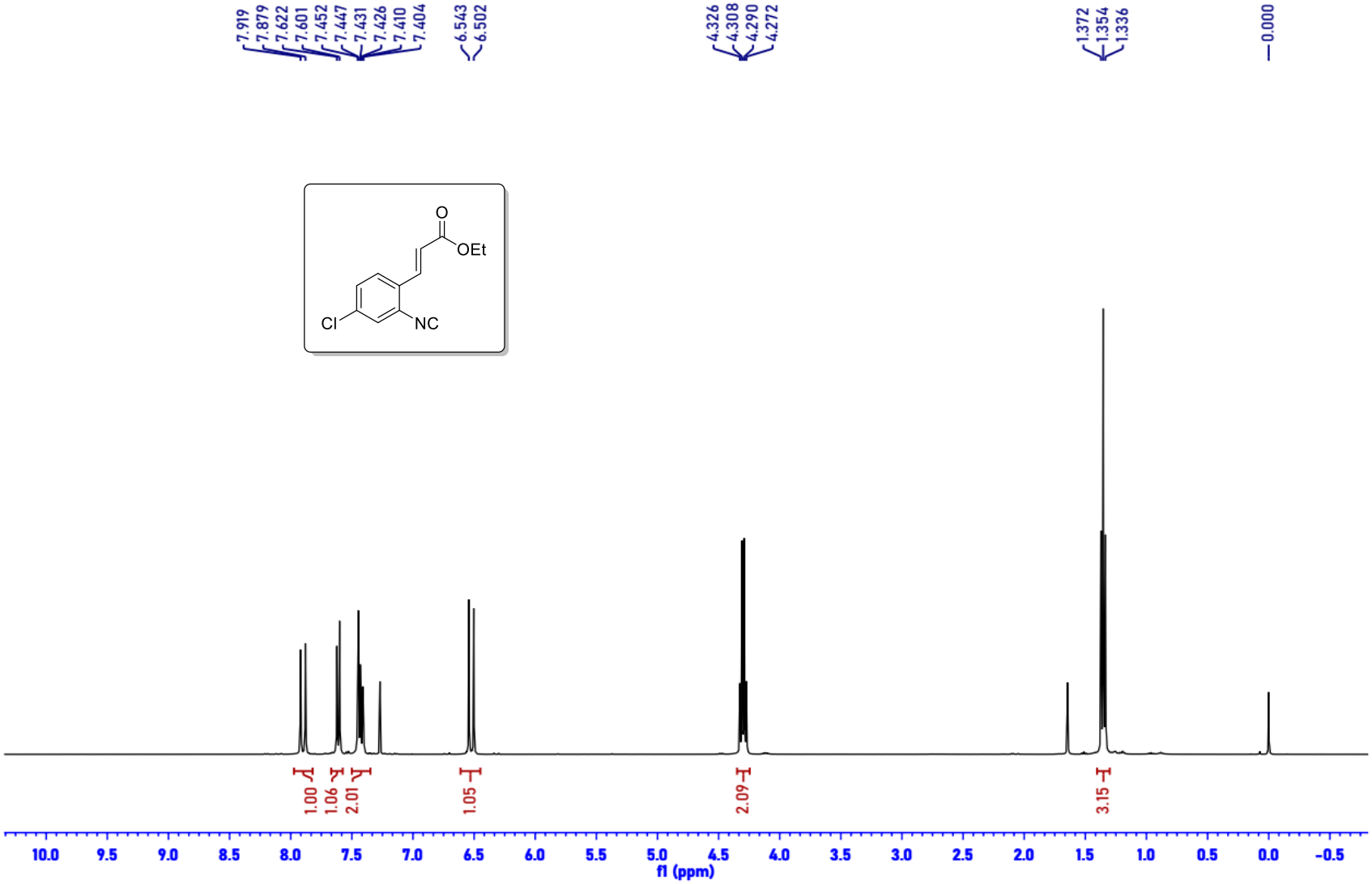
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1fa



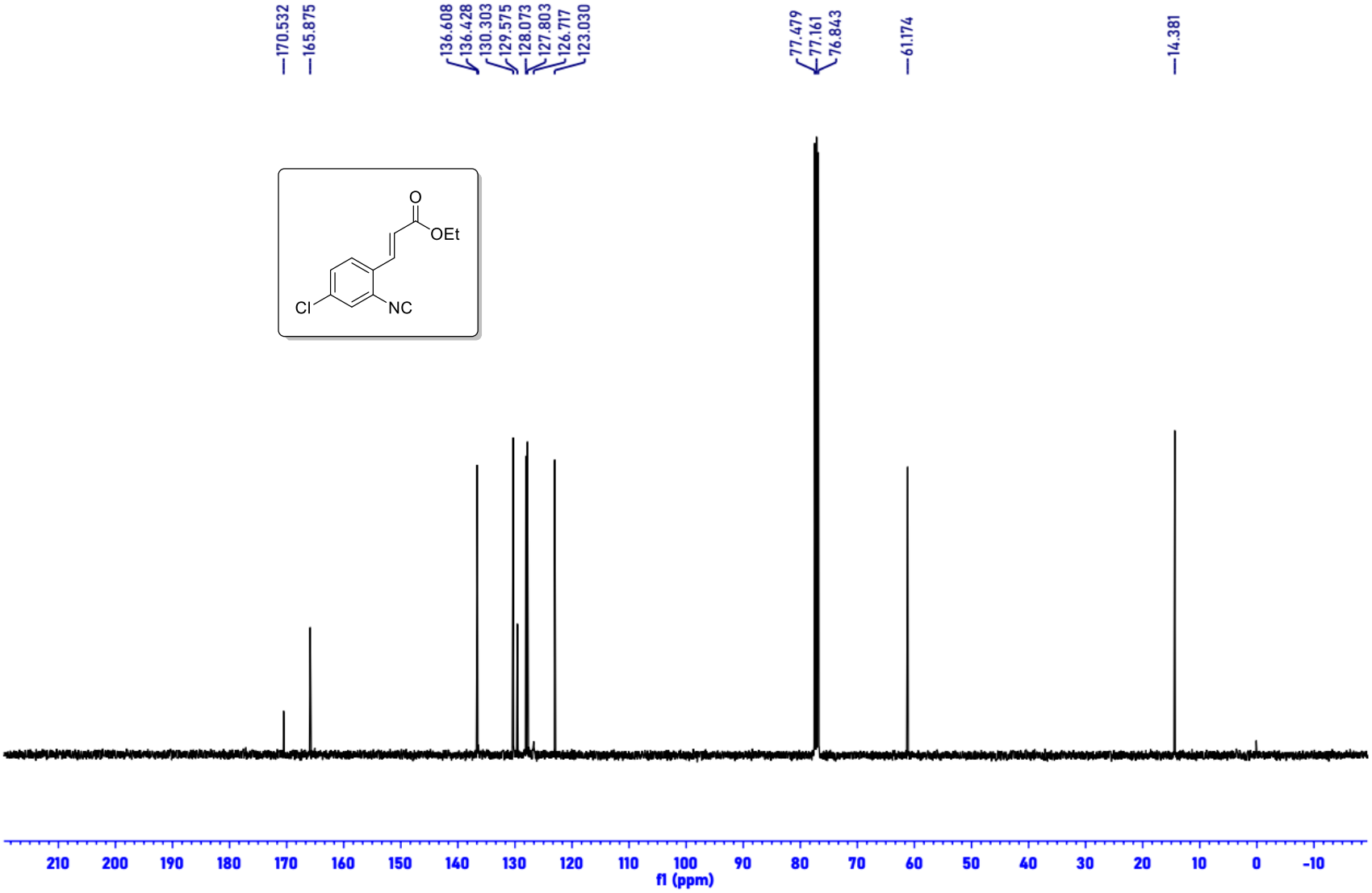
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1fa



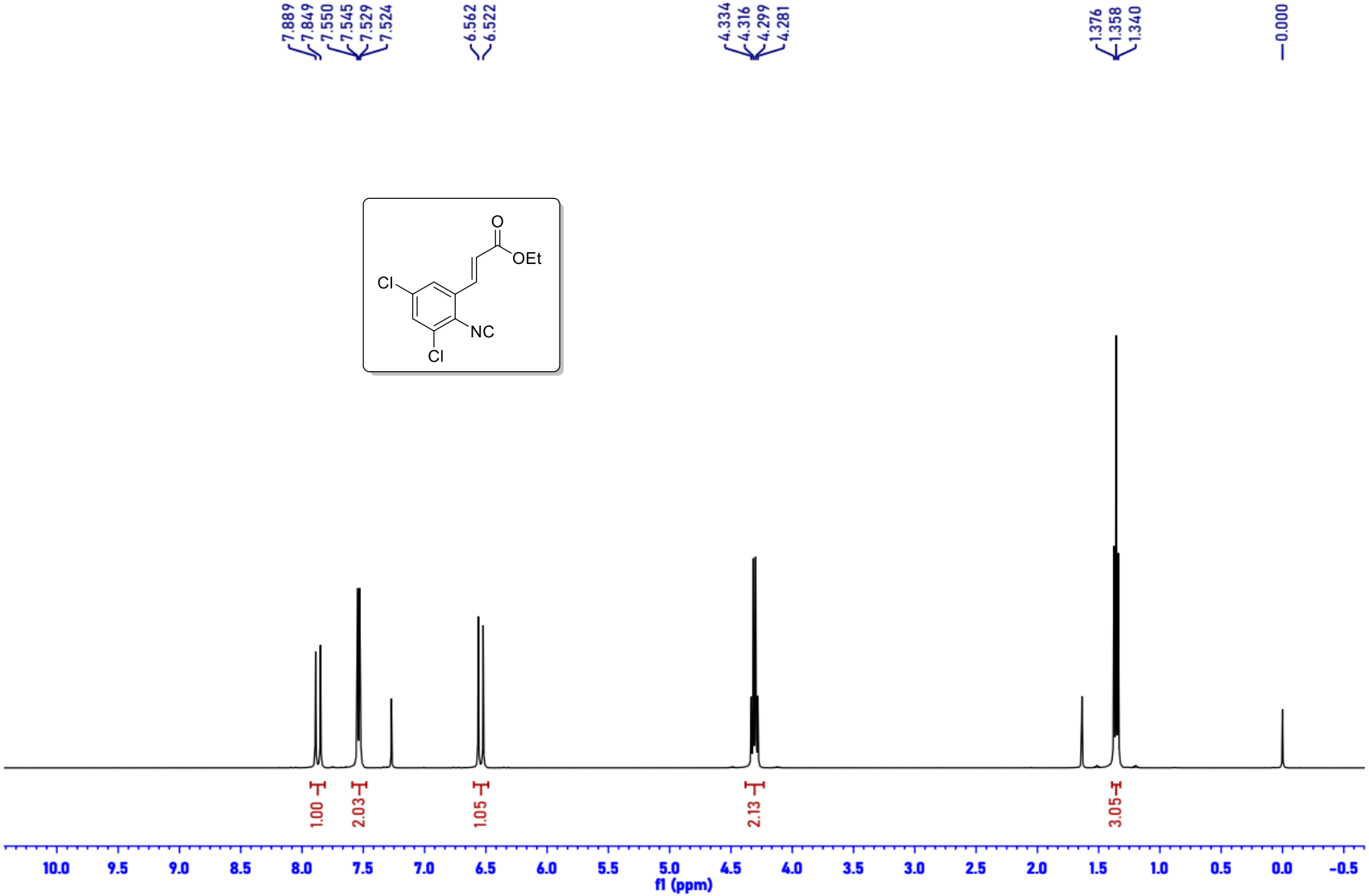
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ga



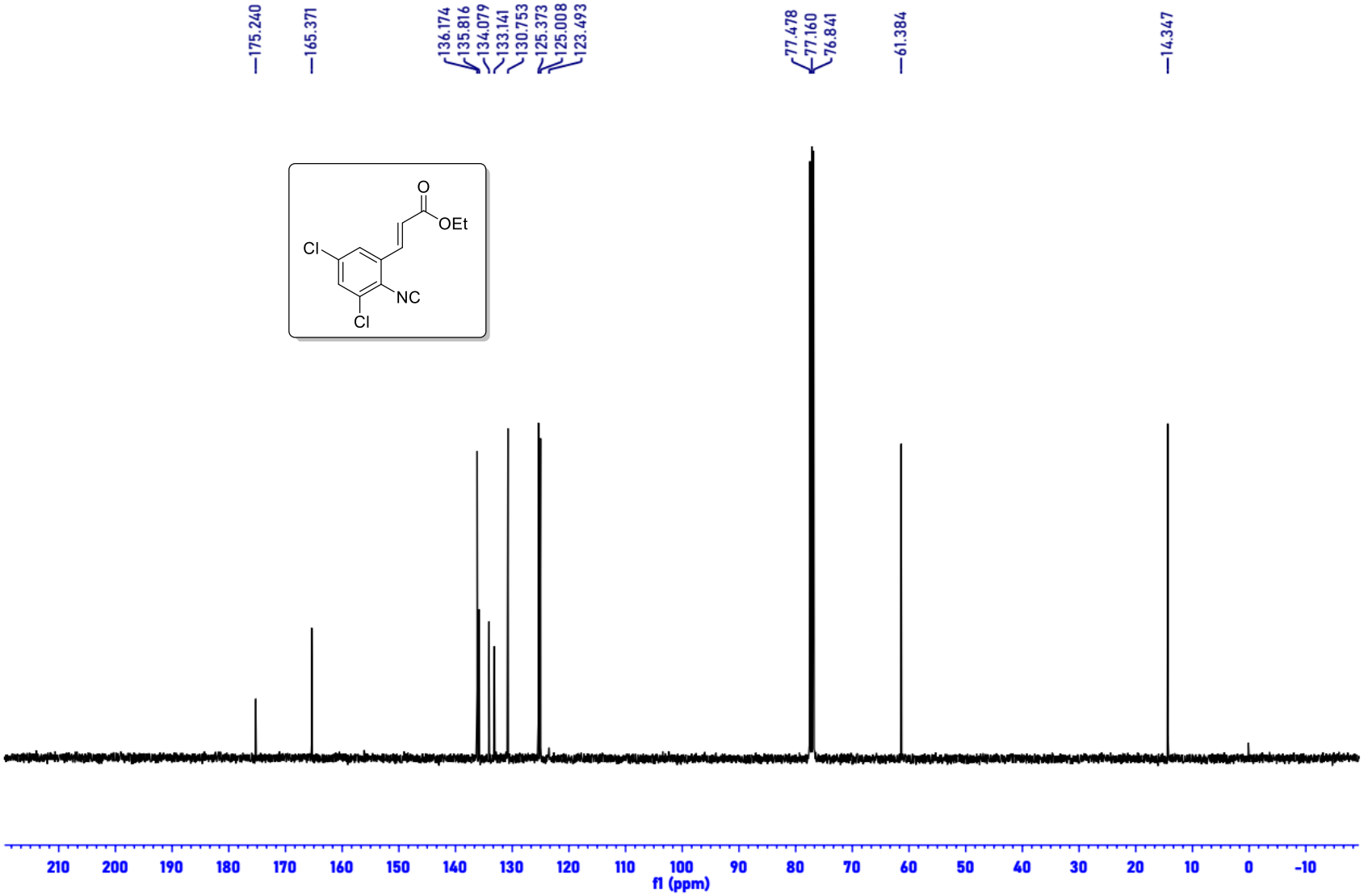
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ga



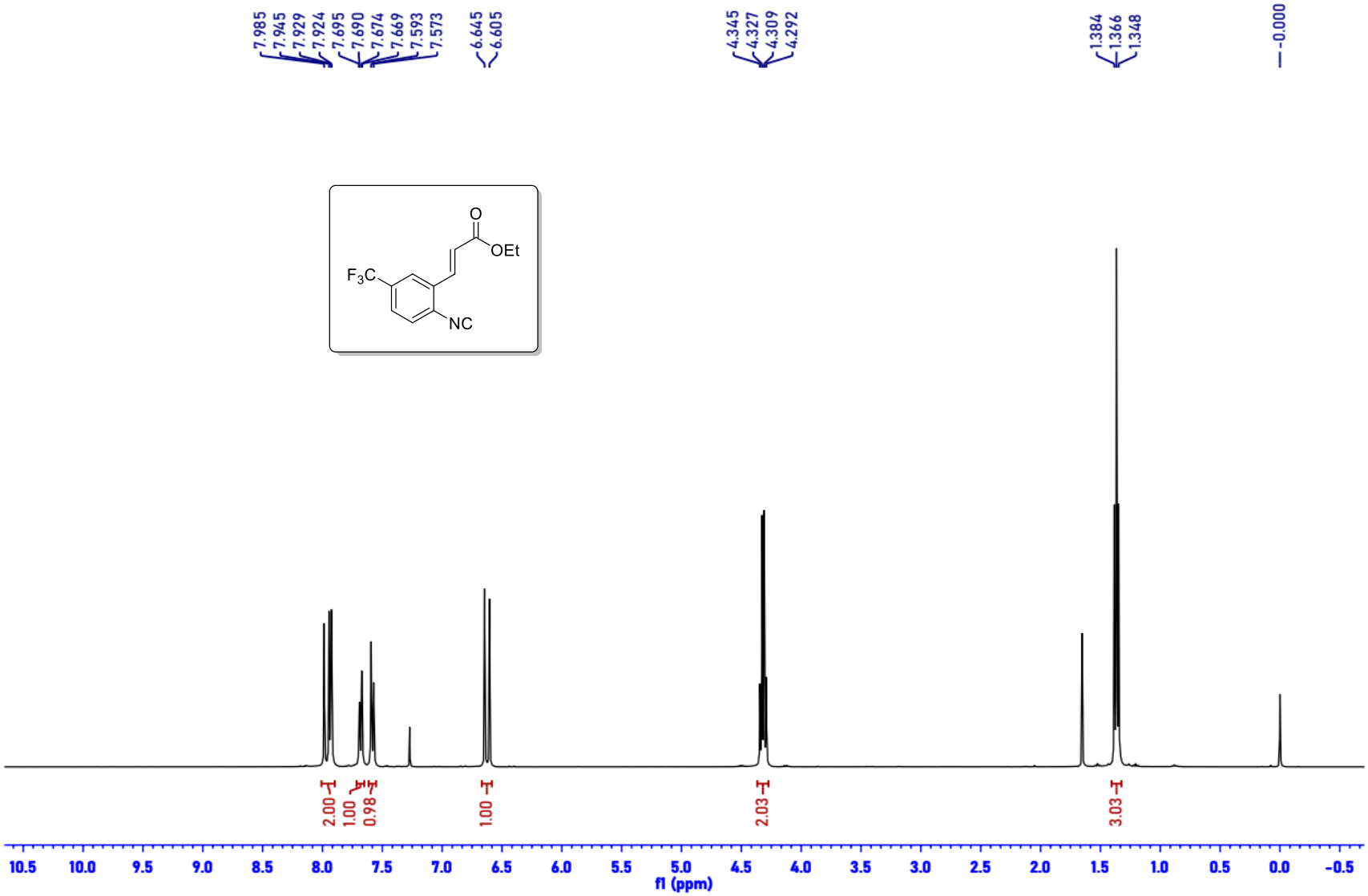
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ha



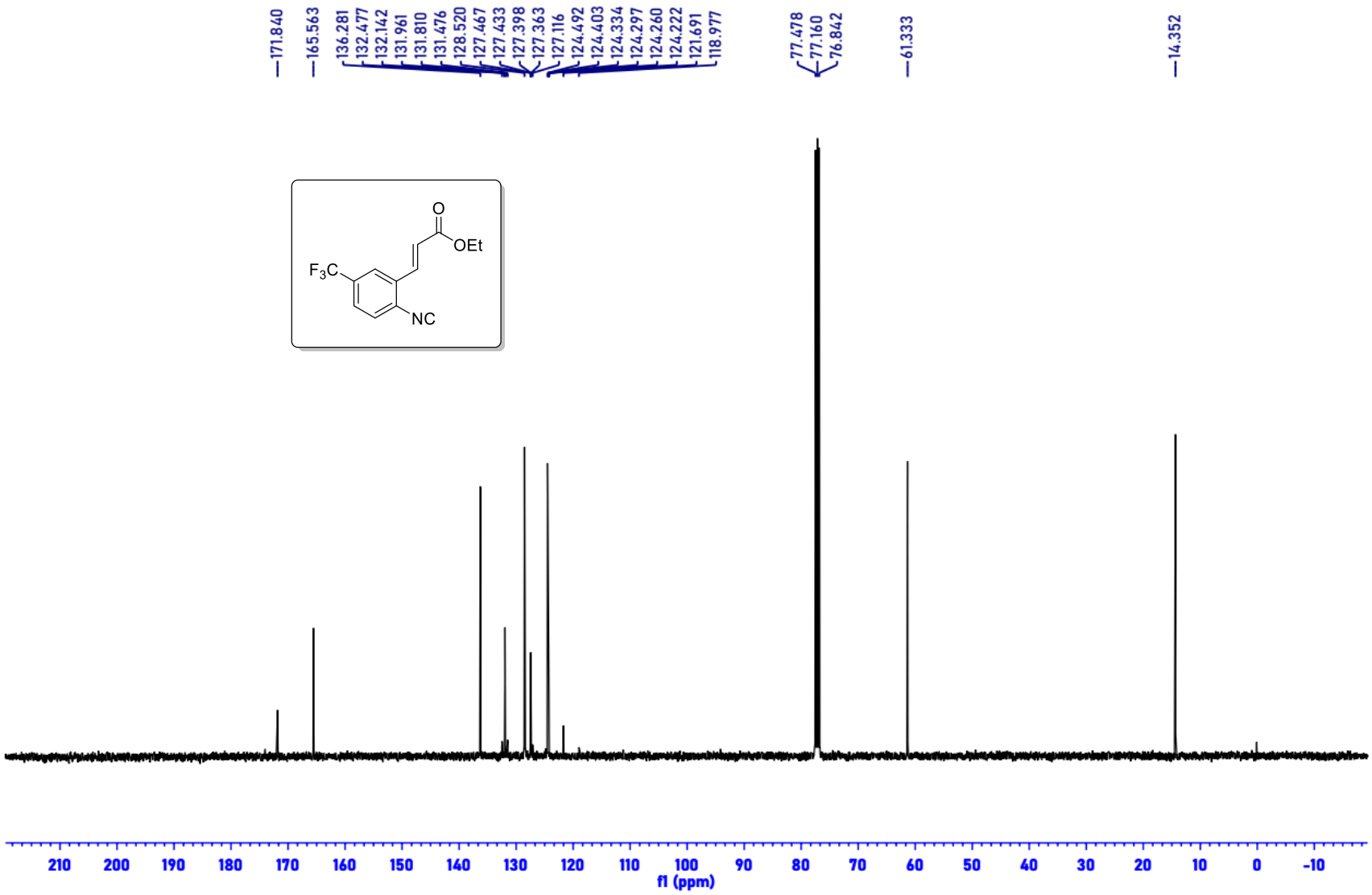
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ha



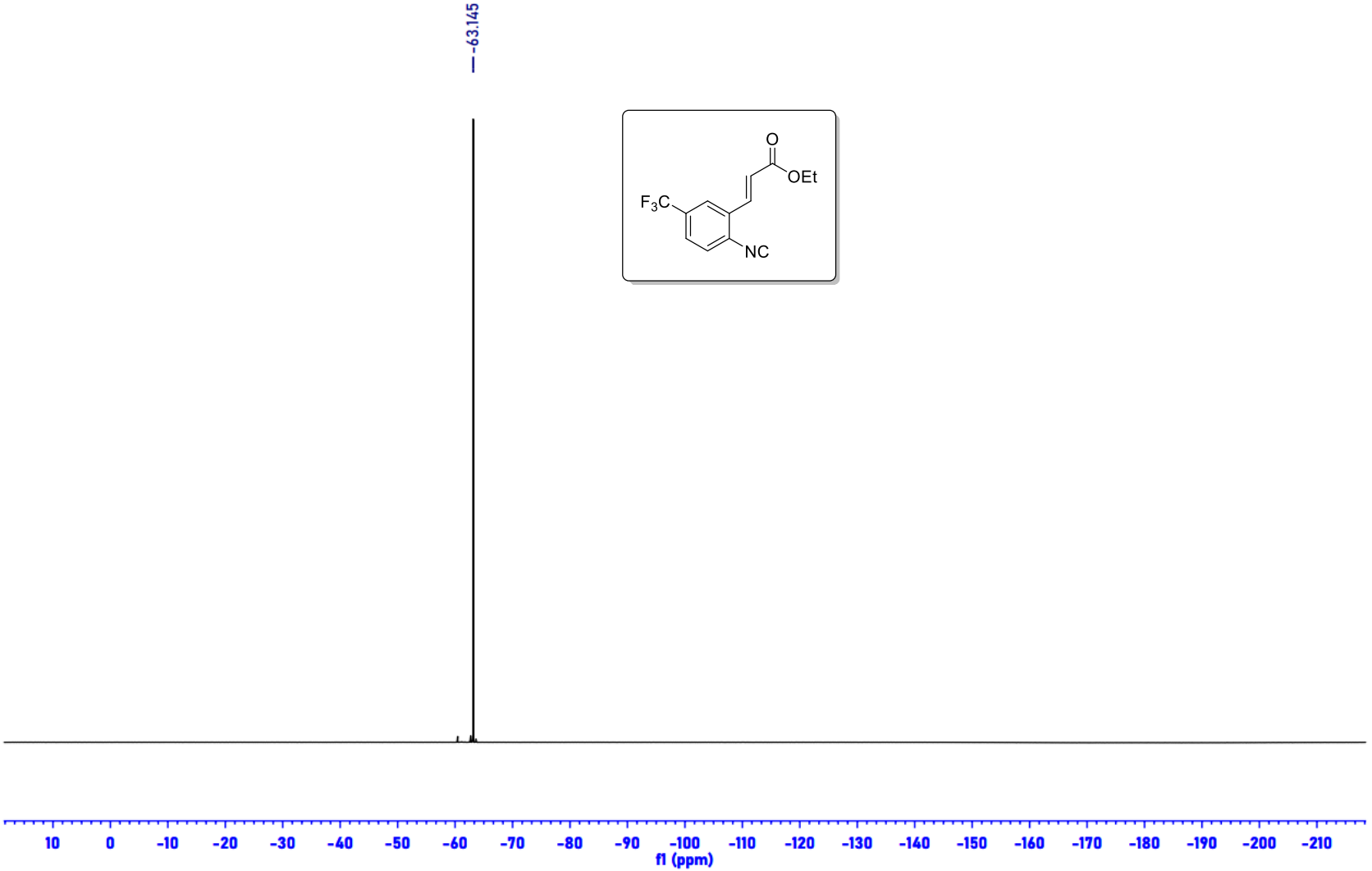
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ia



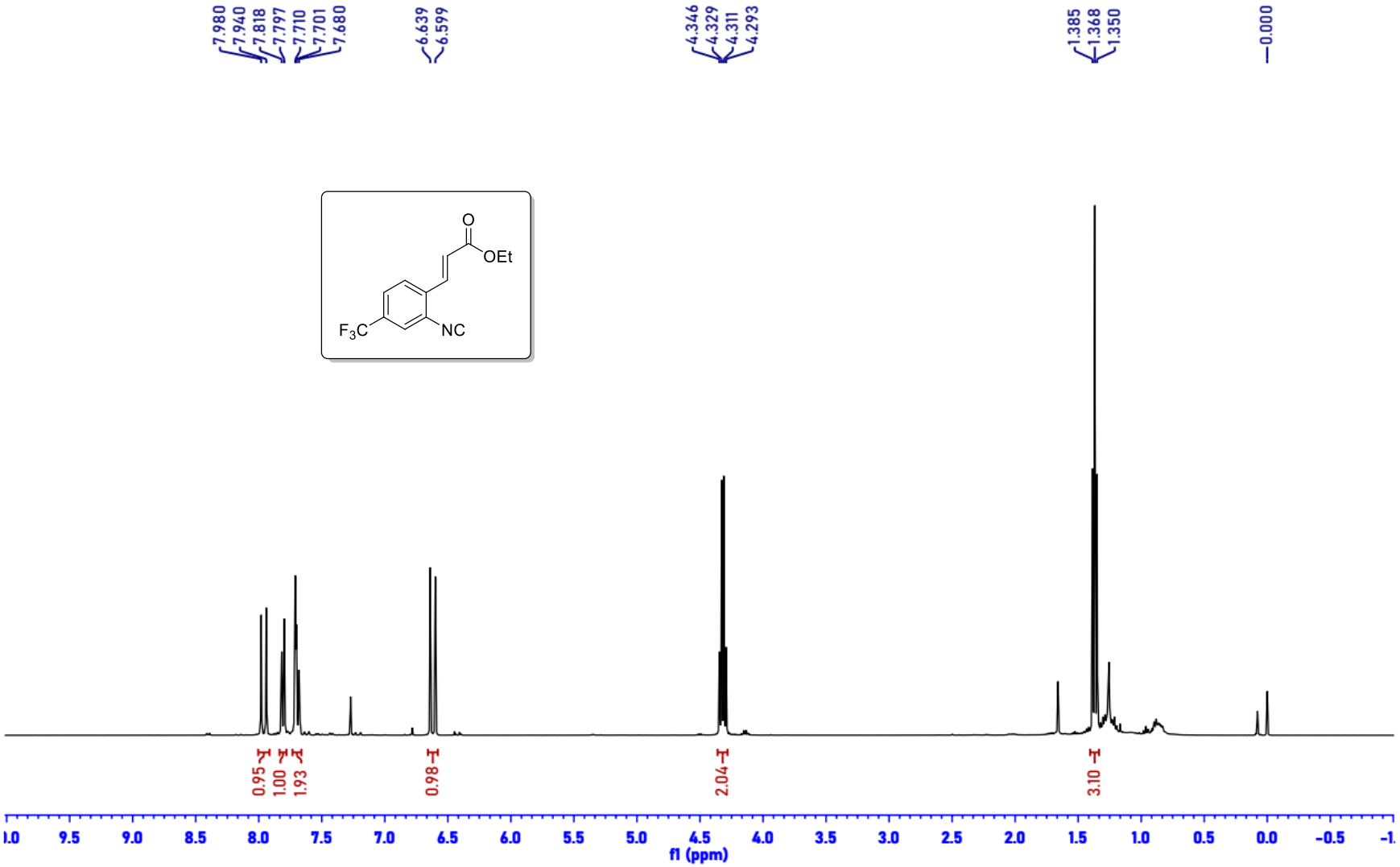
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ia



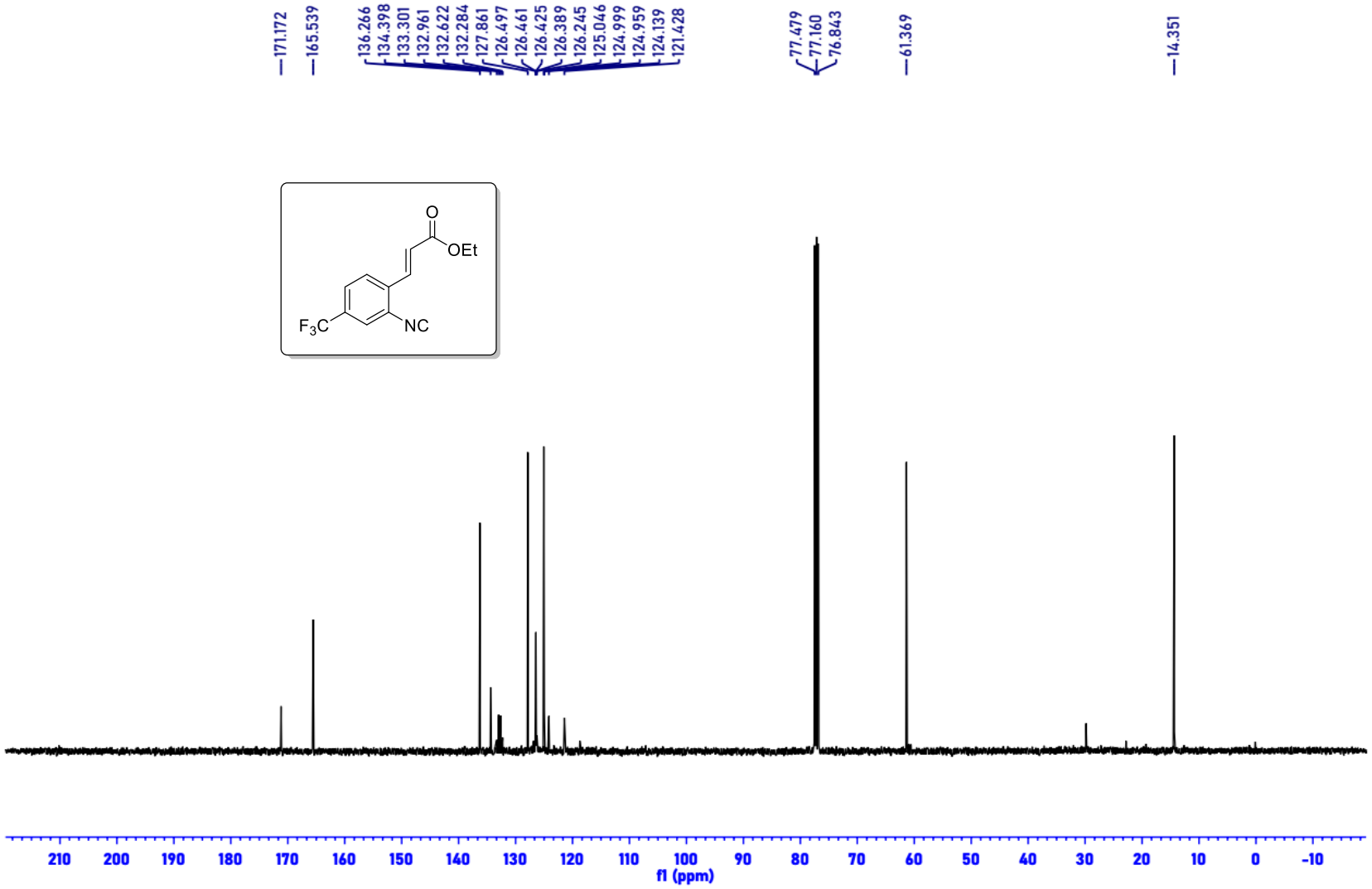
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1ia



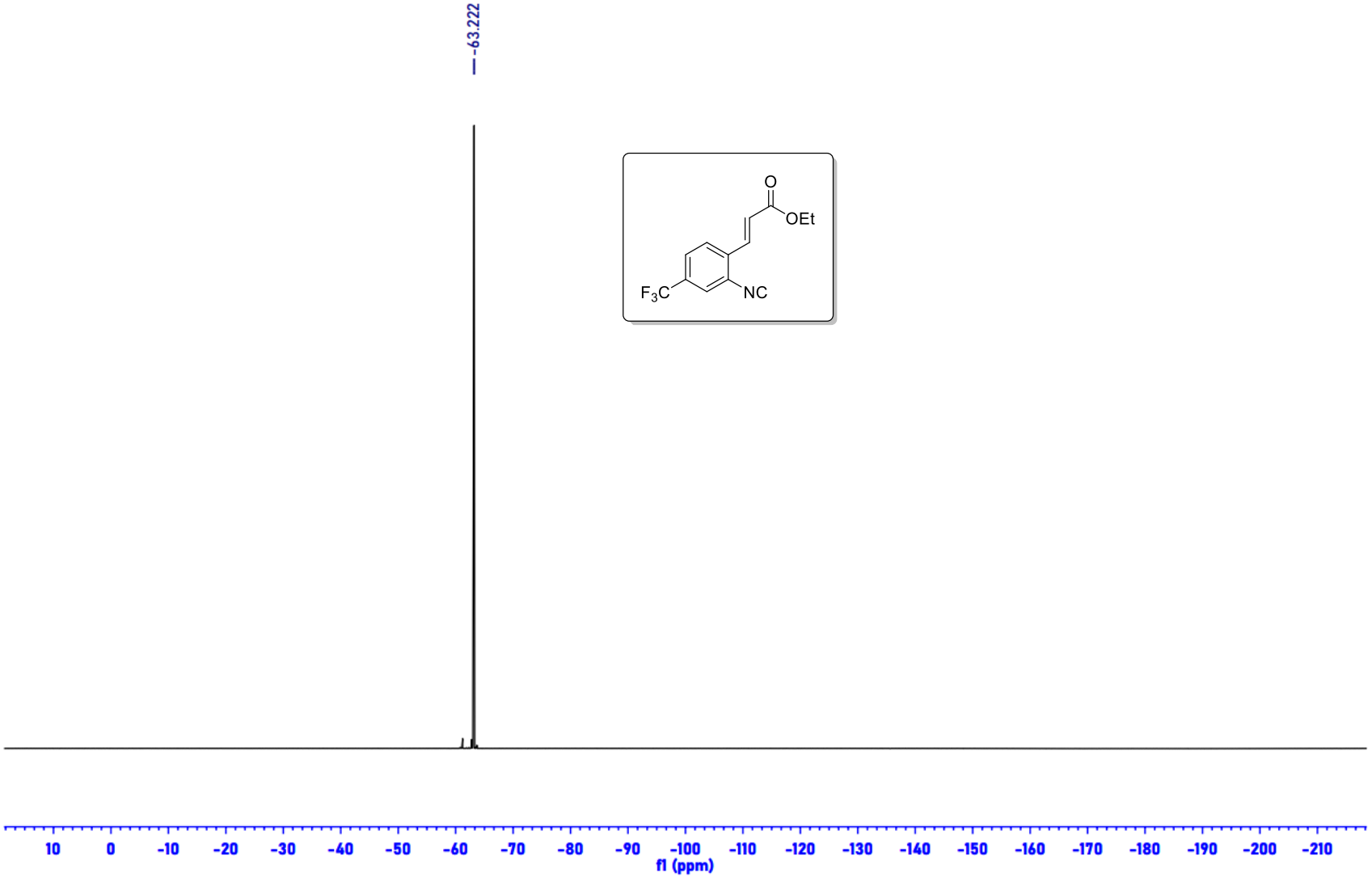
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ja



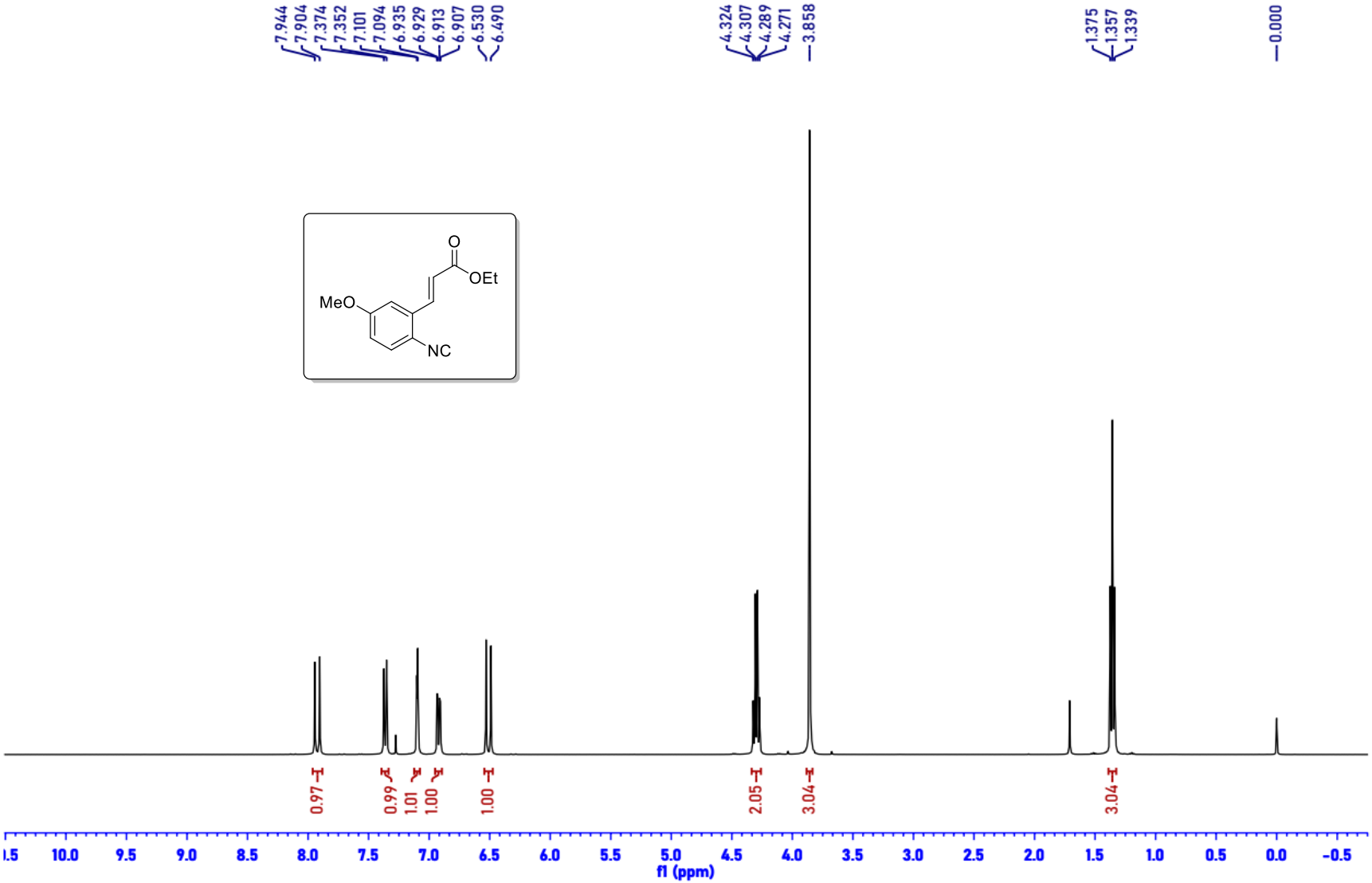
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ja



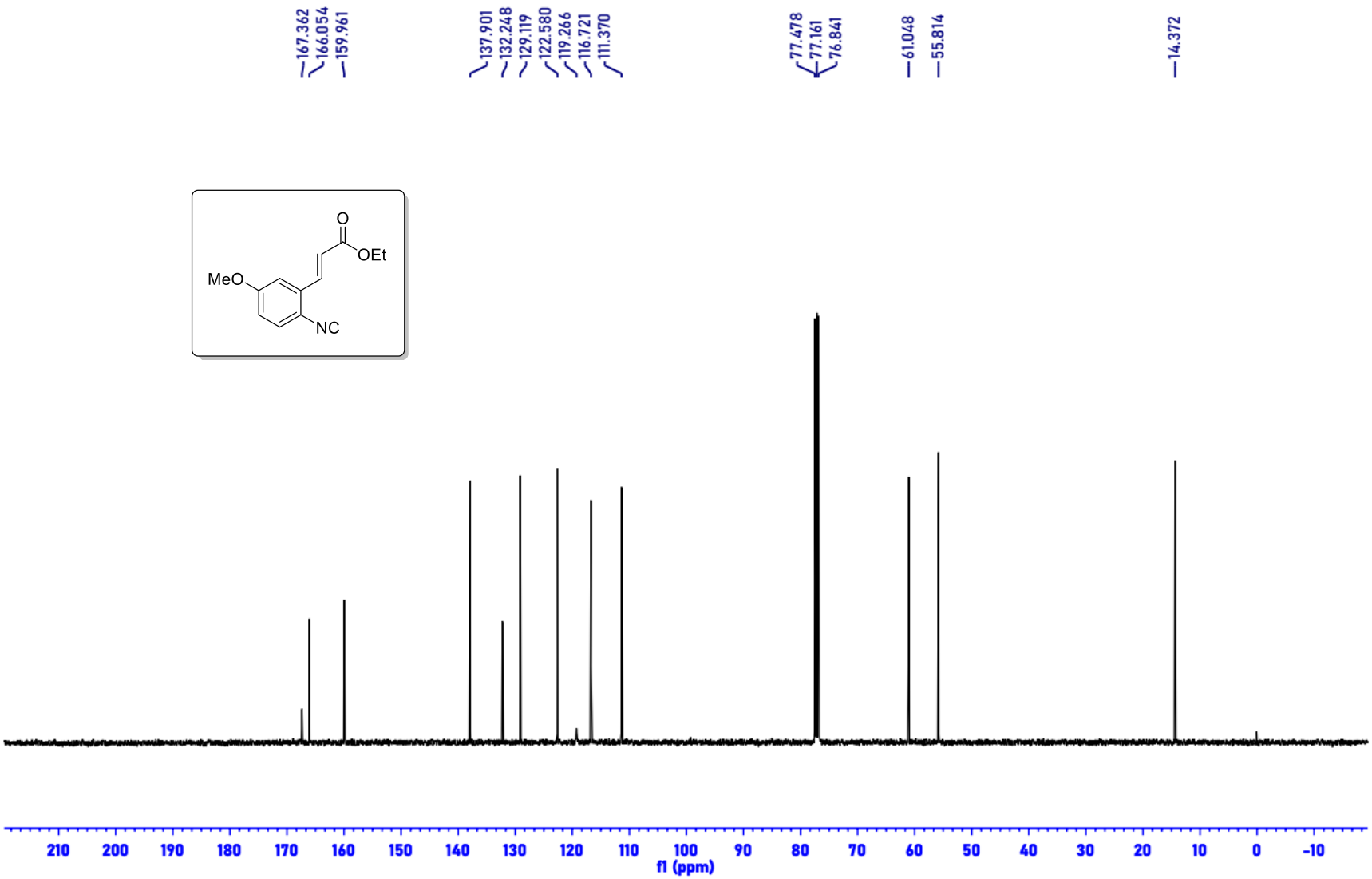
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1ja



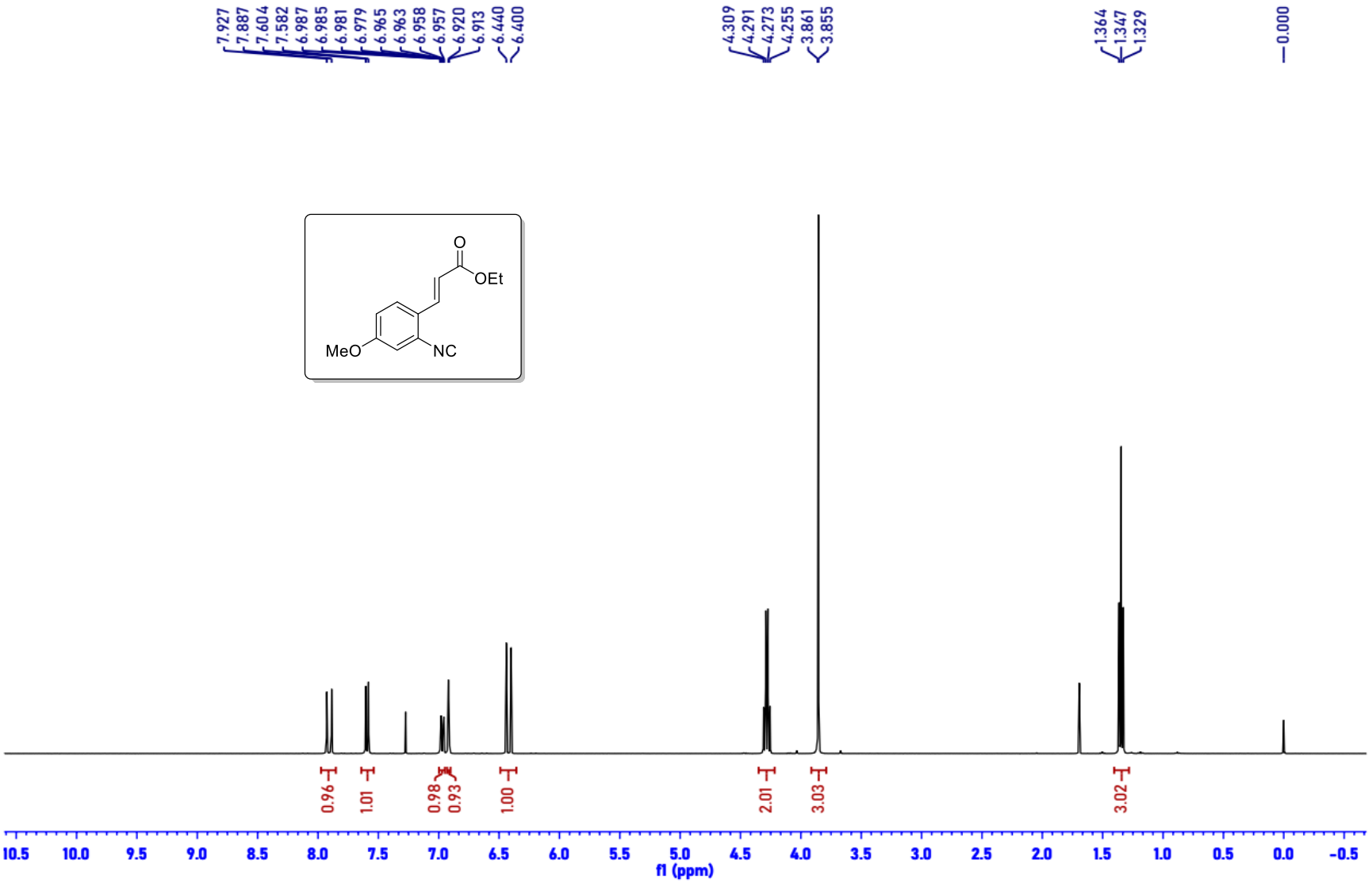
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ka



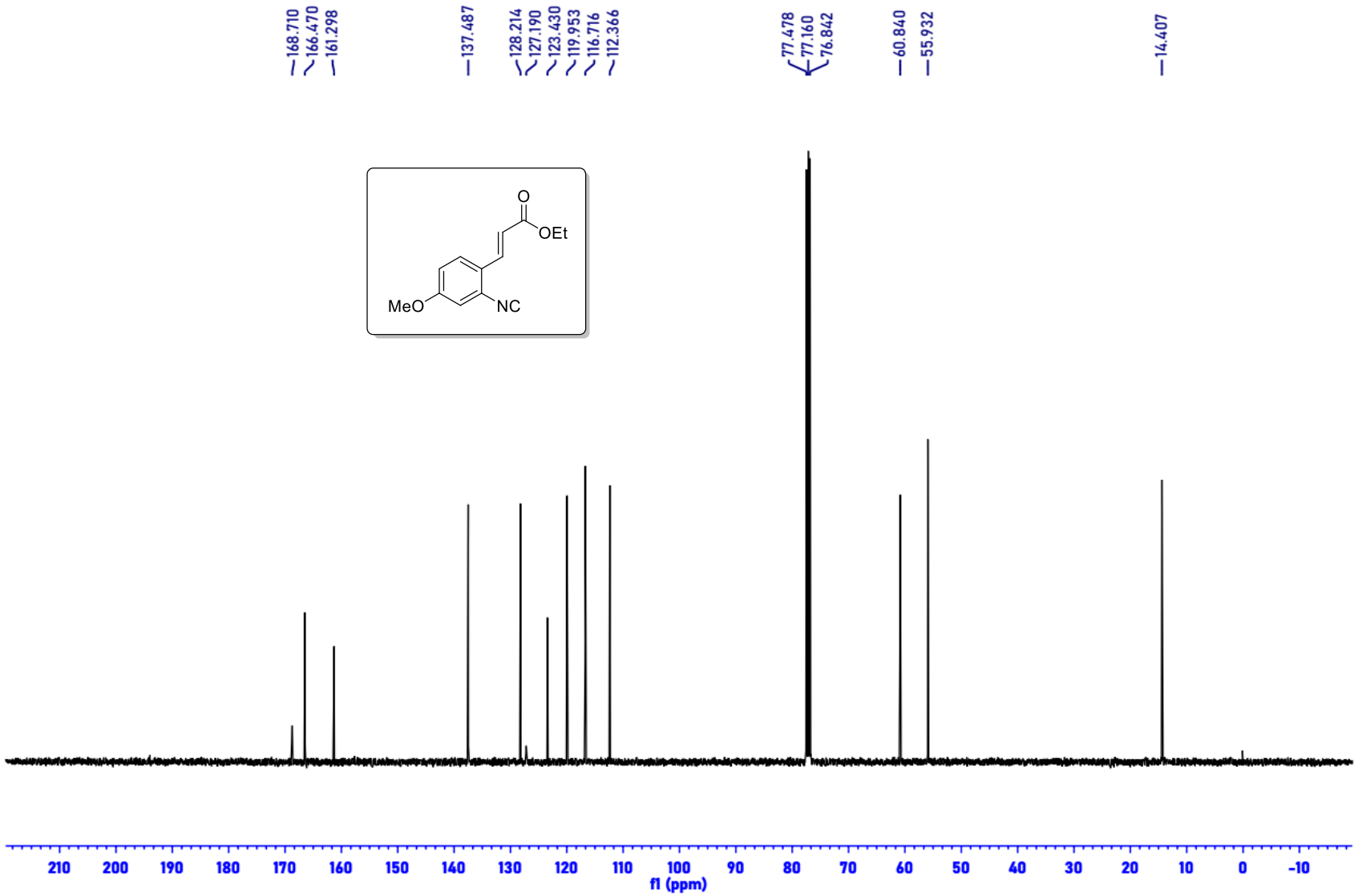
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ka



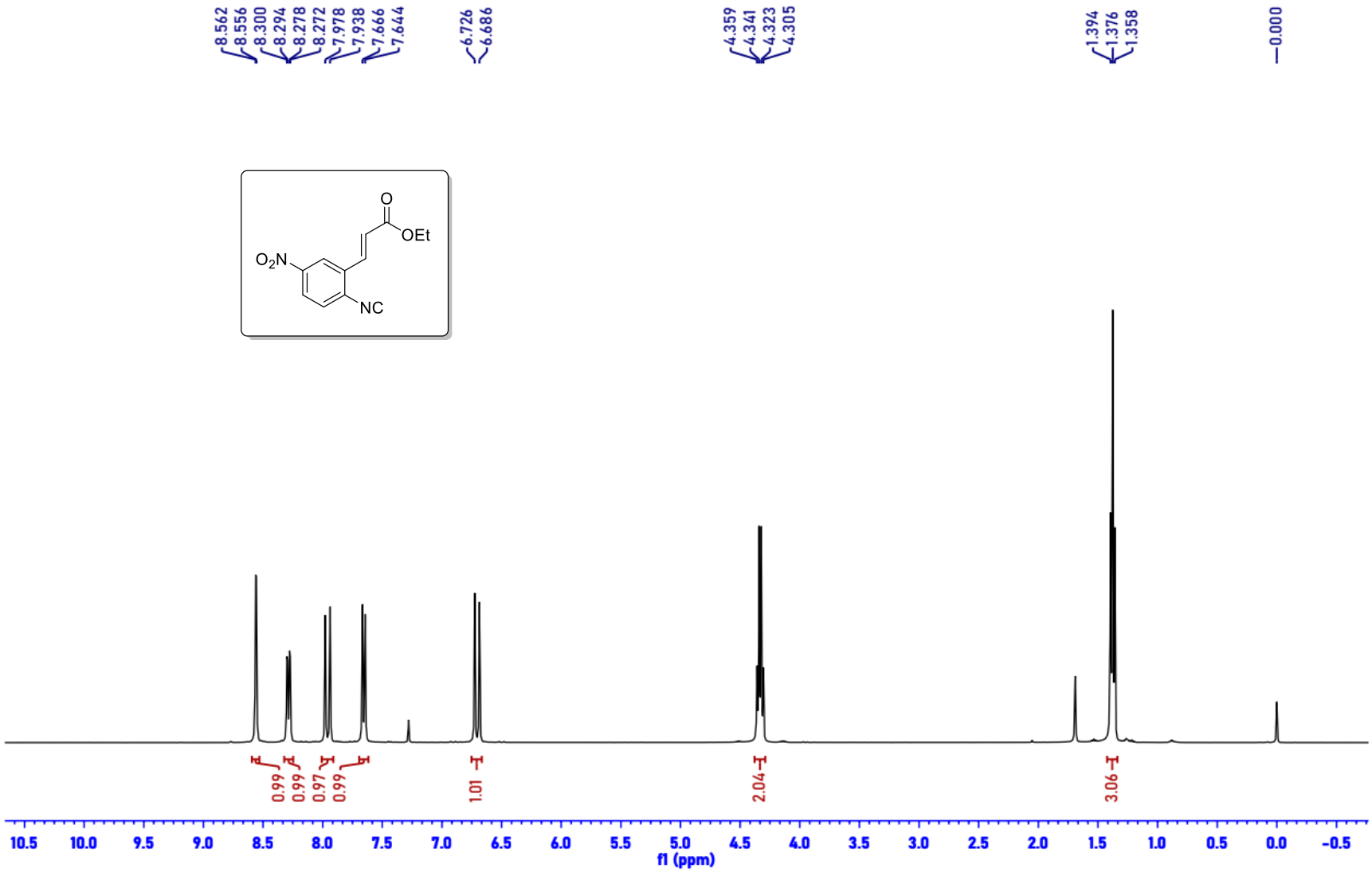
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1la



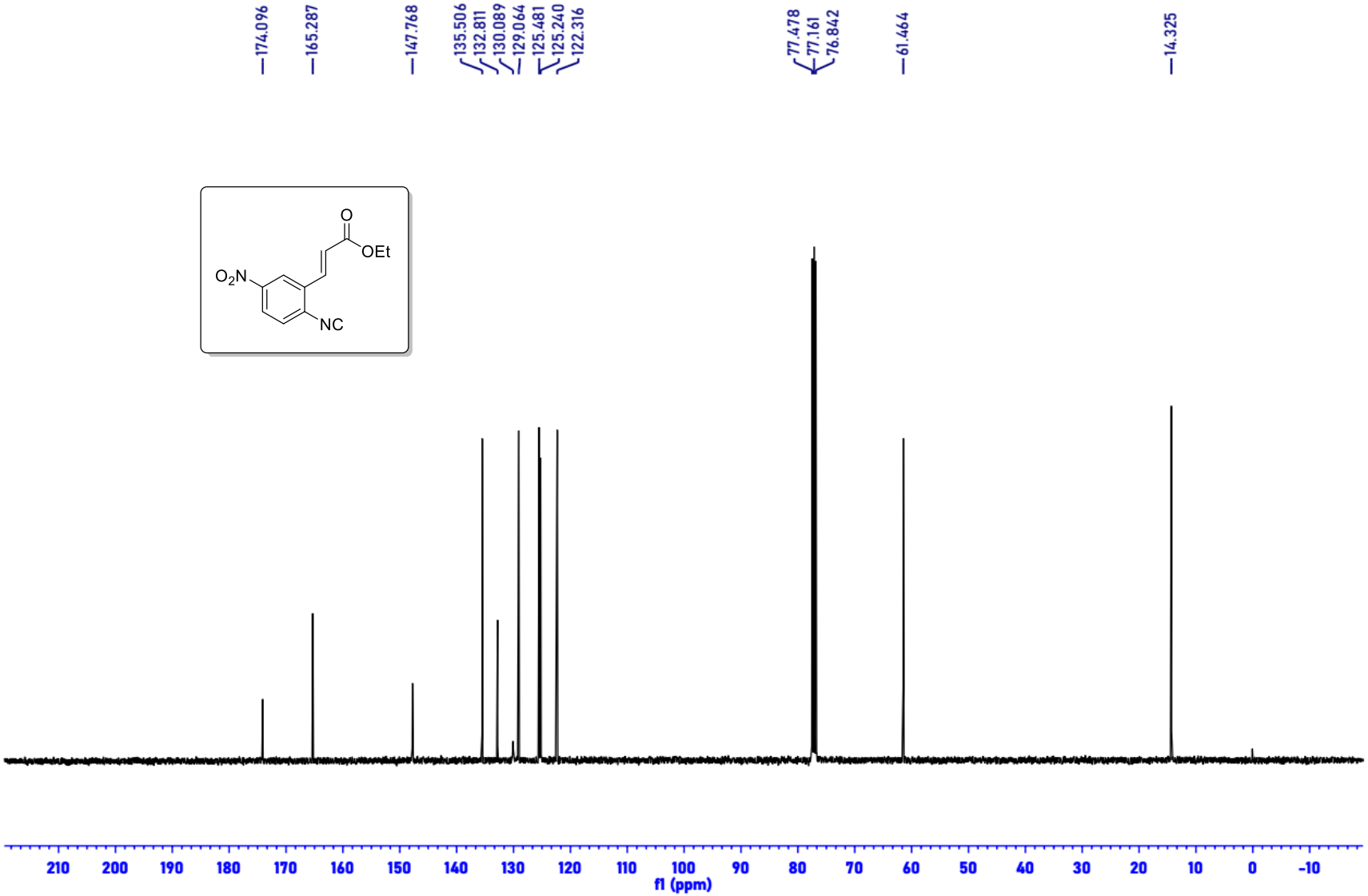
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1la



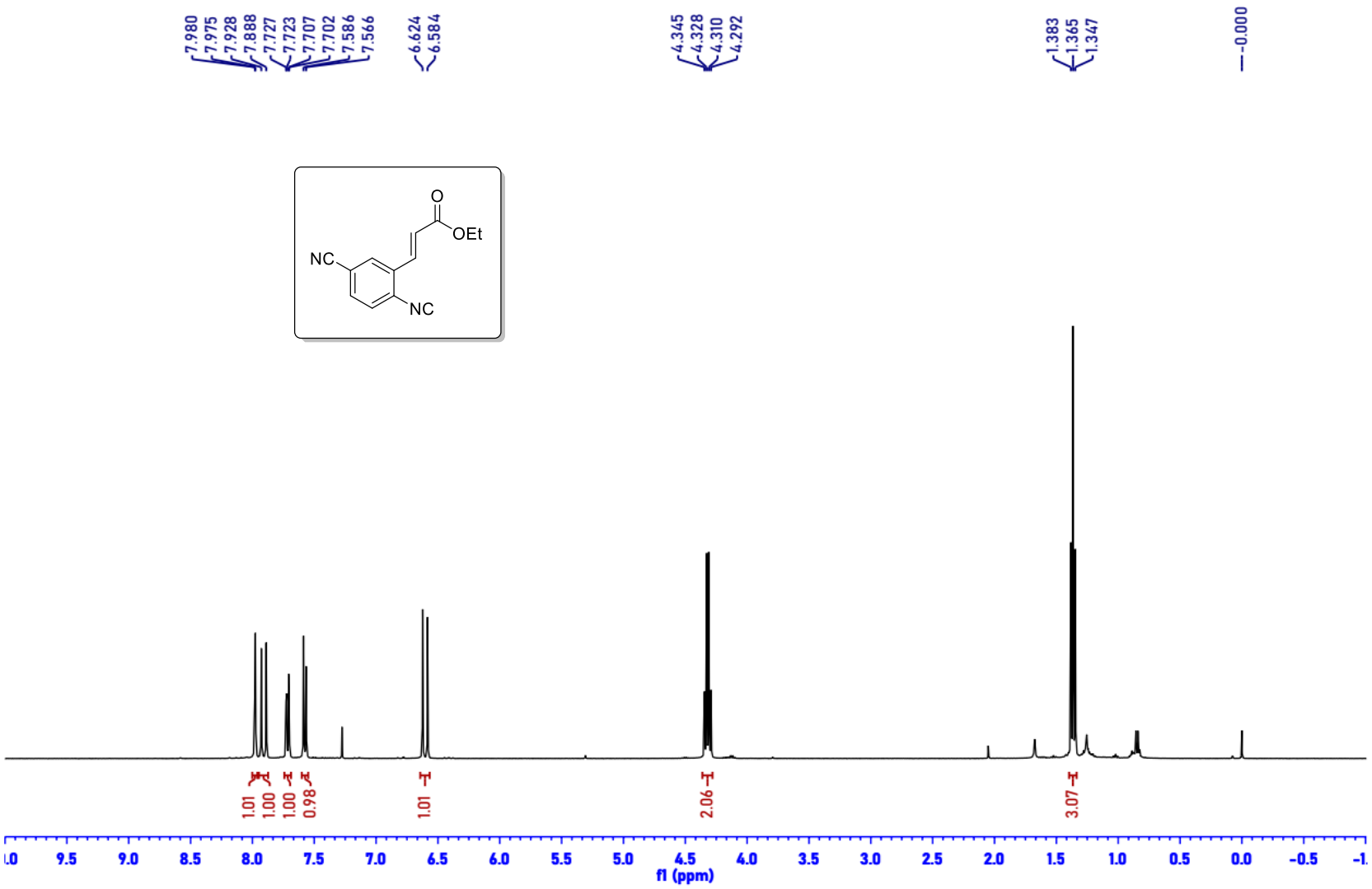
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1ma



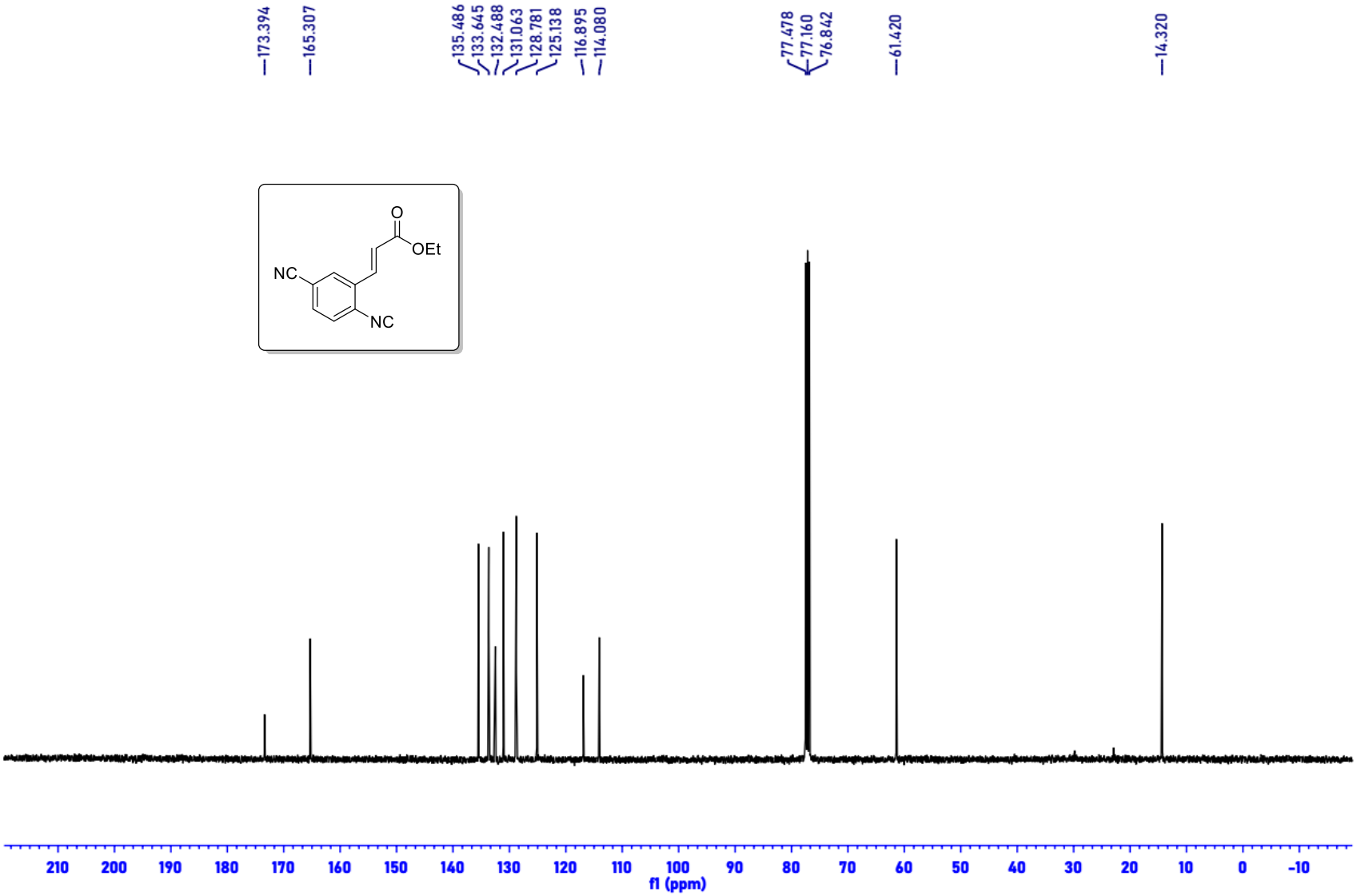
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1ma



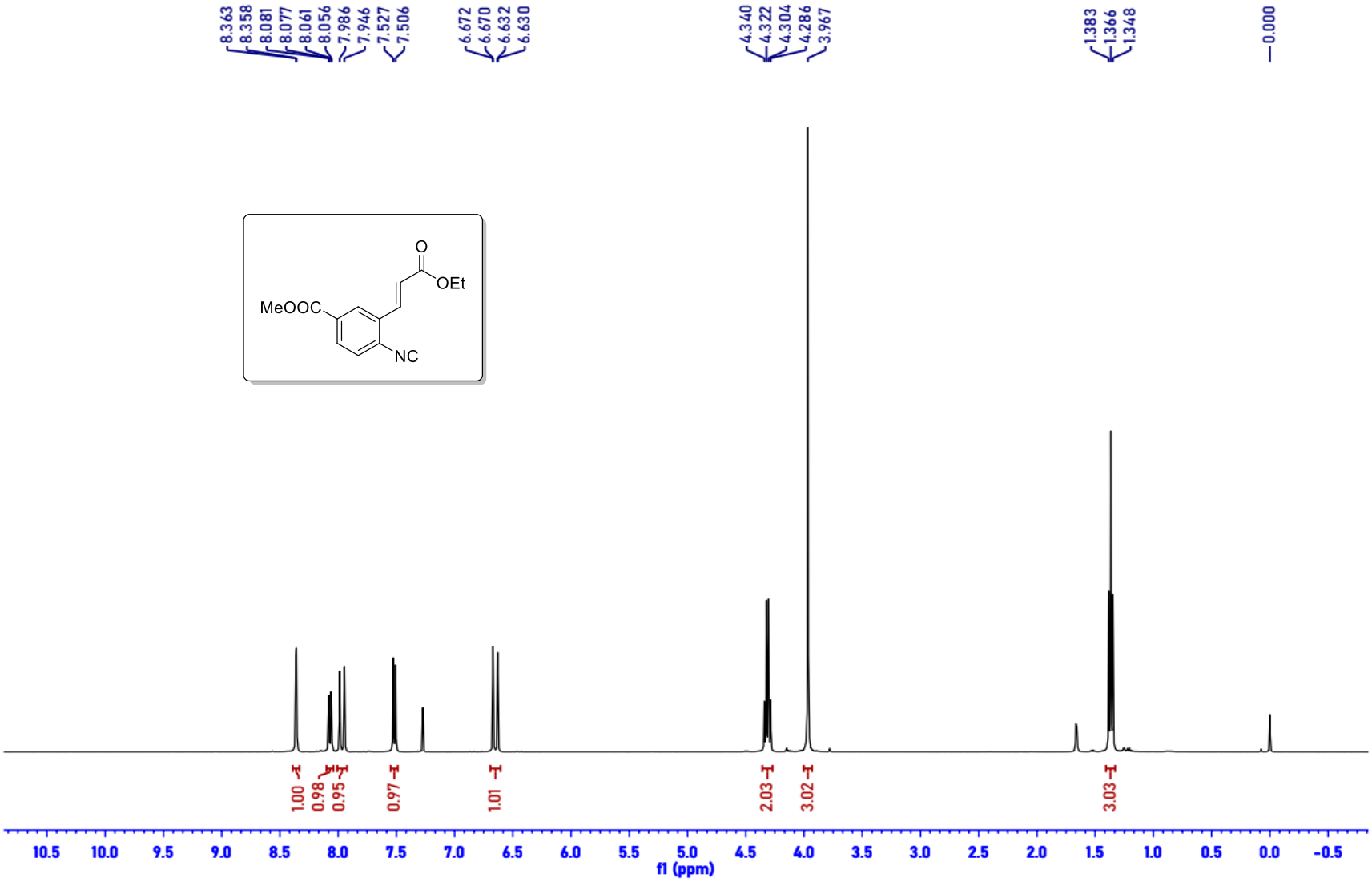
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1na



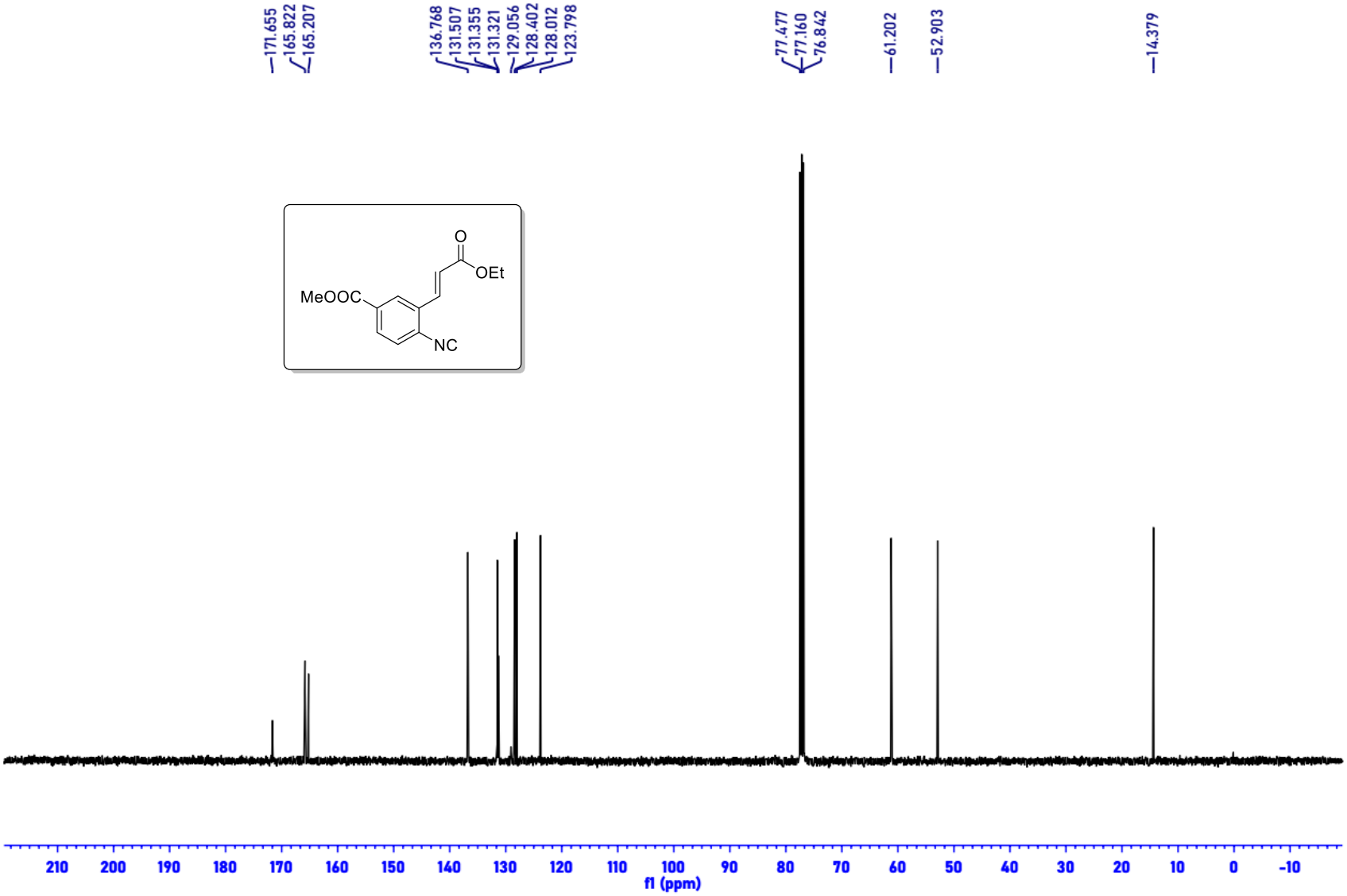
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1na



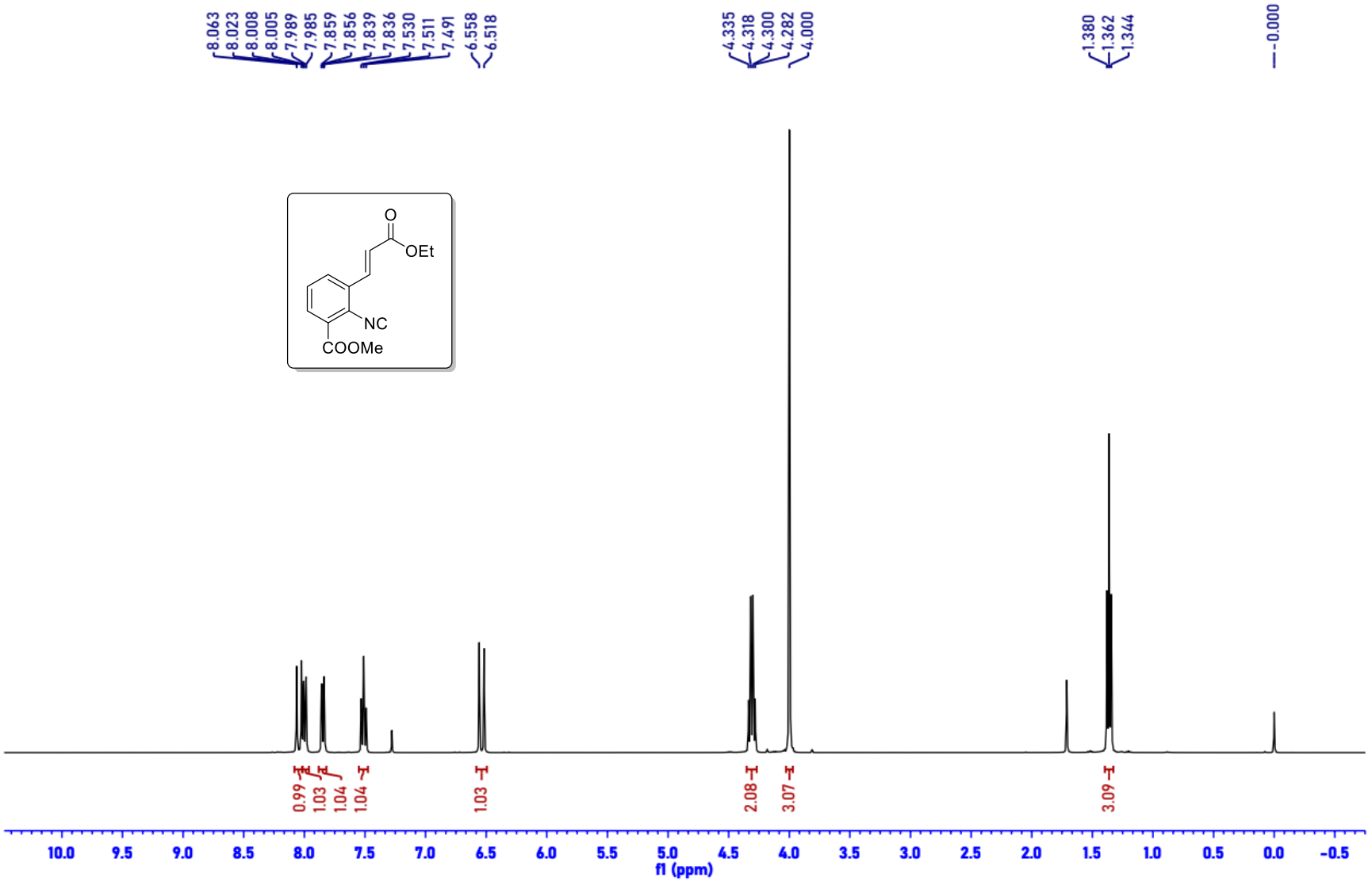
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1oa



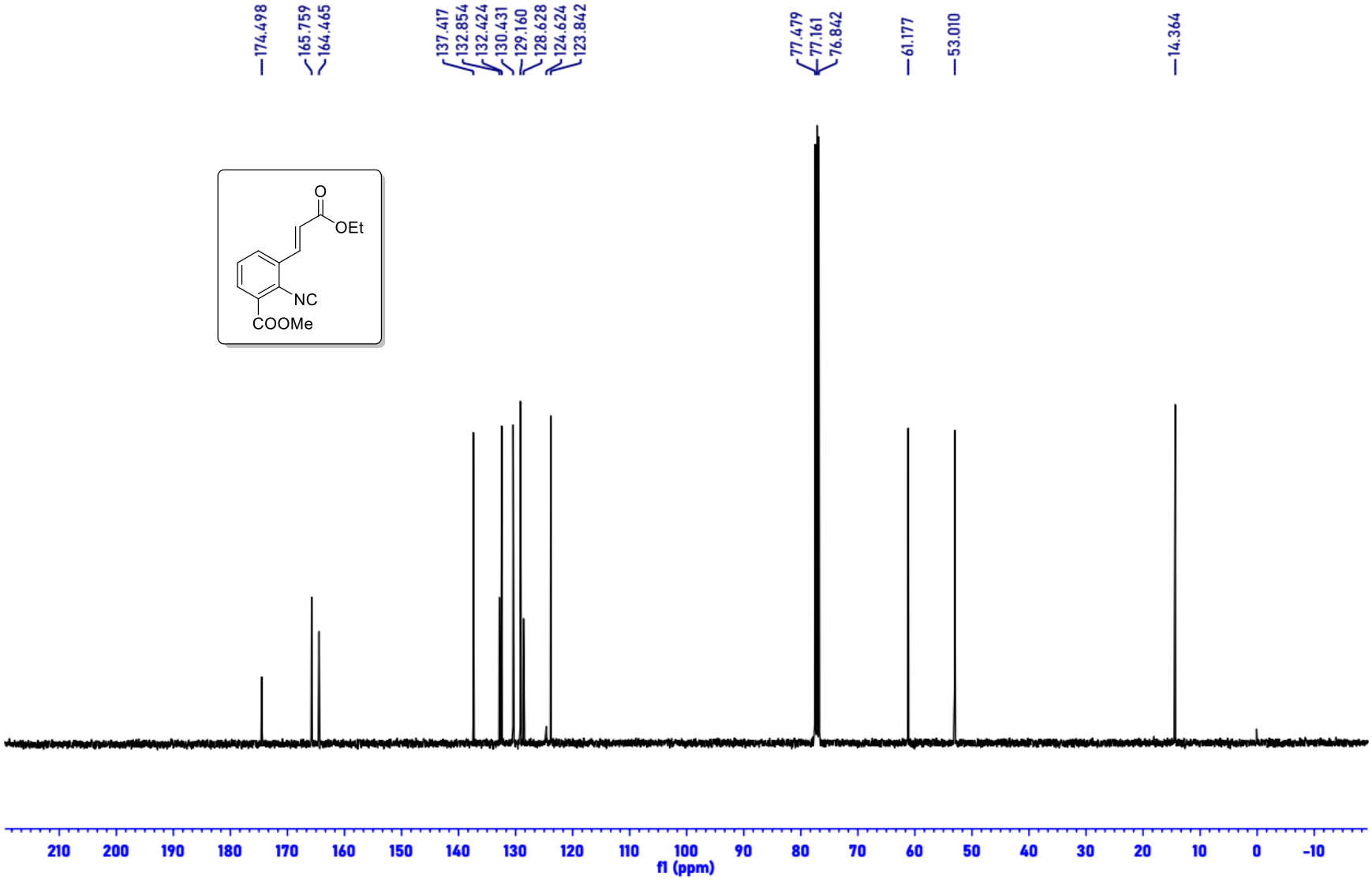
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1oa



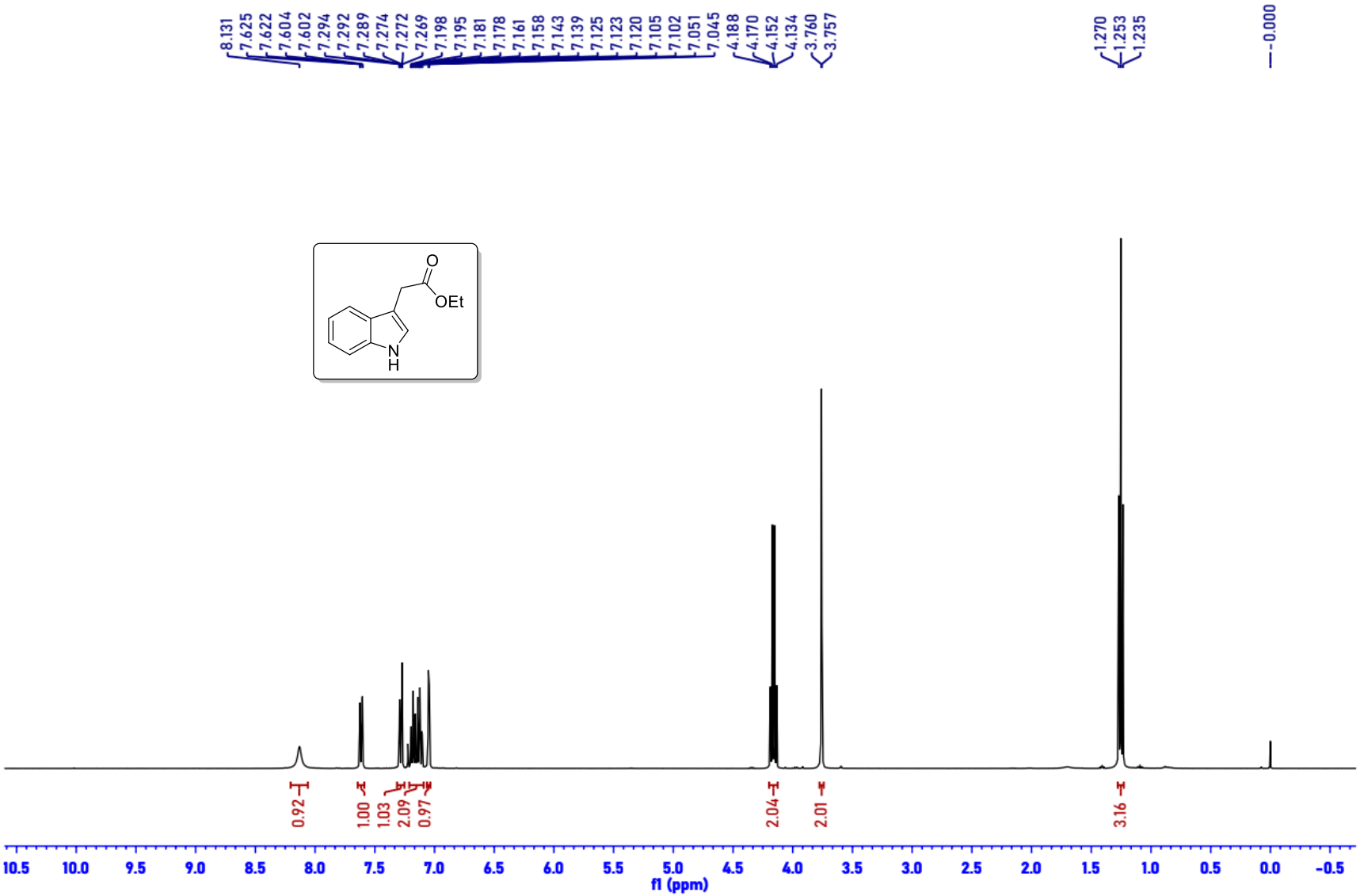
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 1pa



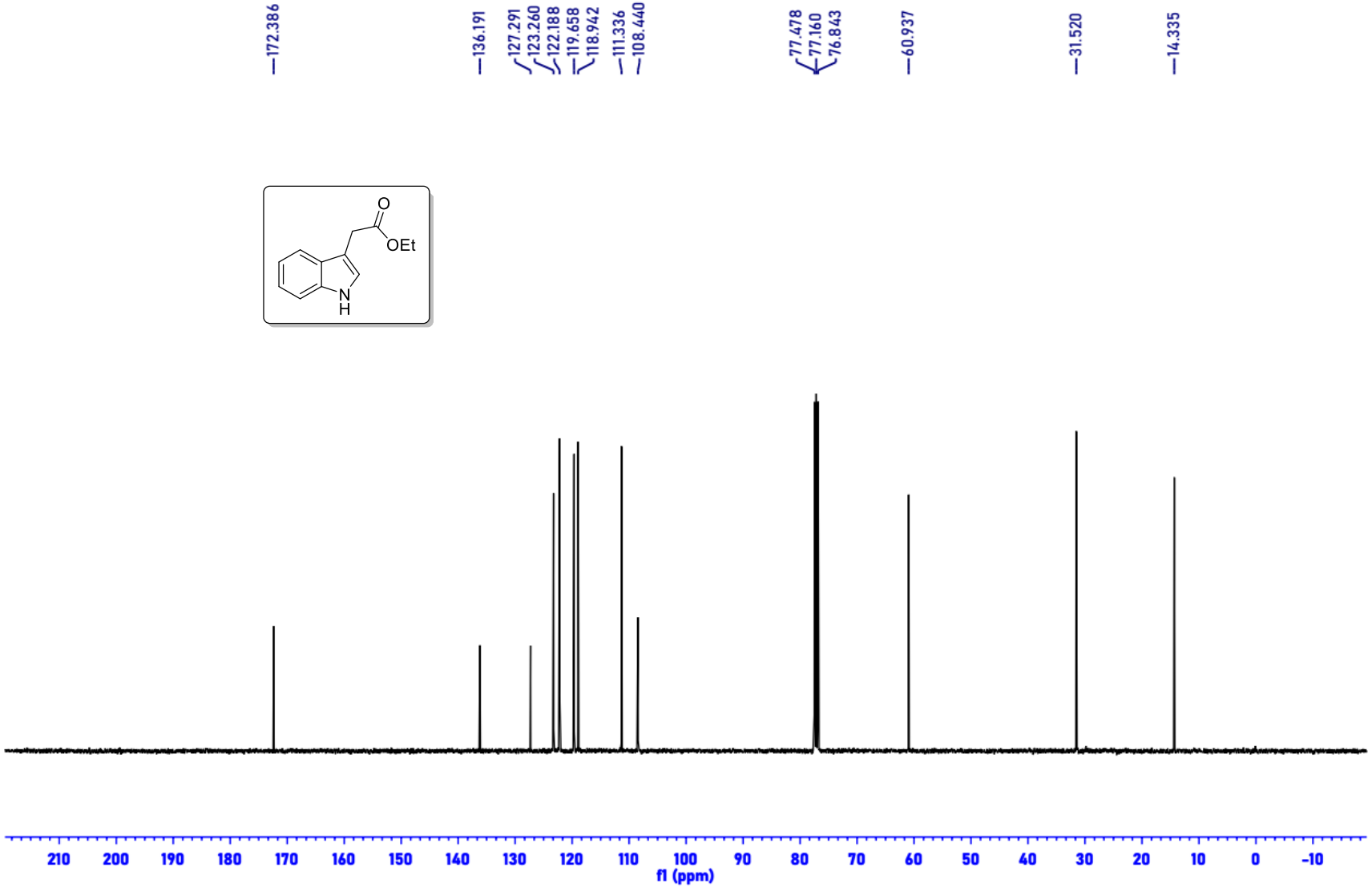
^{13}C NMR (400 MHz, $CDCl_3$) spectra for 1pa



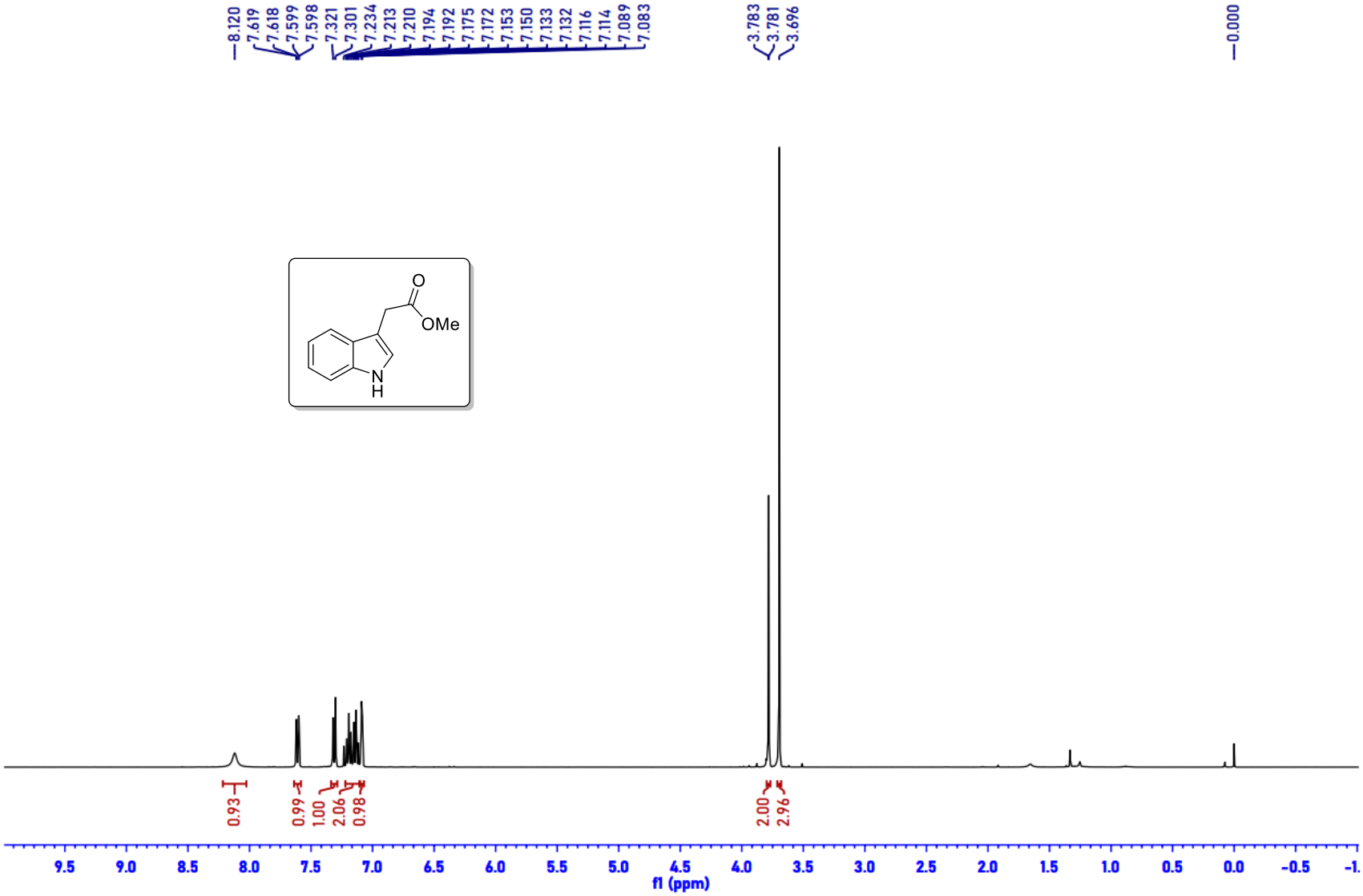
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aa



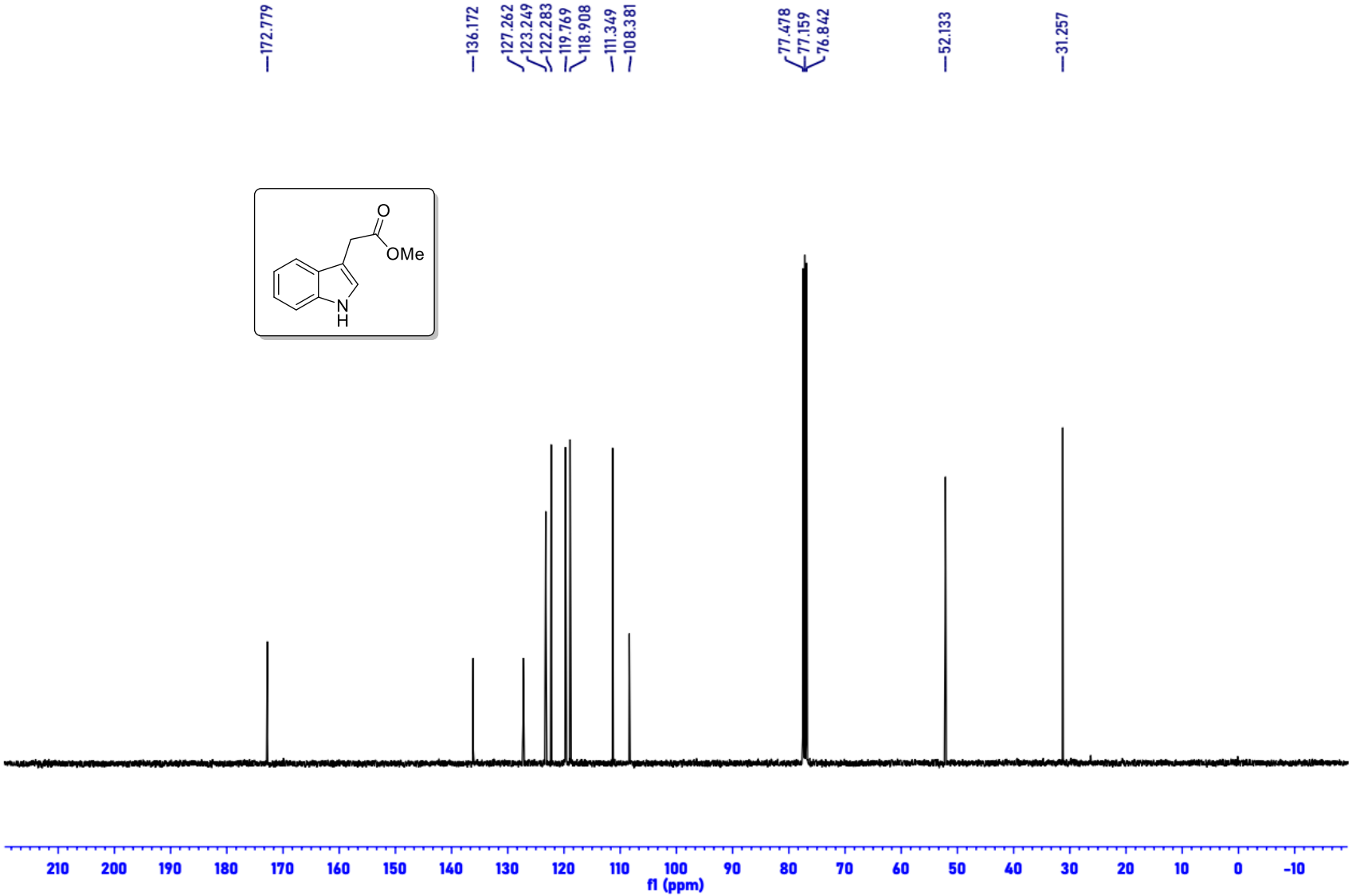
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2aa



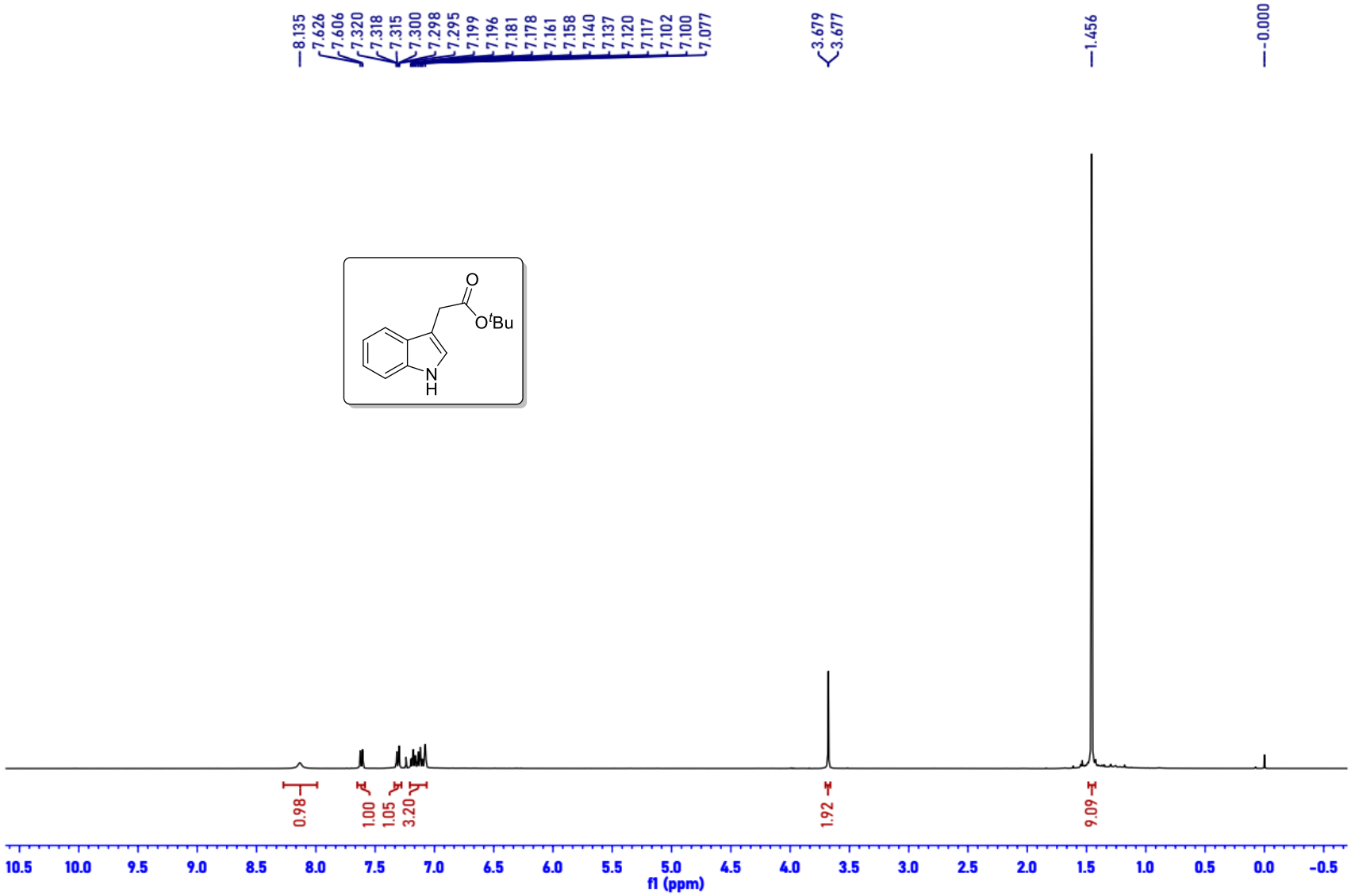
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ab



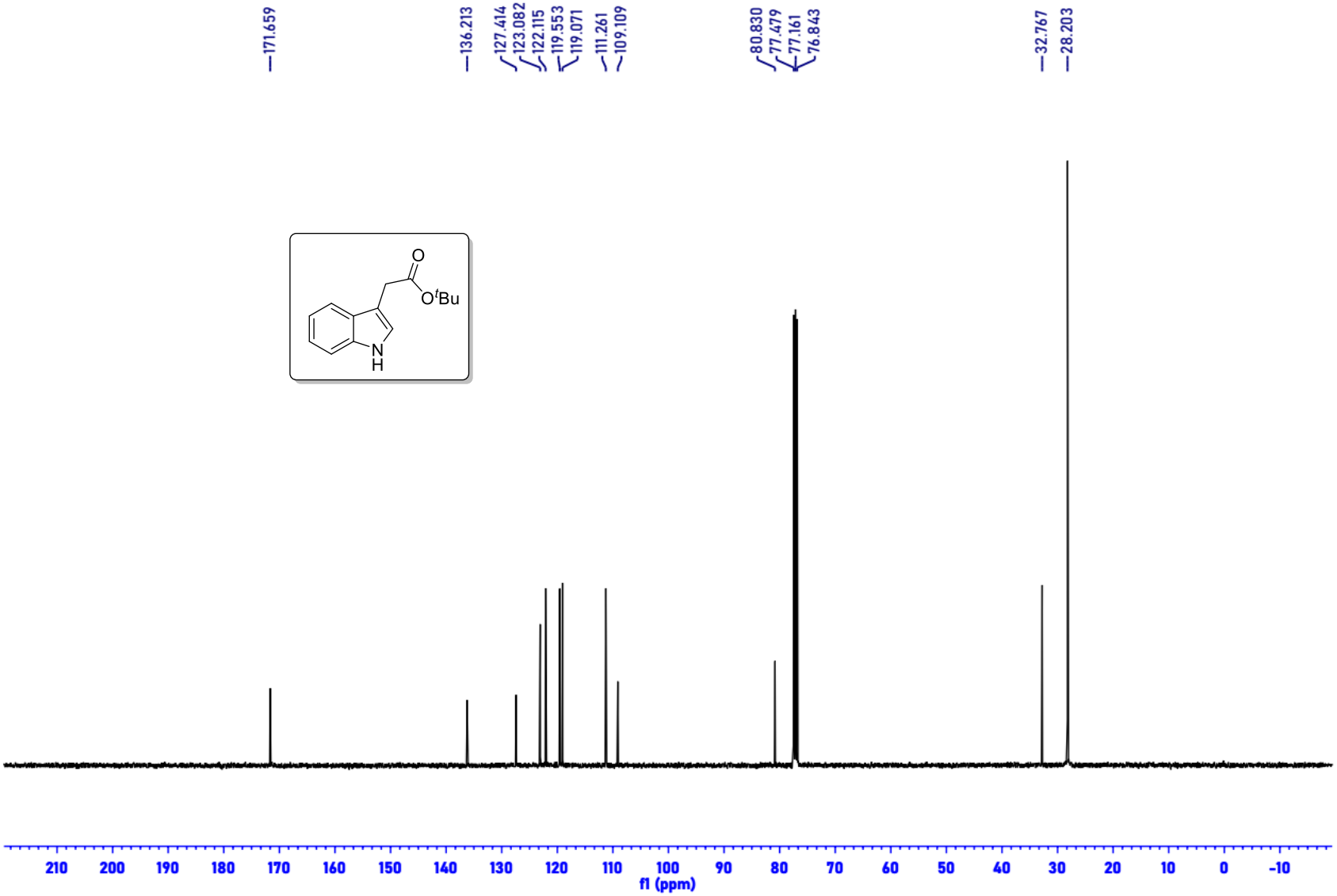
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ab



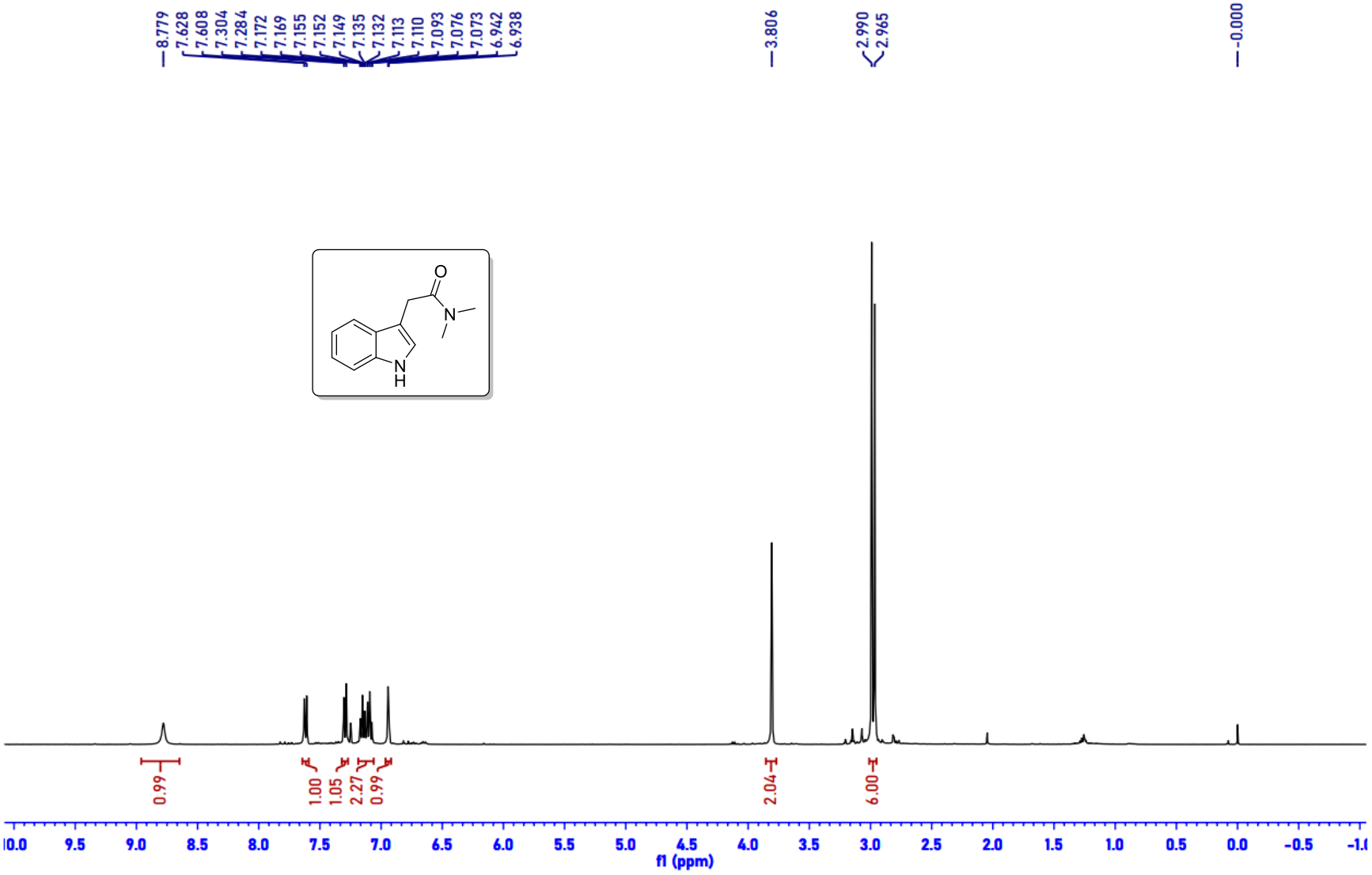
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ac



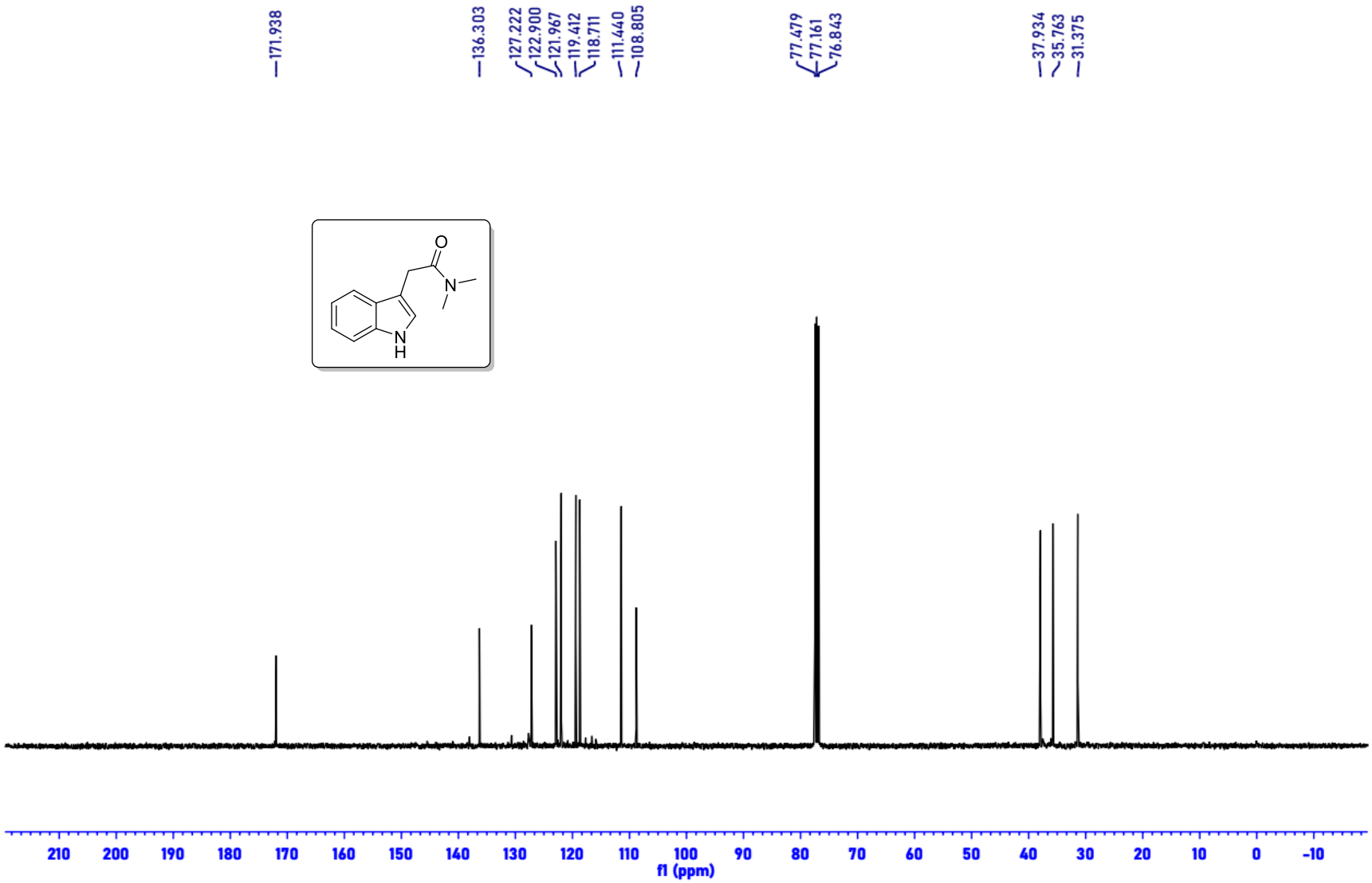
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ac



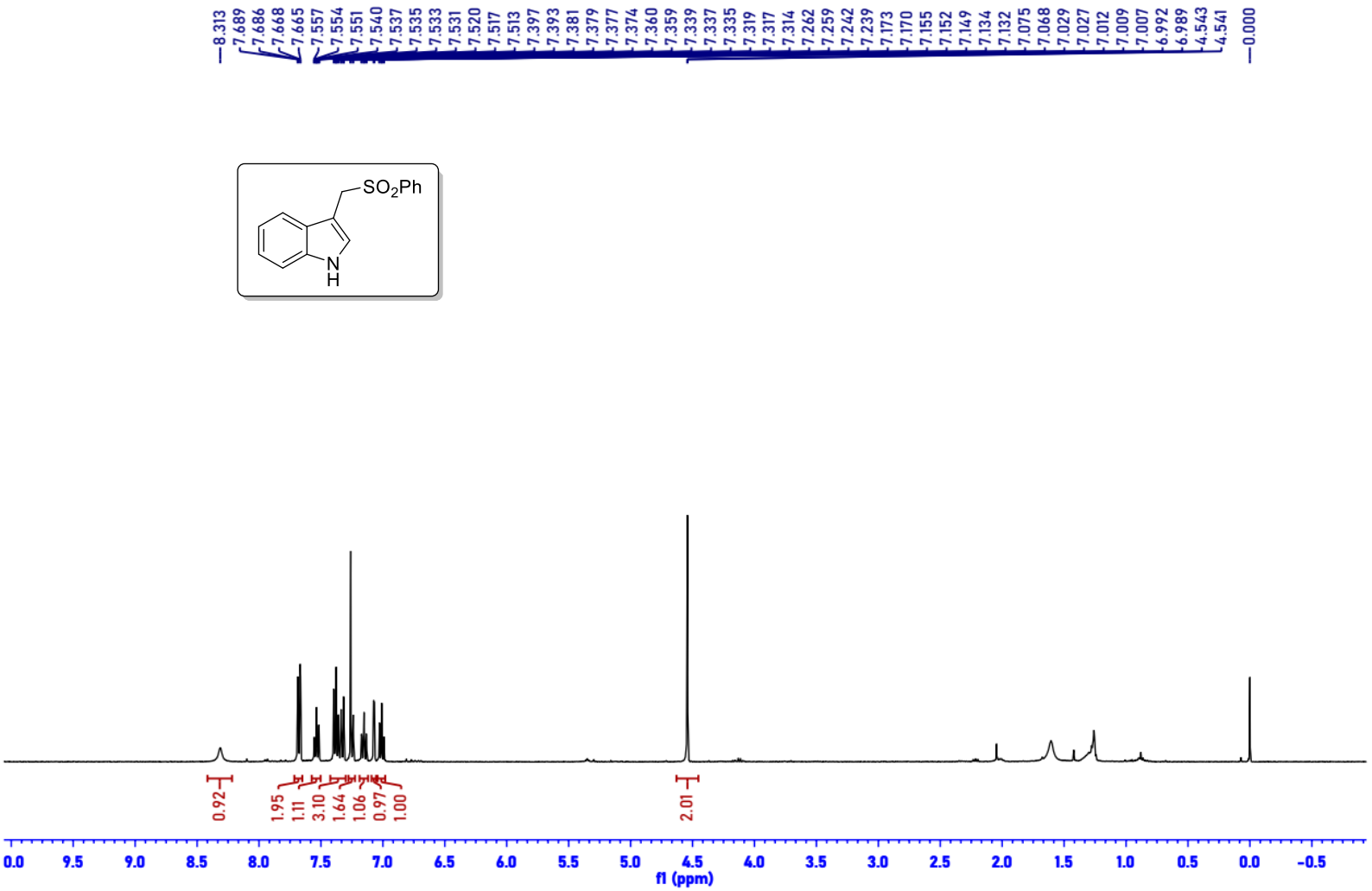
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ad



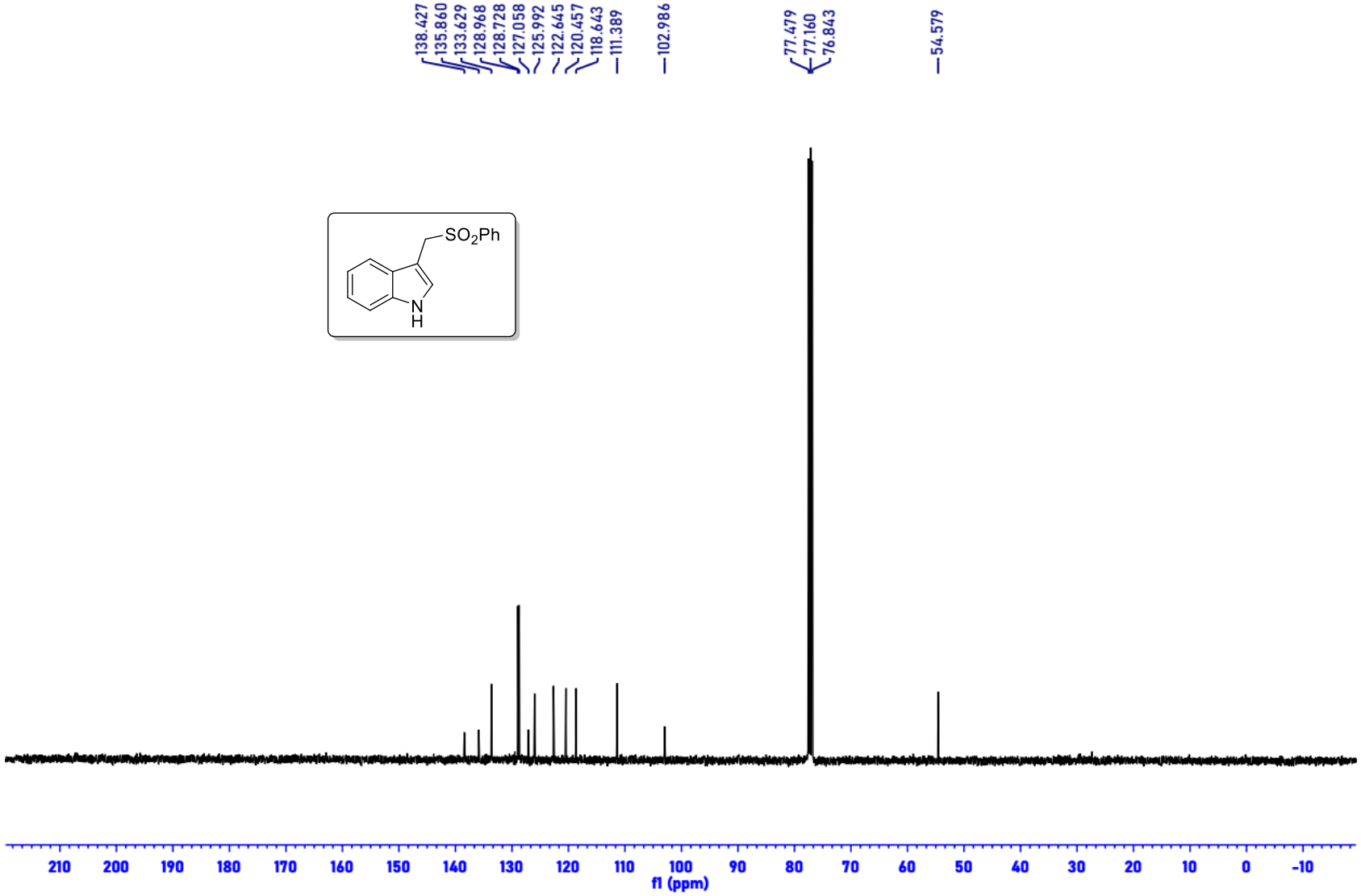
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ad



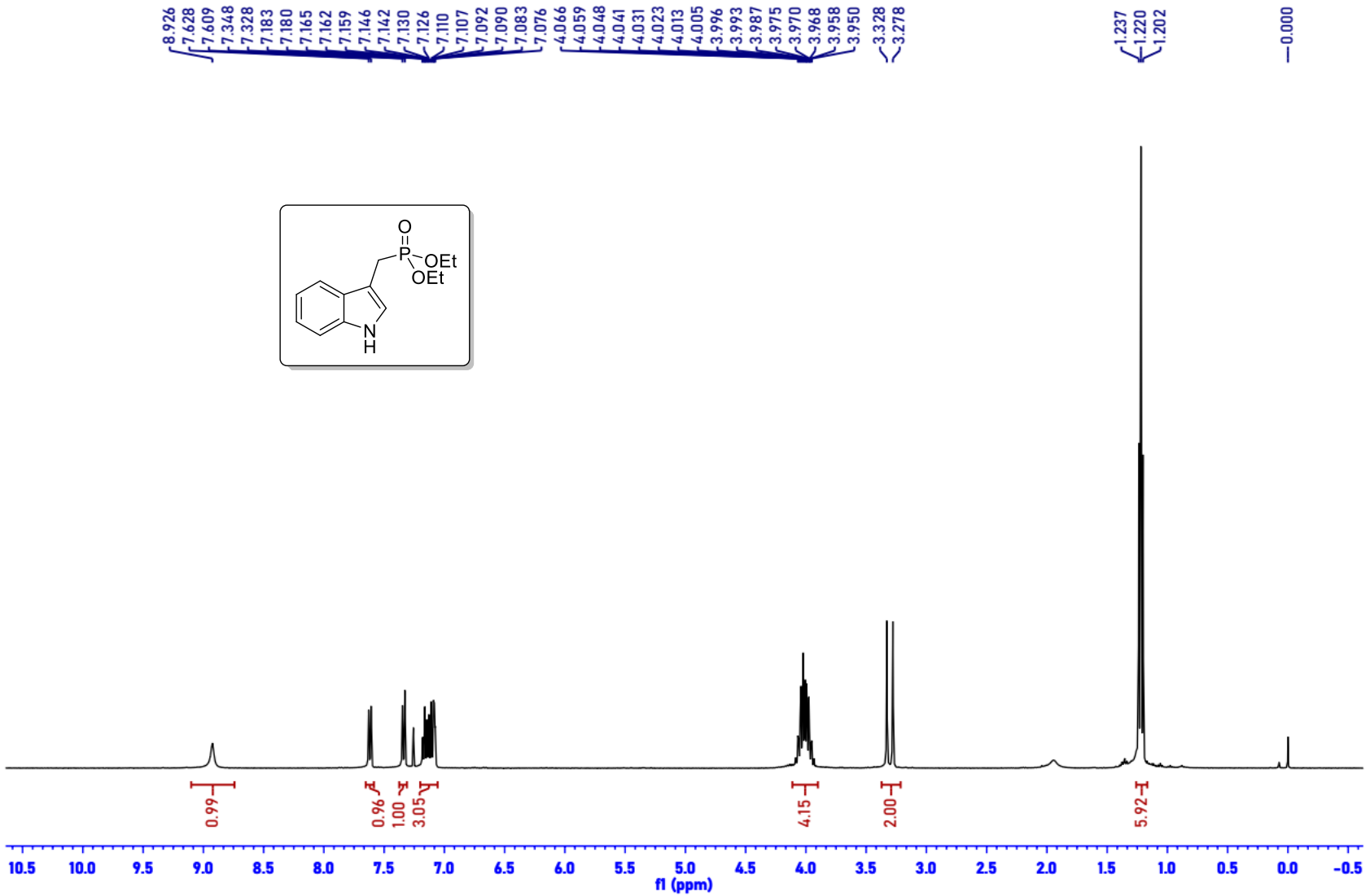
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ae



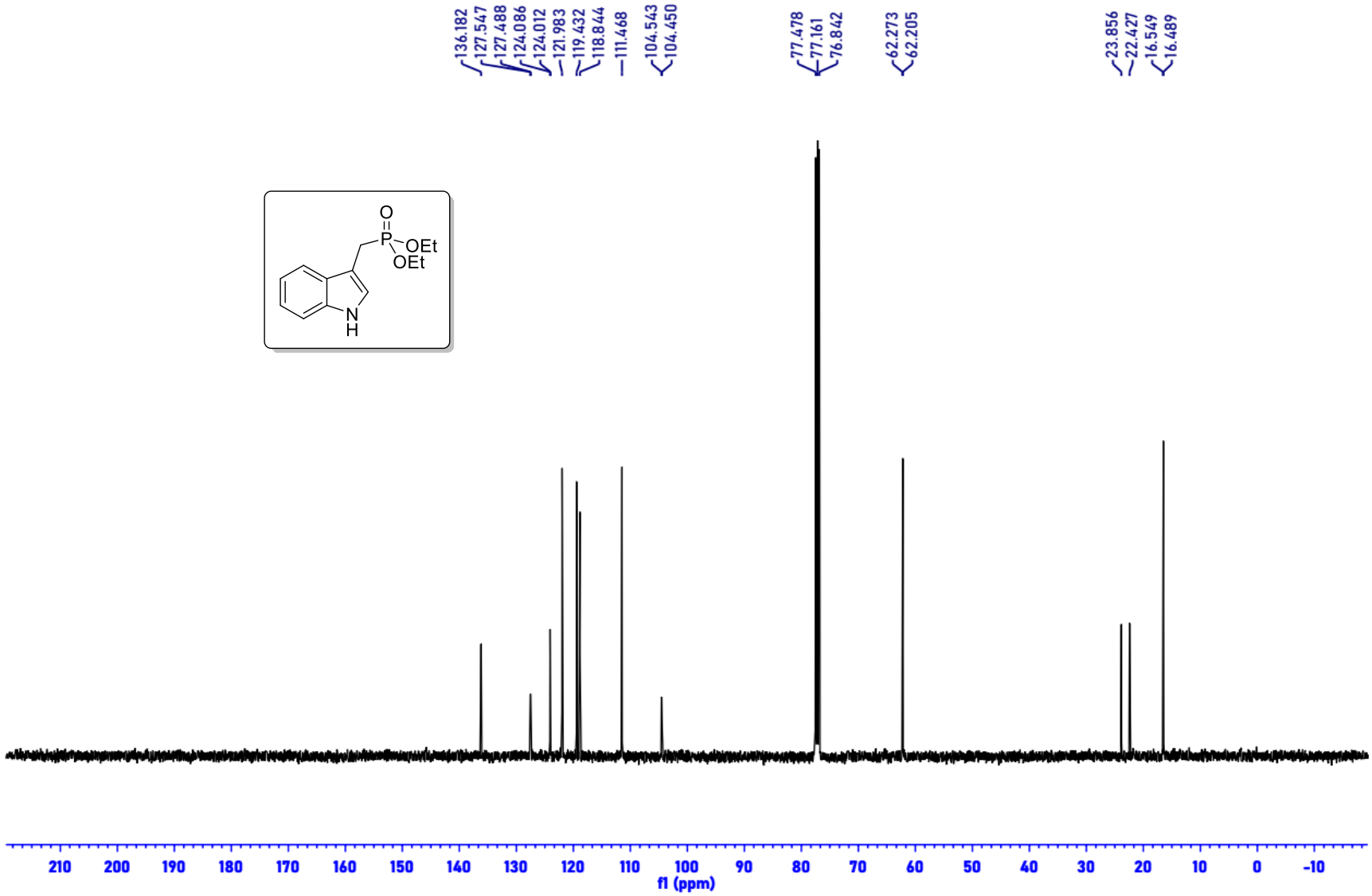
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ae



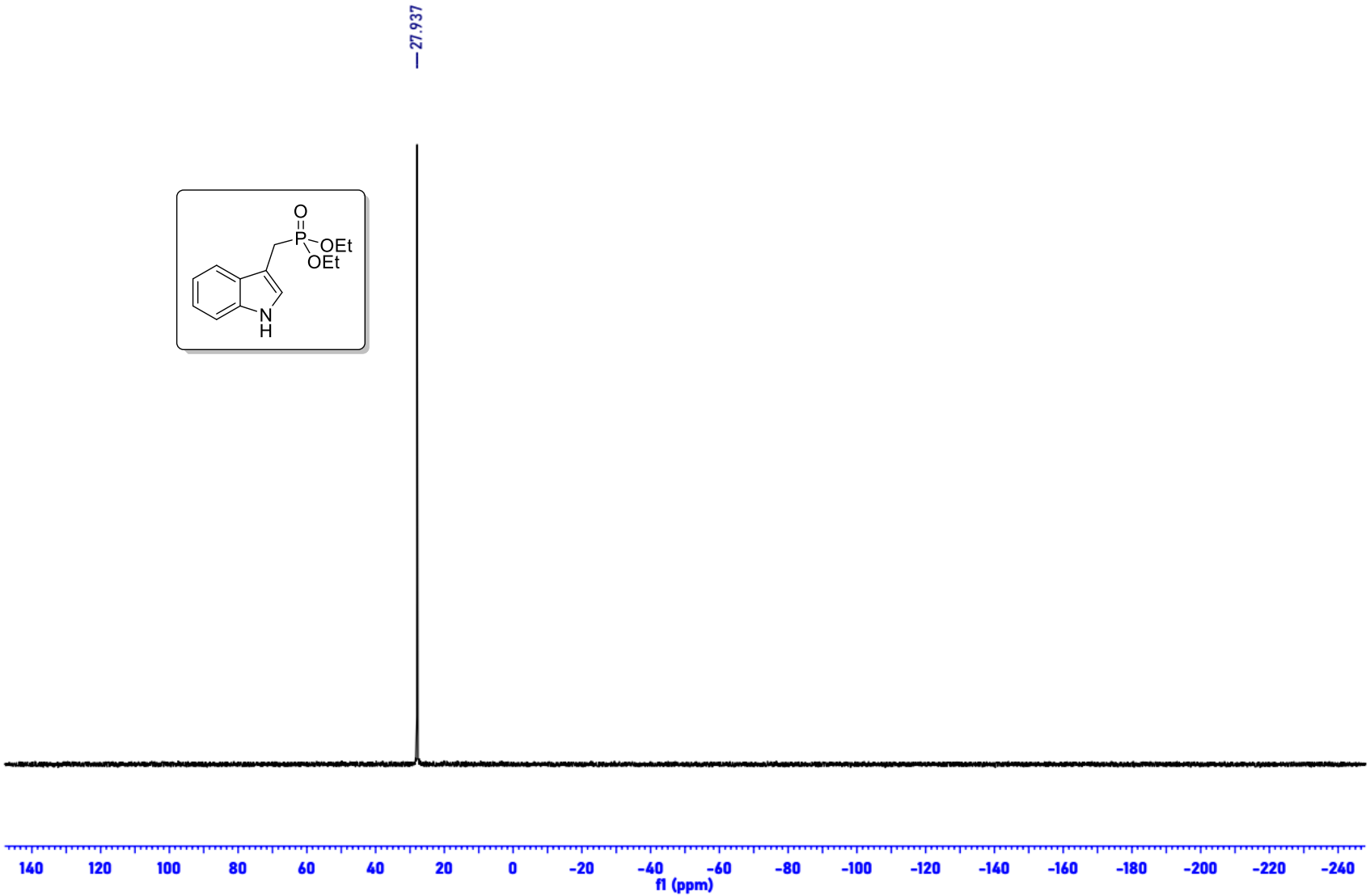
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2af



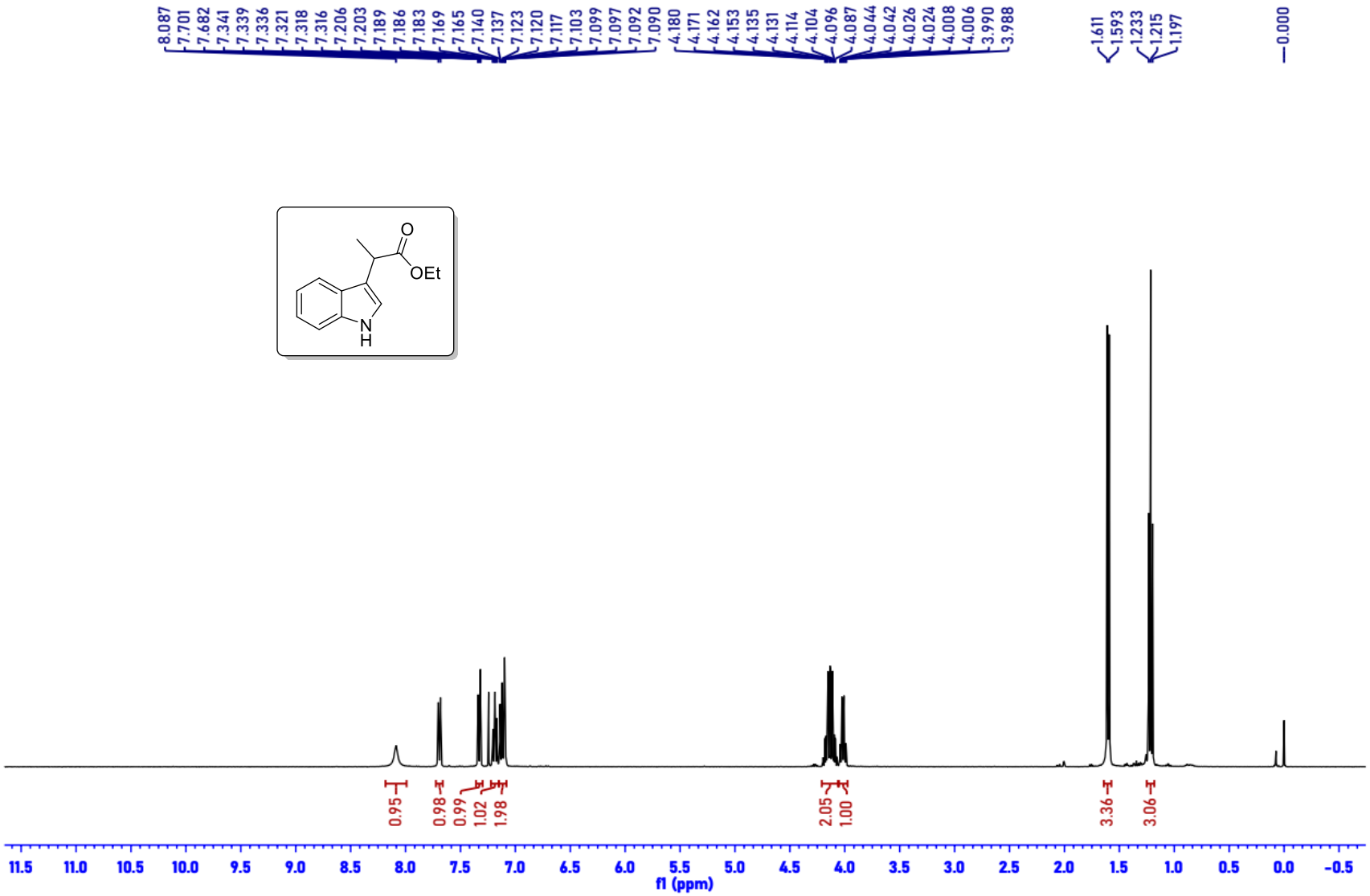
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2af



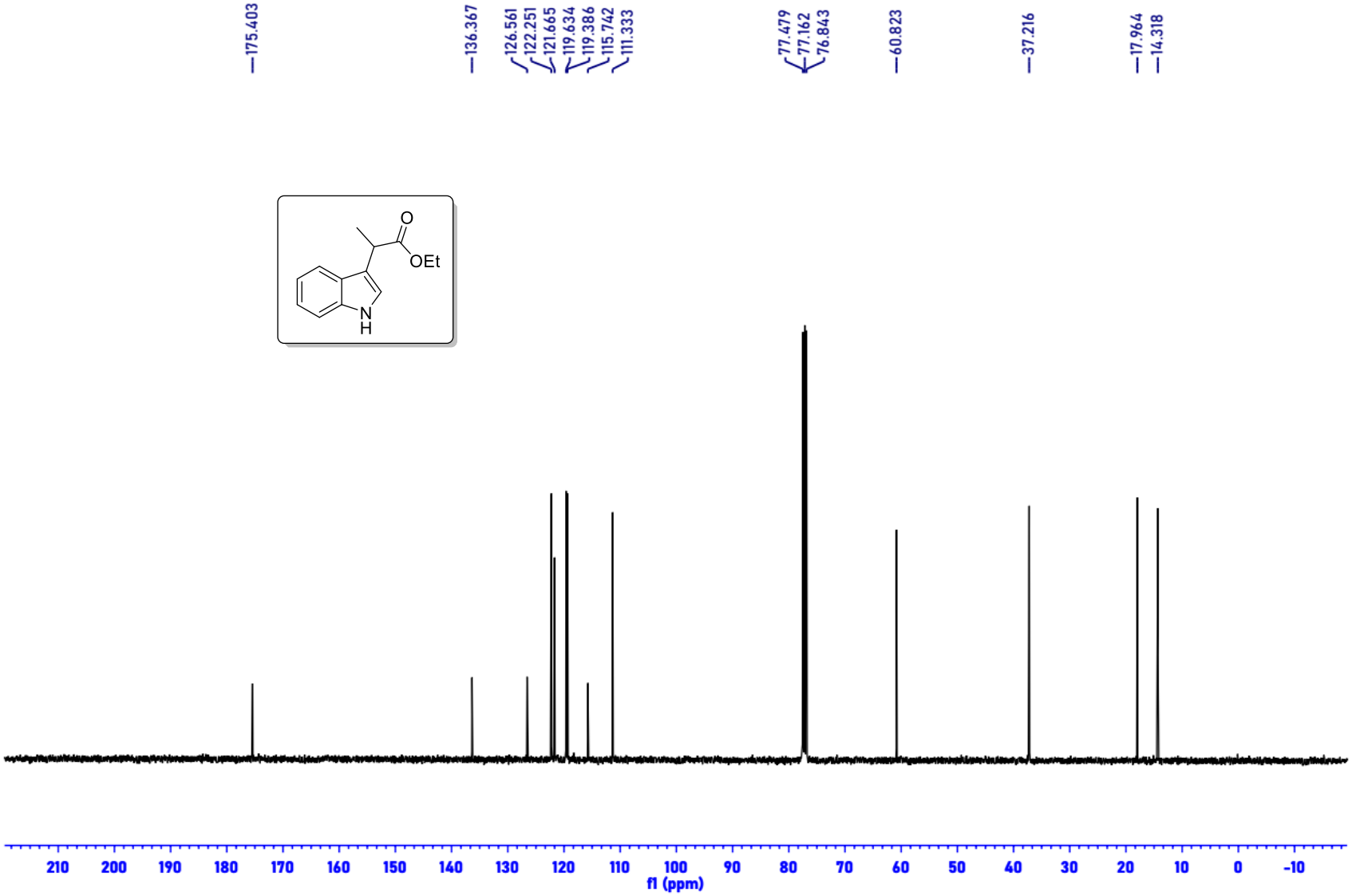
^{31}P NMR (162 MHz, $CDCl_3$) spectra for 2af



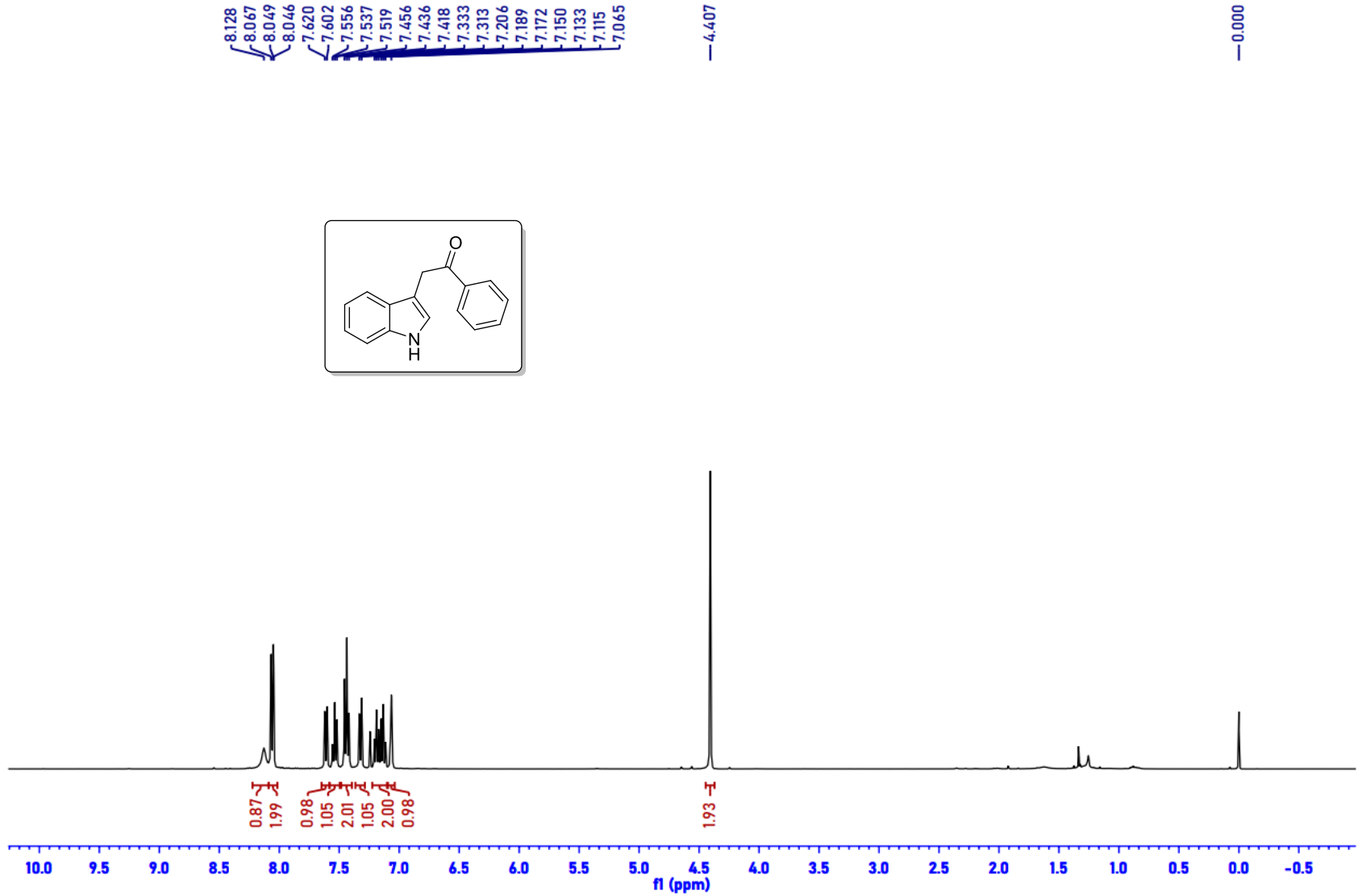
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ag



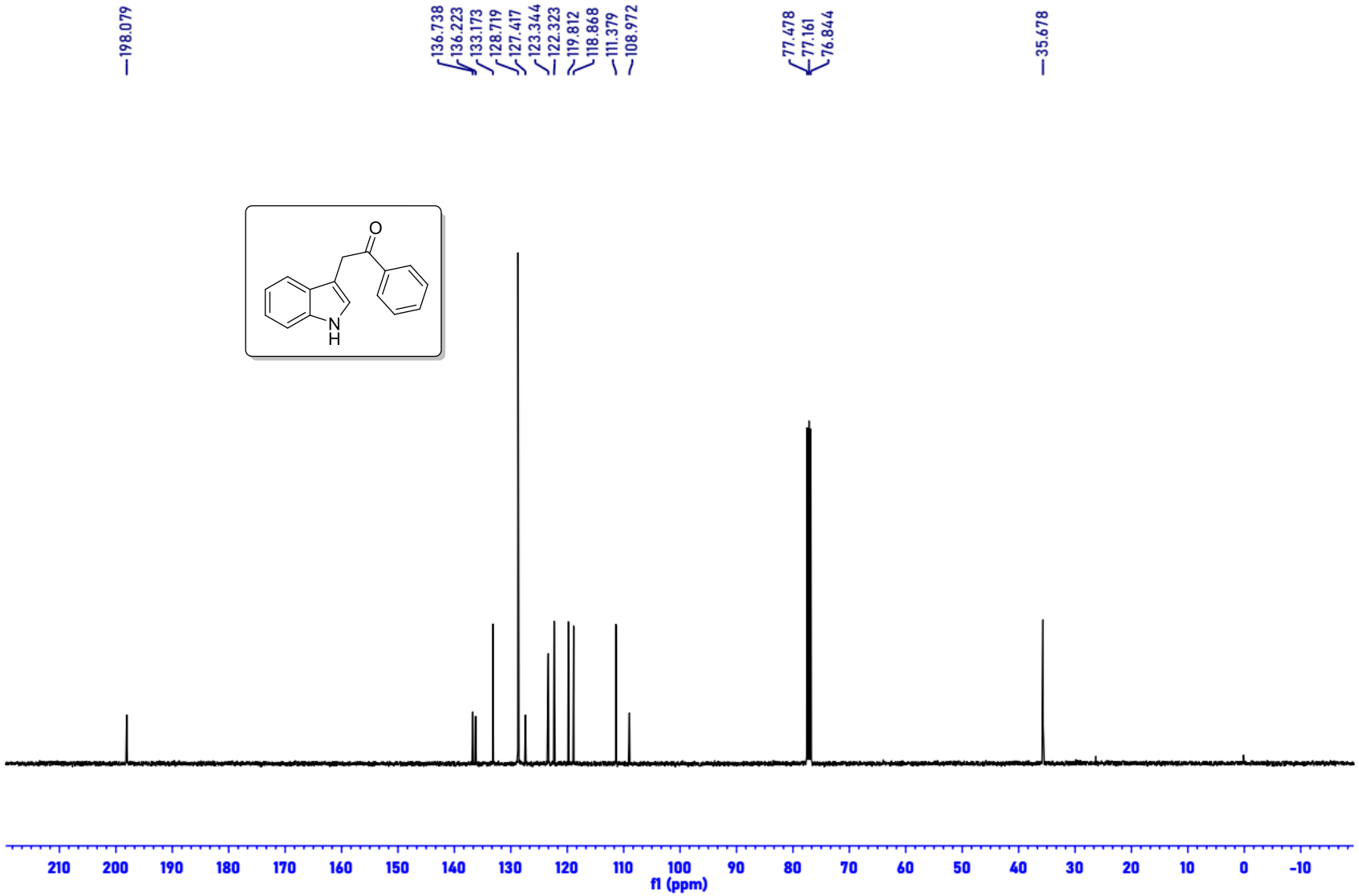
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ag



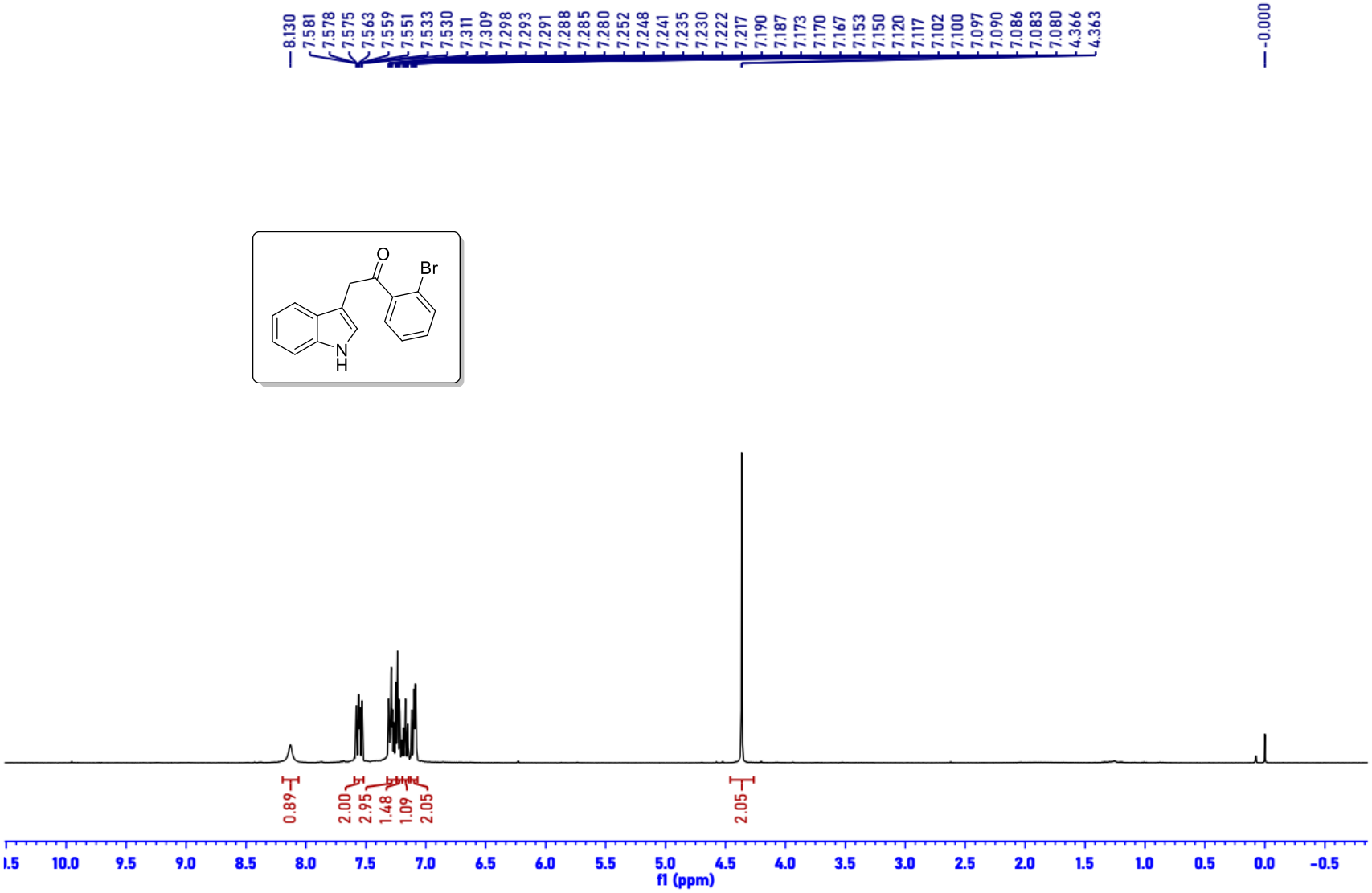
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ah



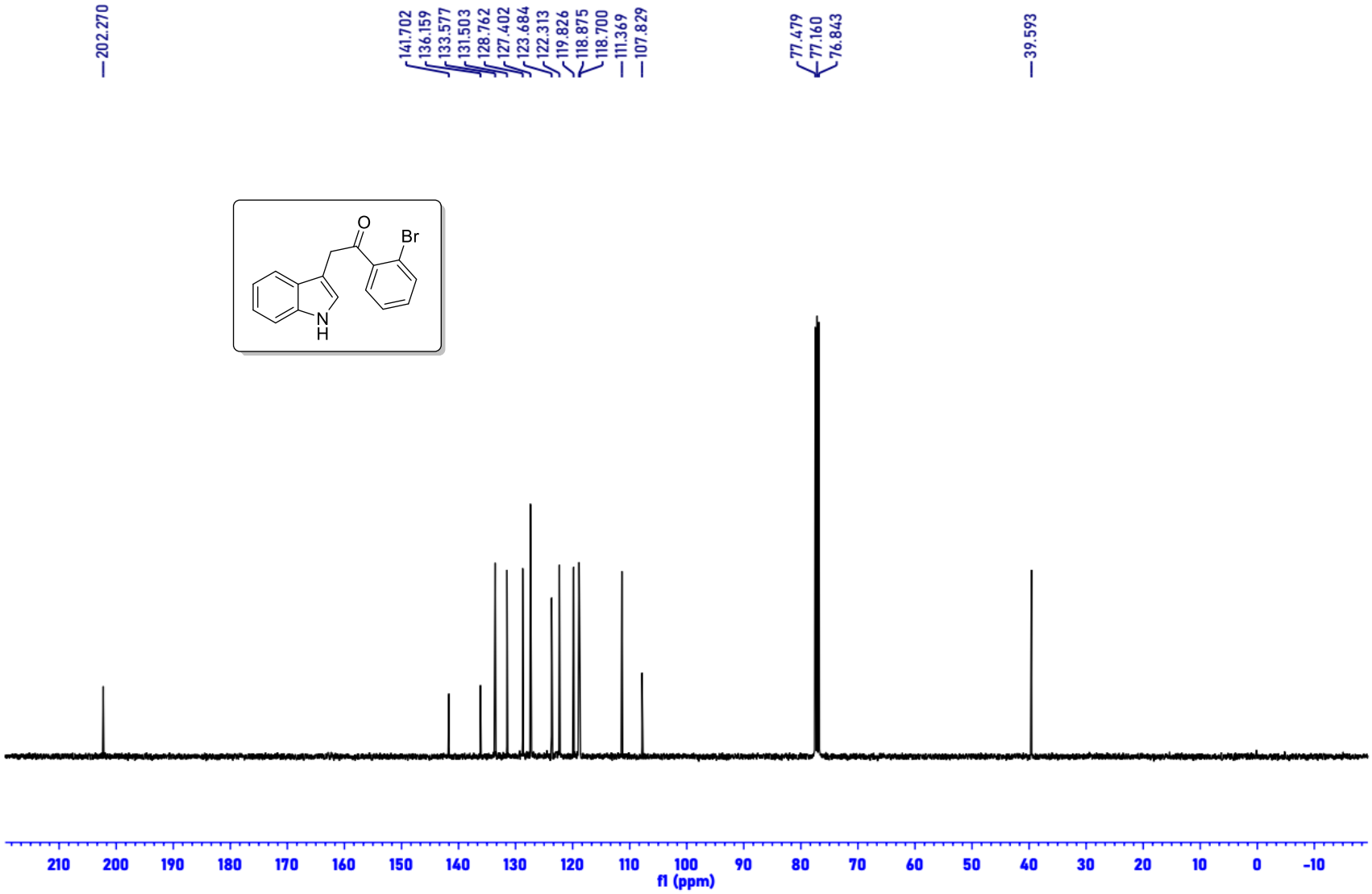
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ah



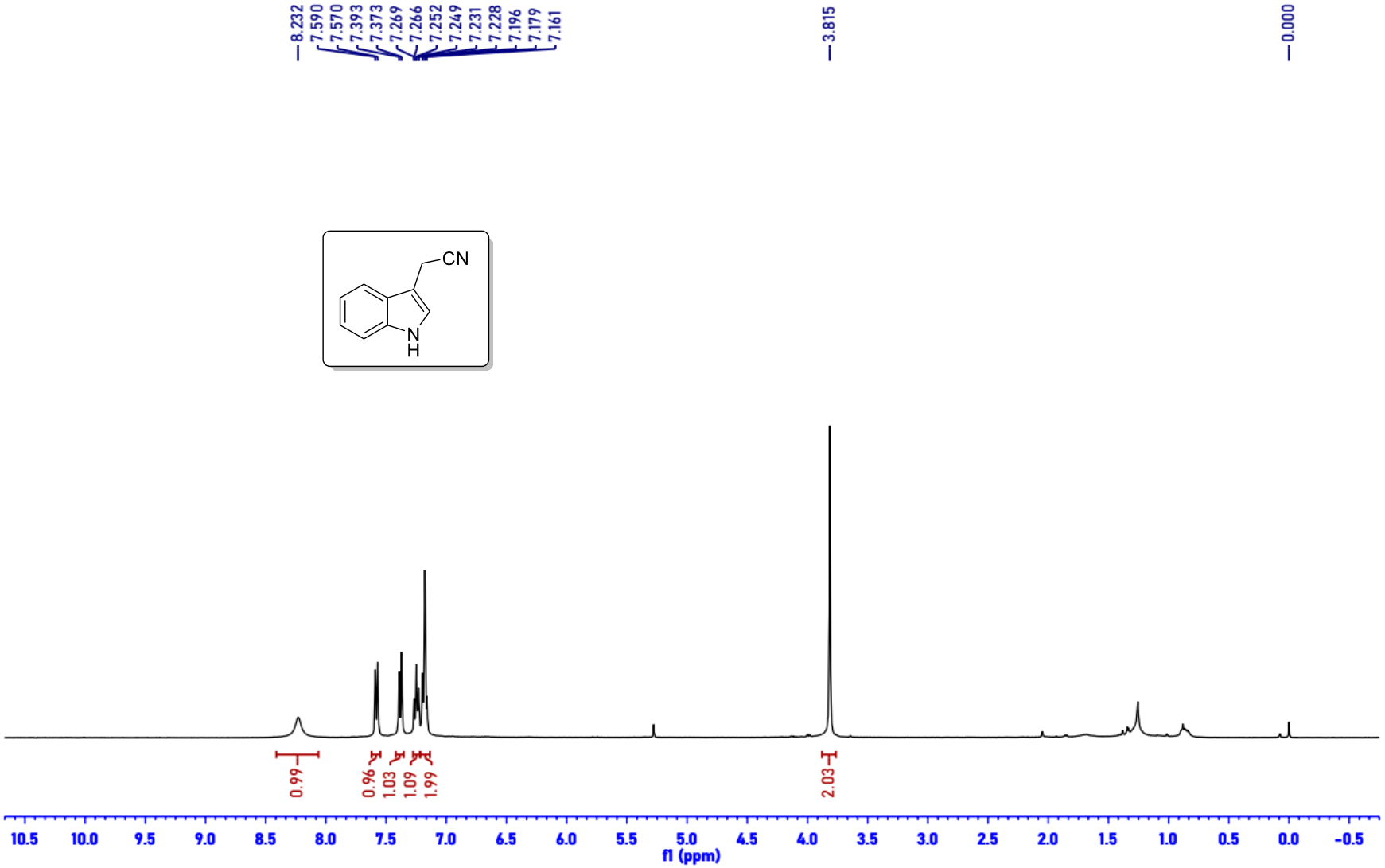
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ai



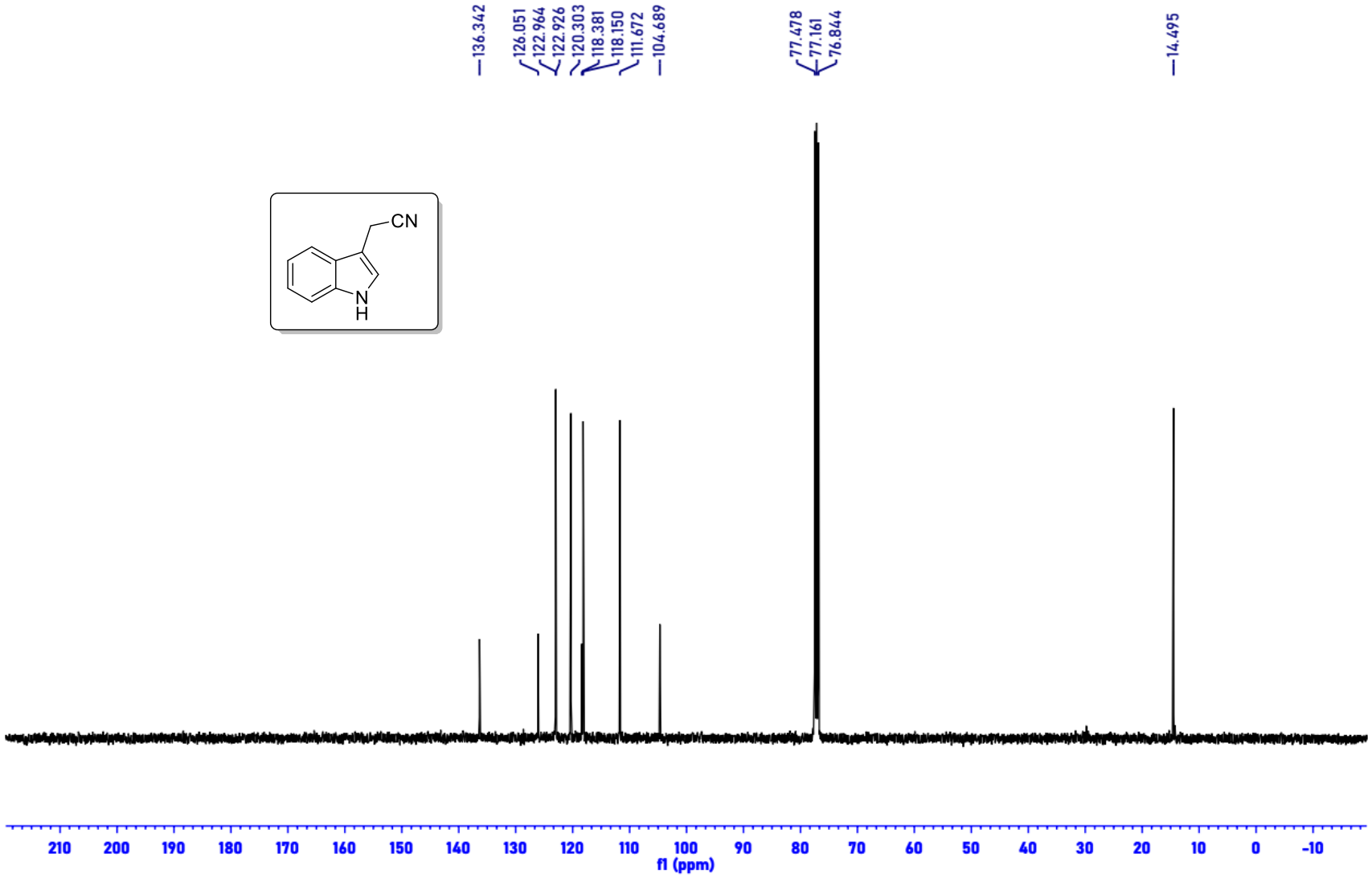
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ai



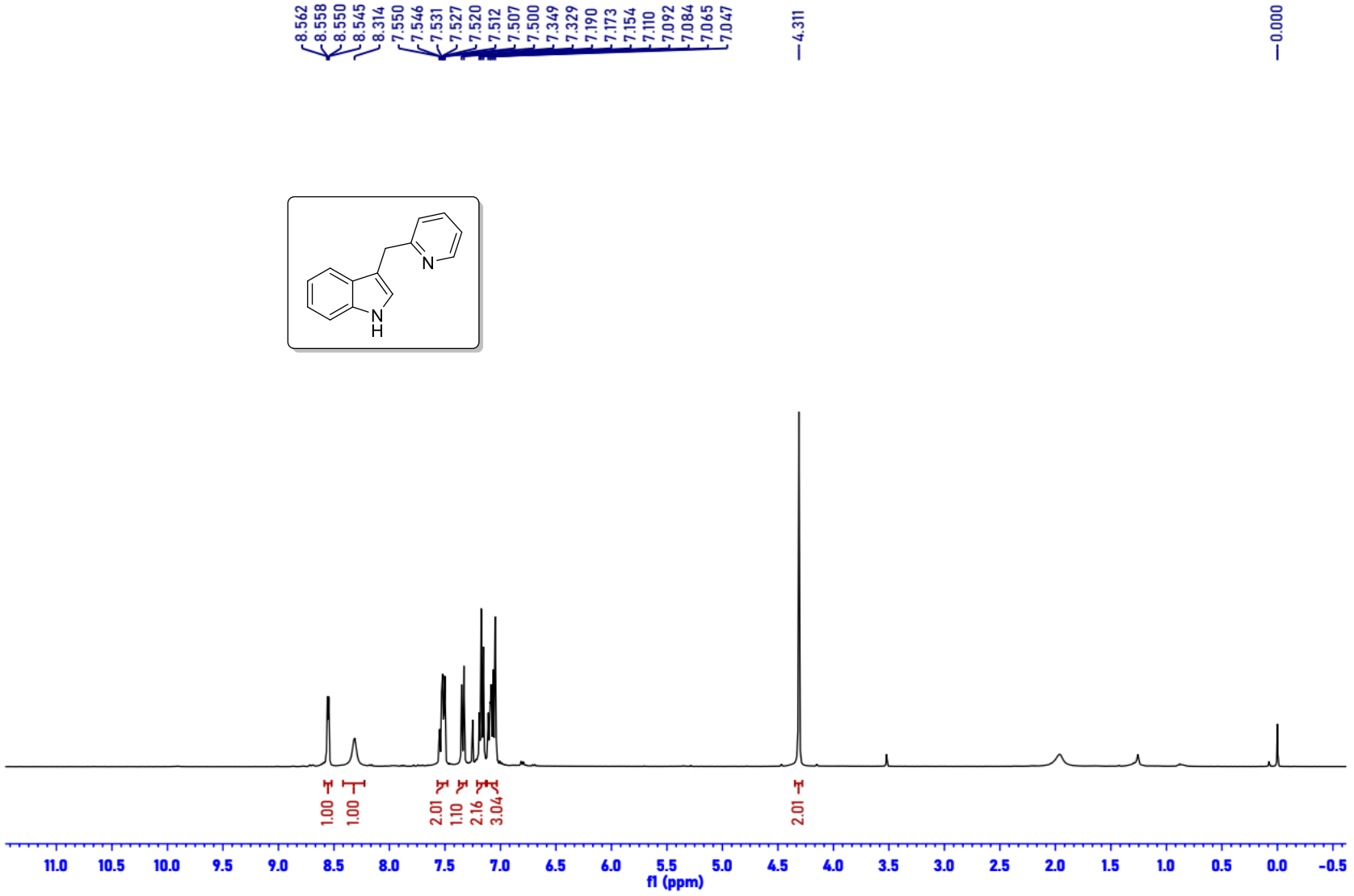
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aj



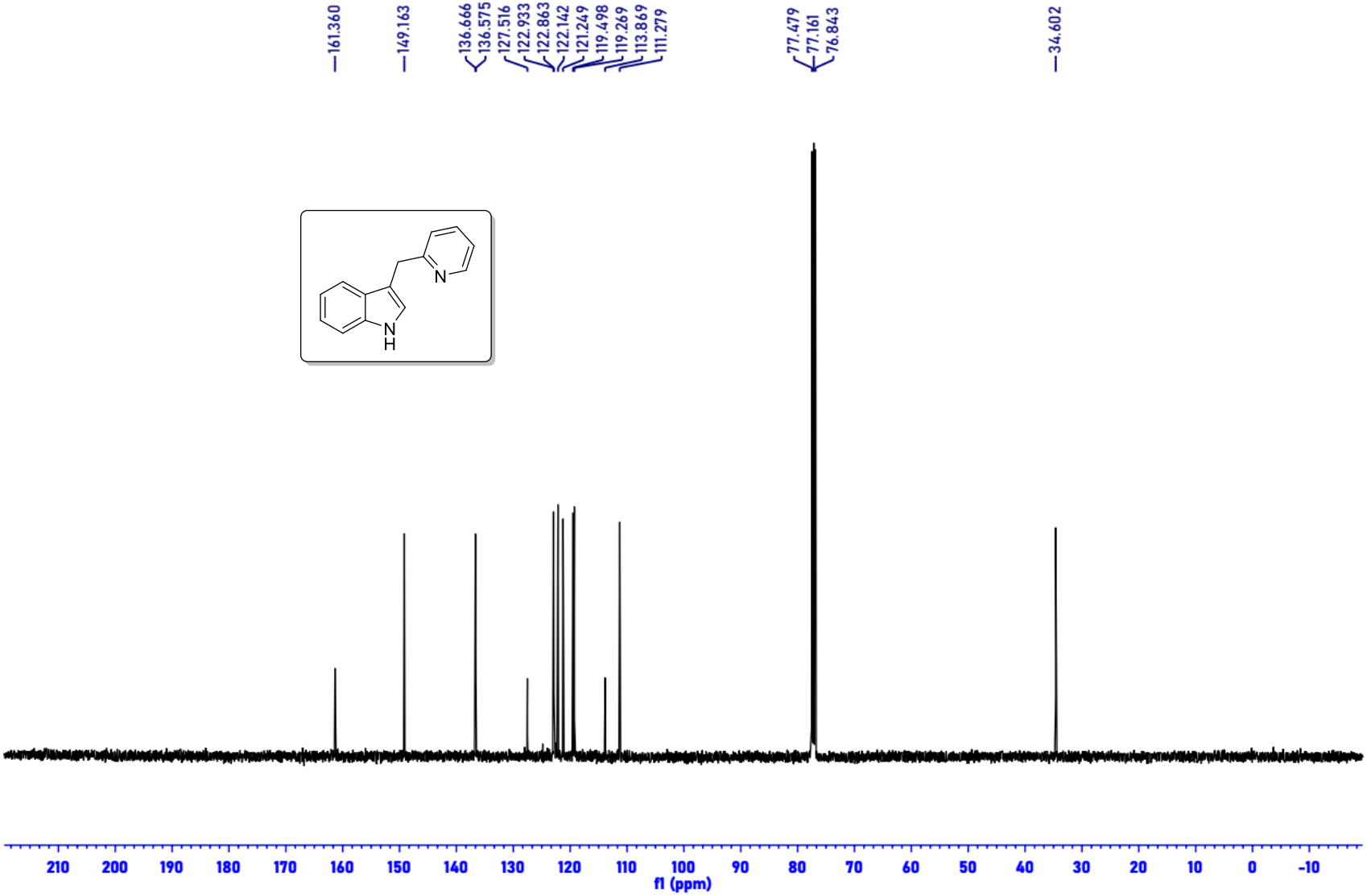
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2aj



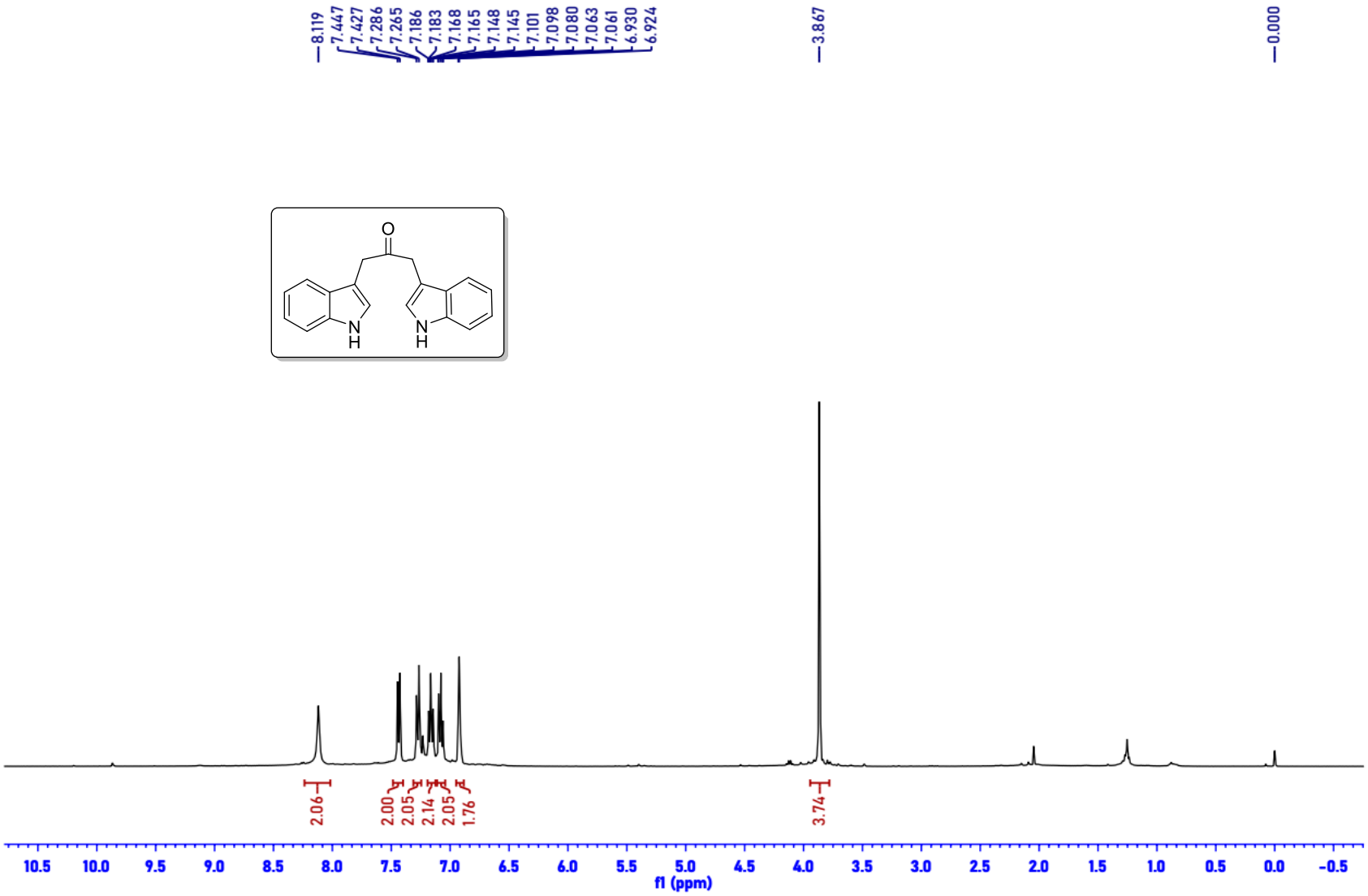
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ak



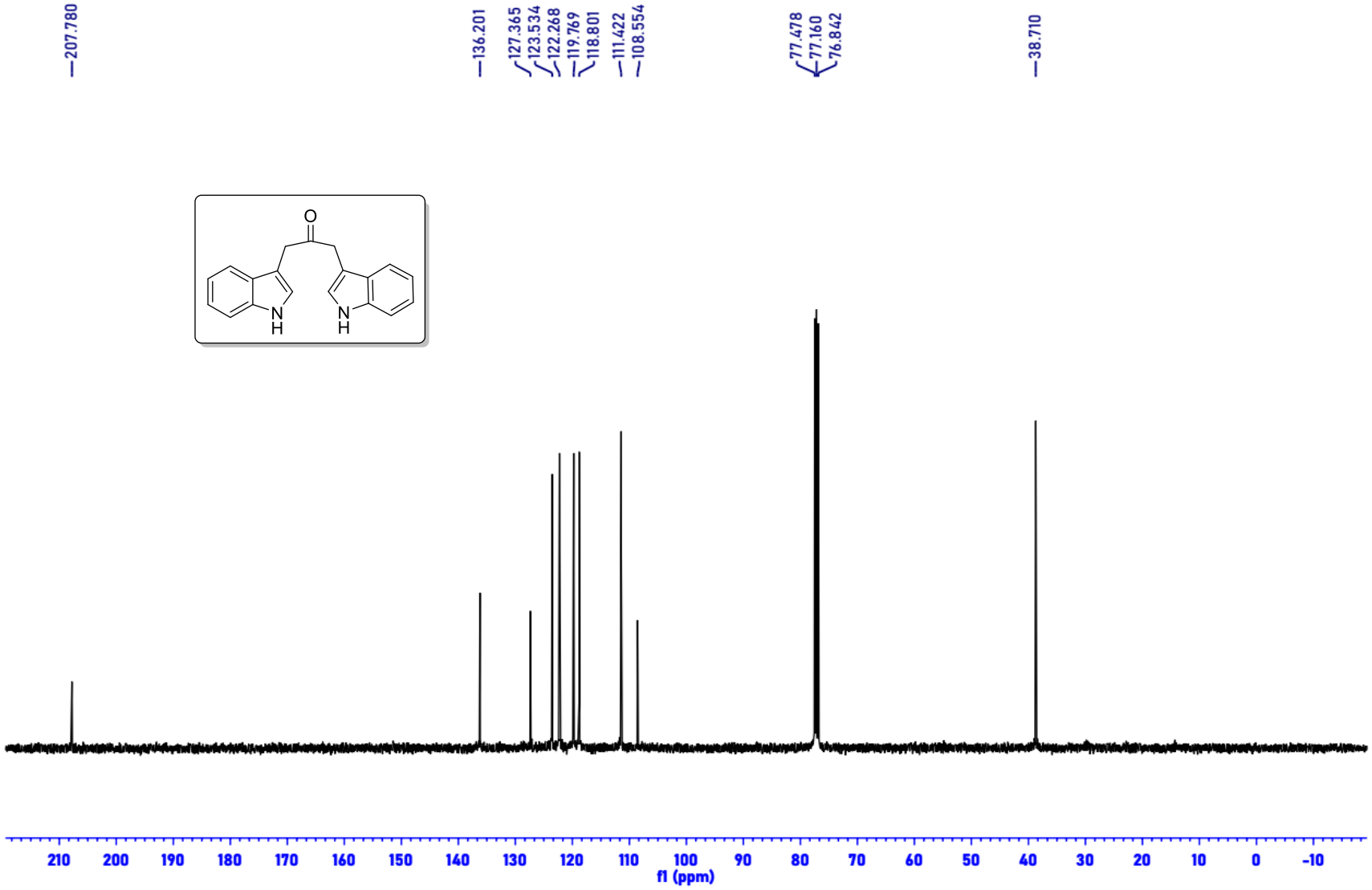
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ak



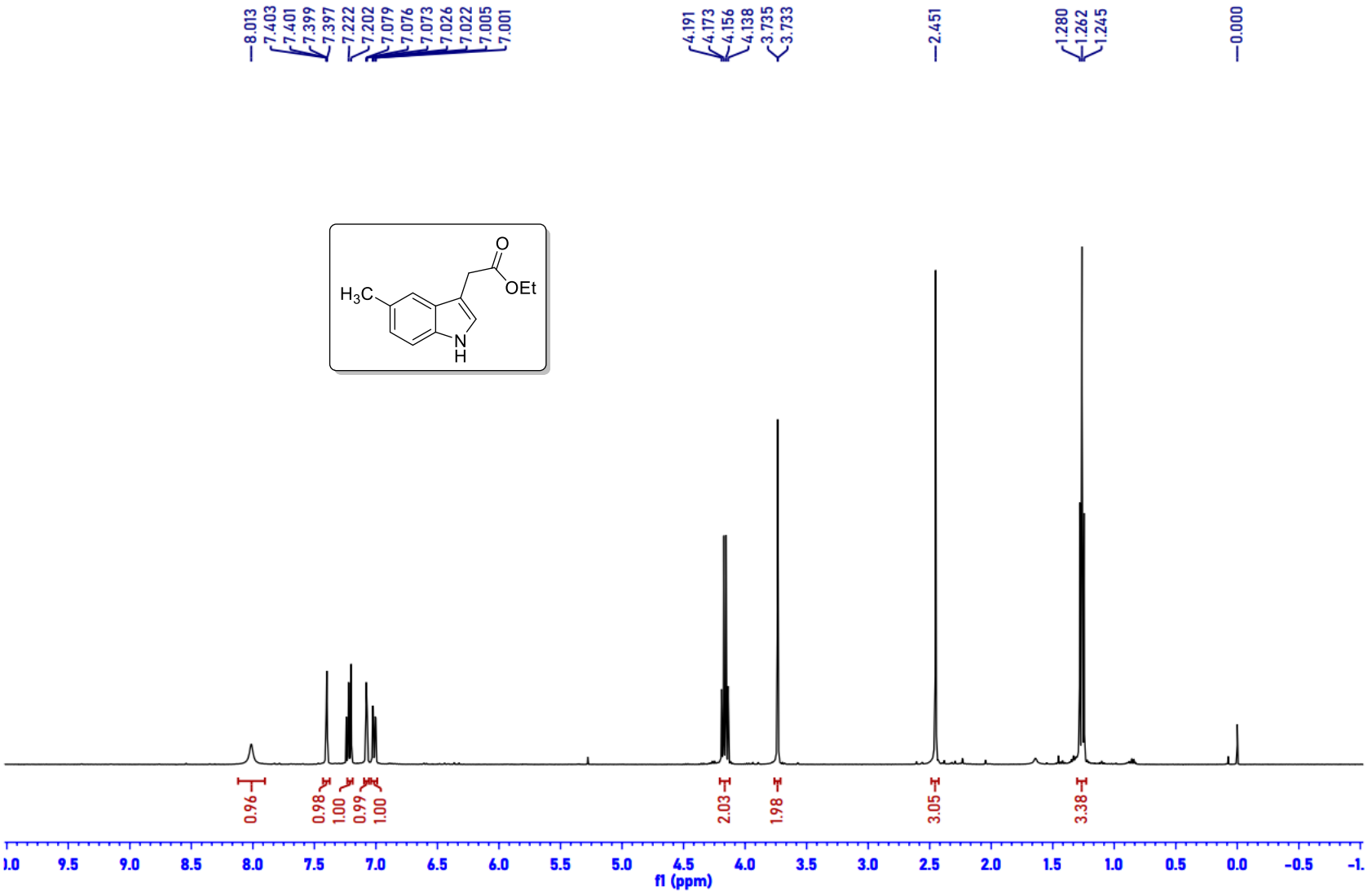
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2al



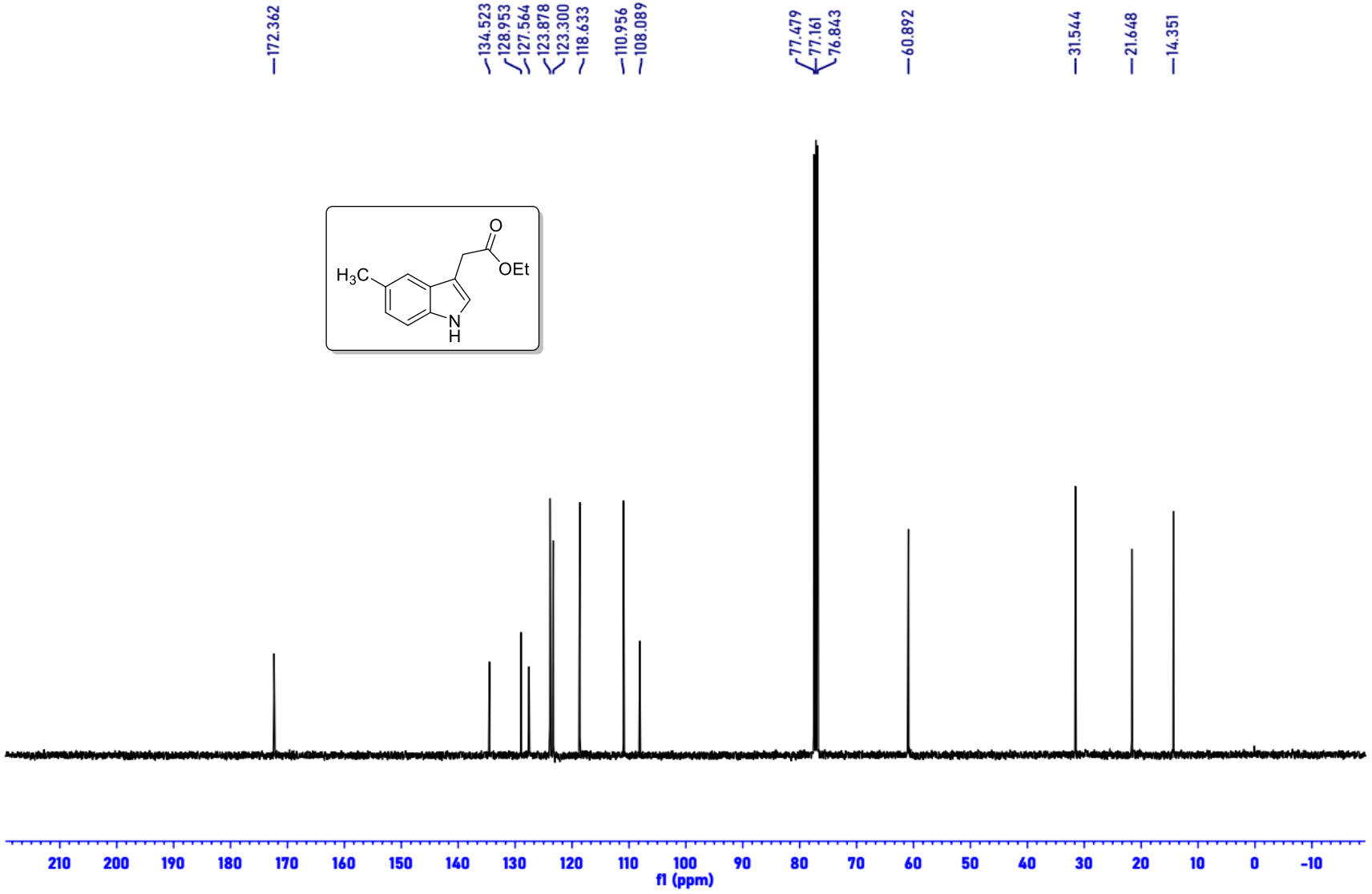
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2al



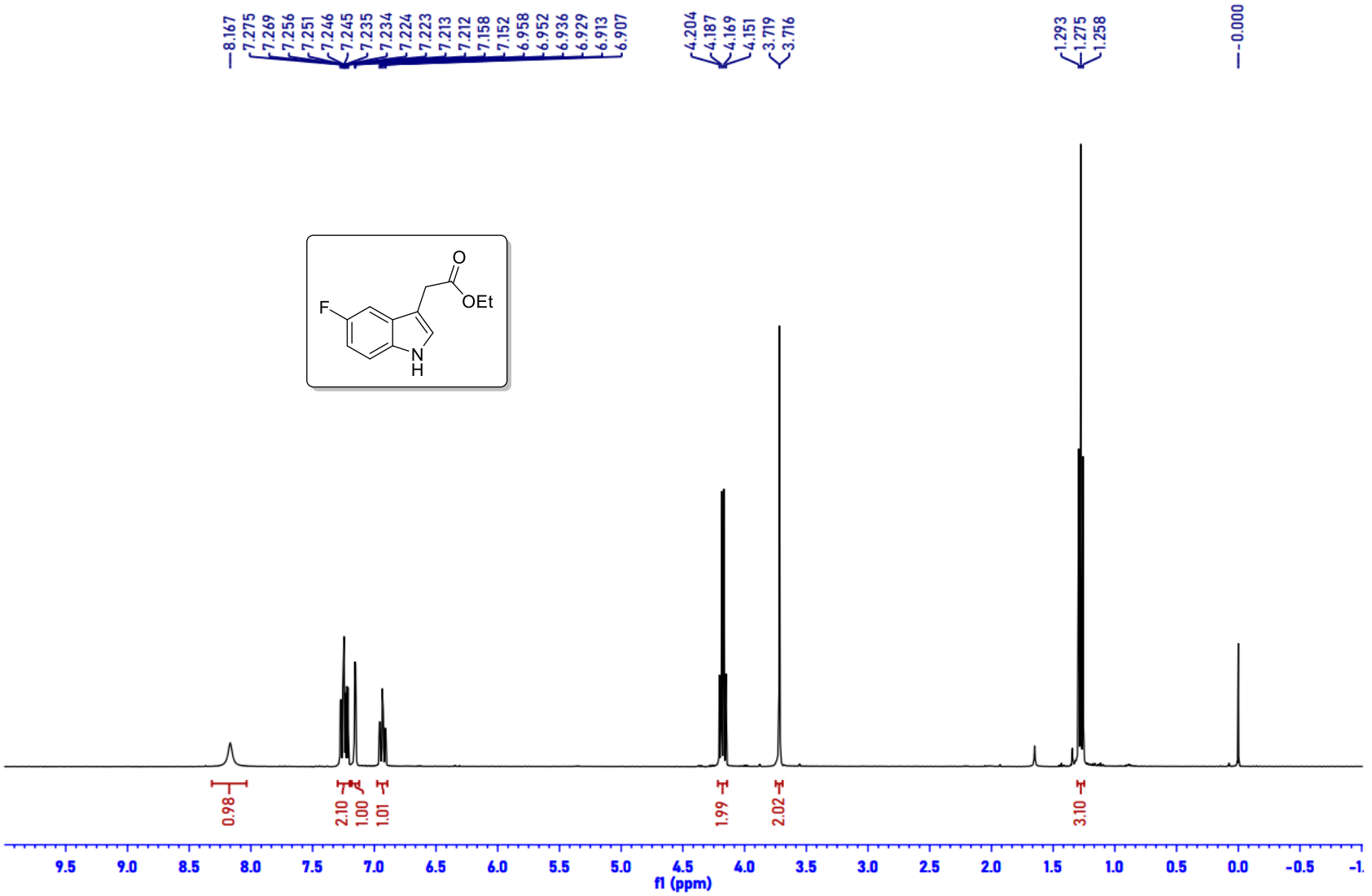
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ba



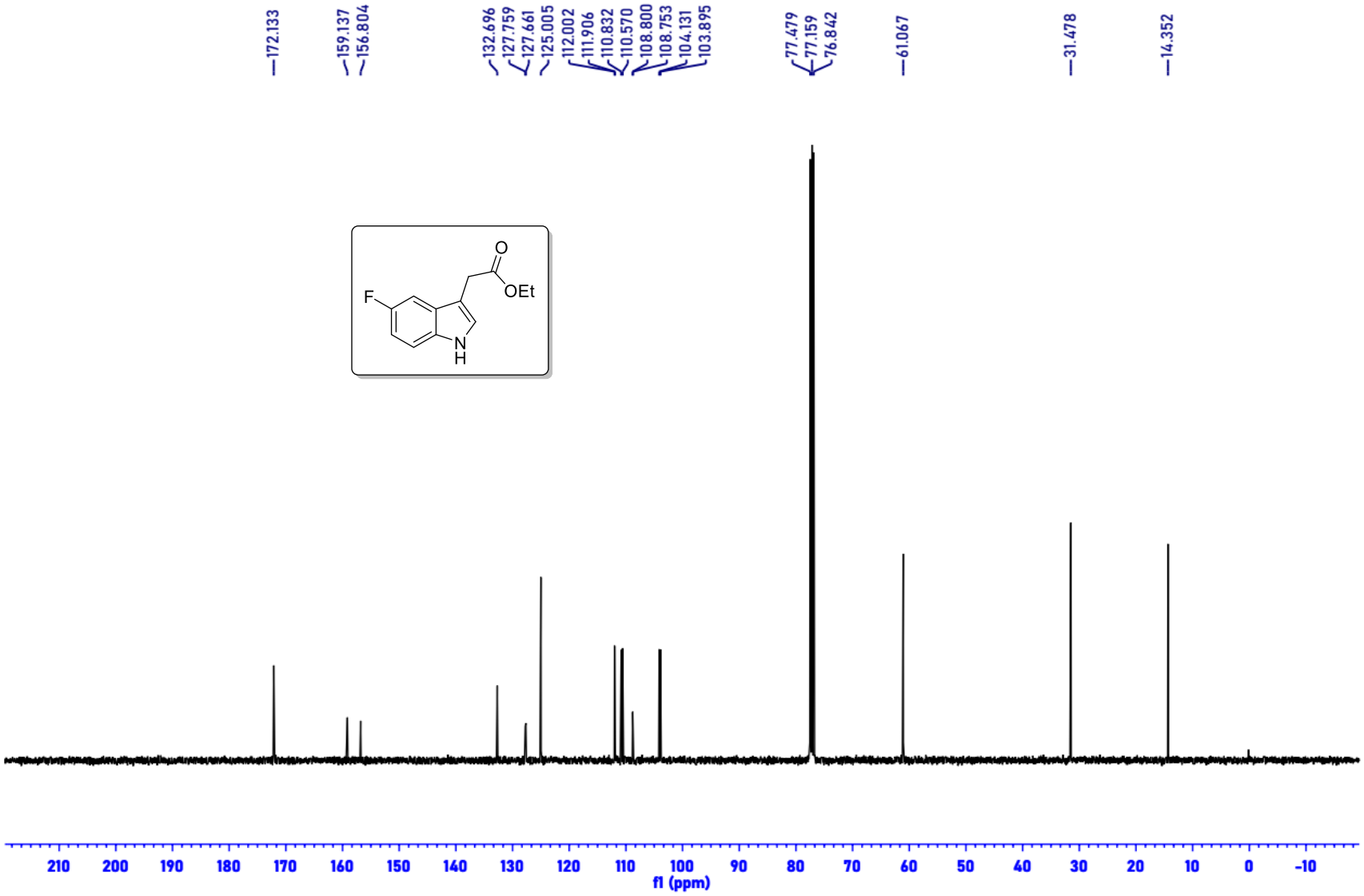
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ba



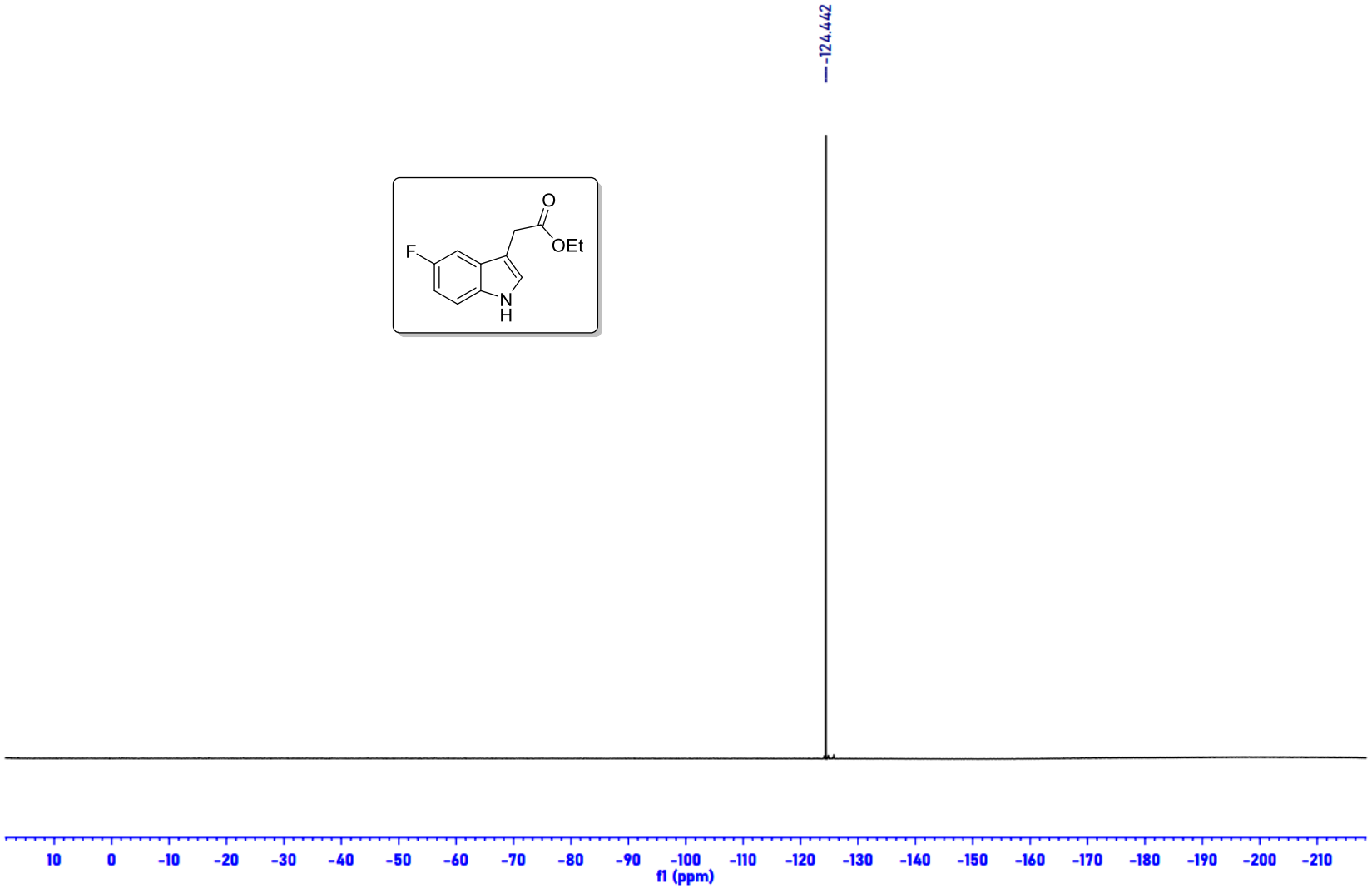
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ca



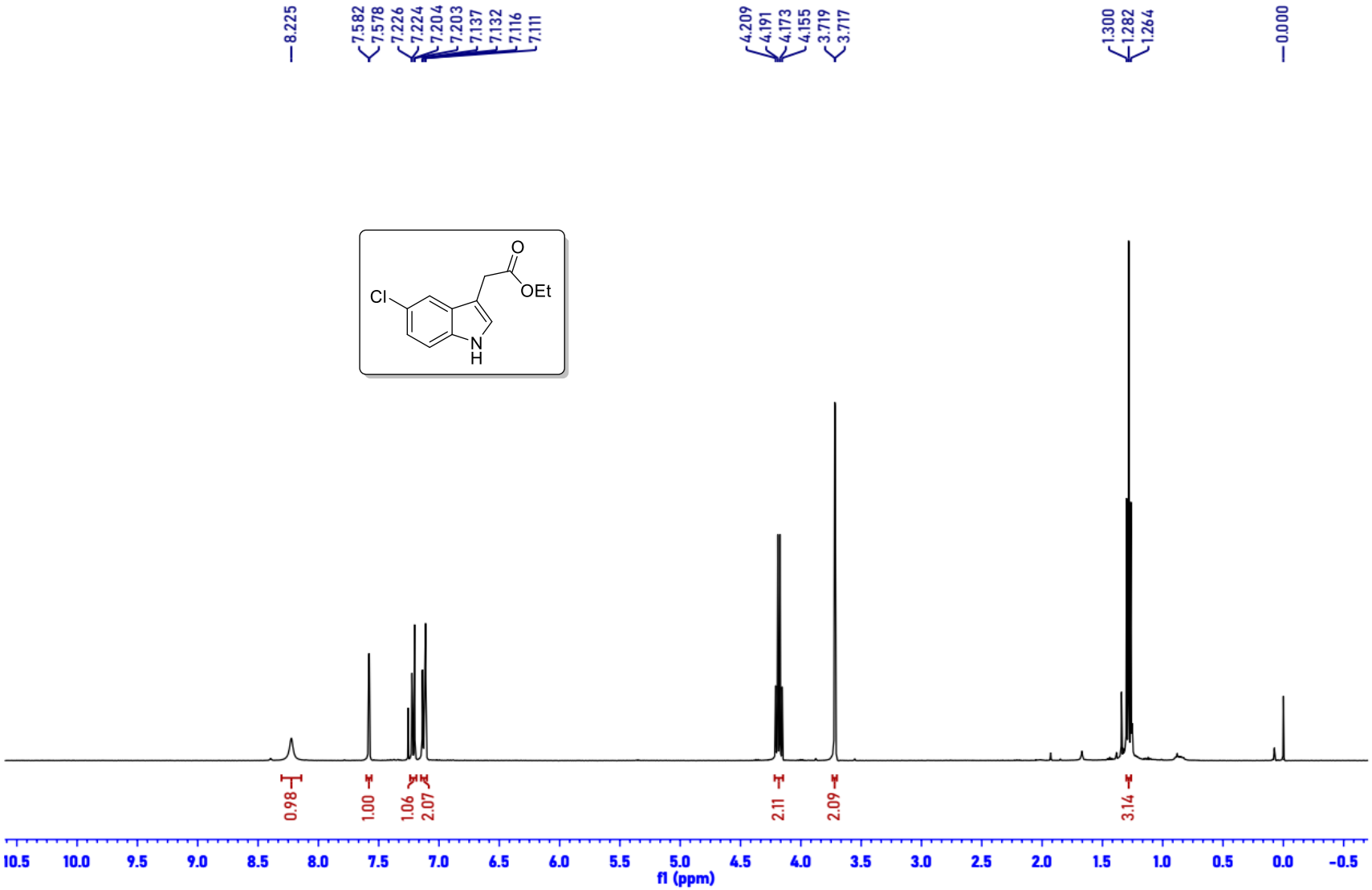
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ca



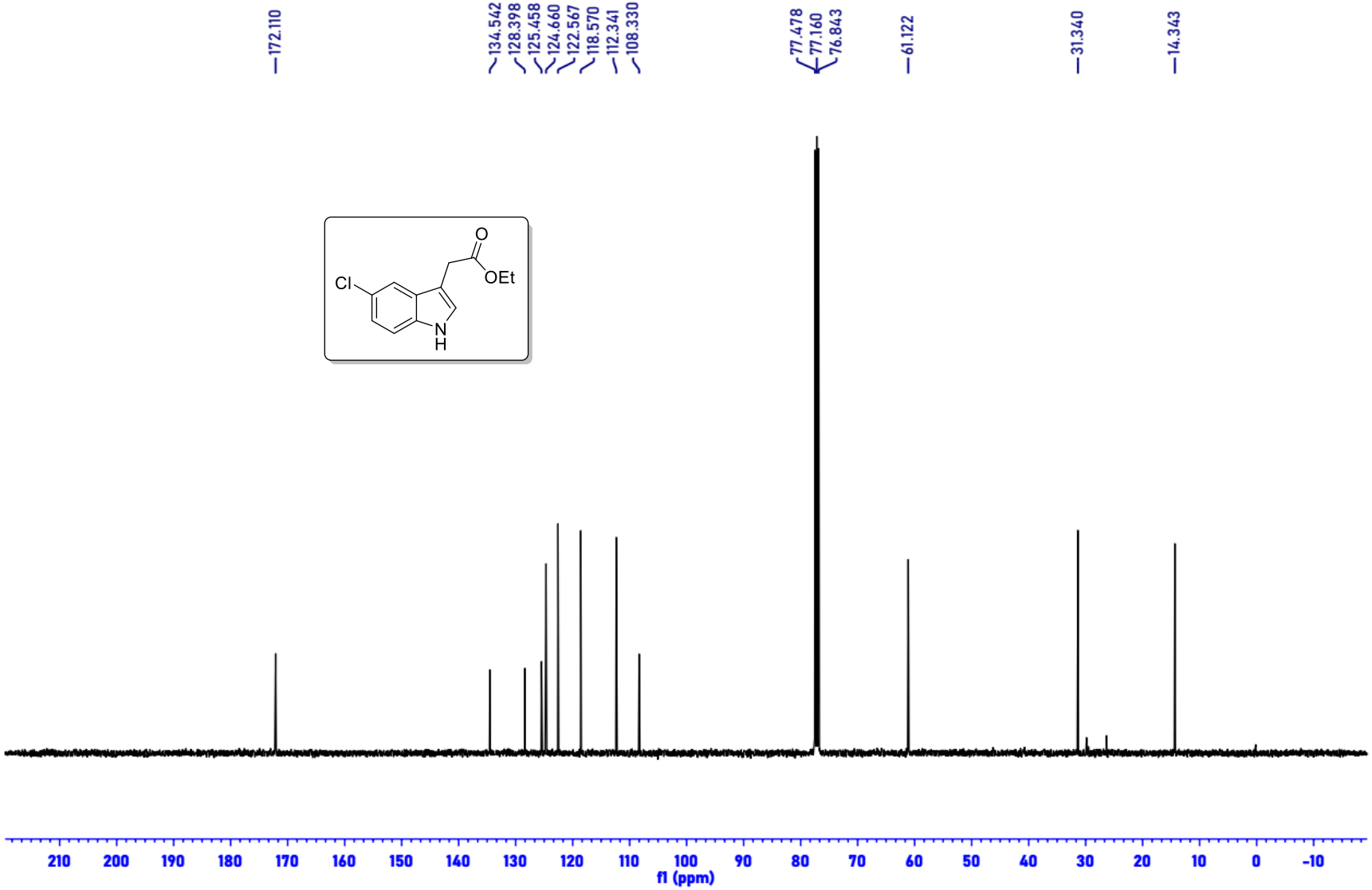
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 2ca



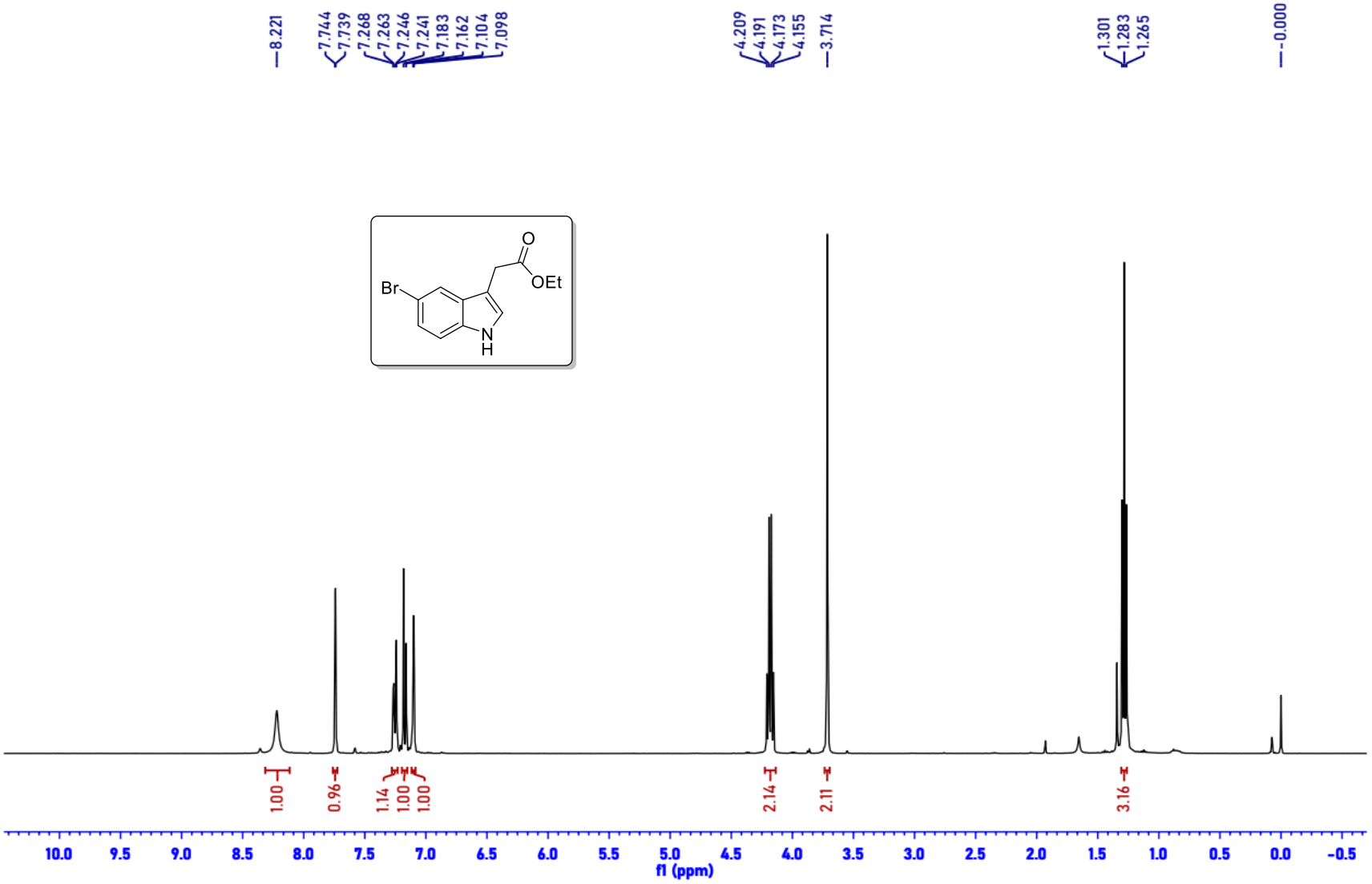
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2da



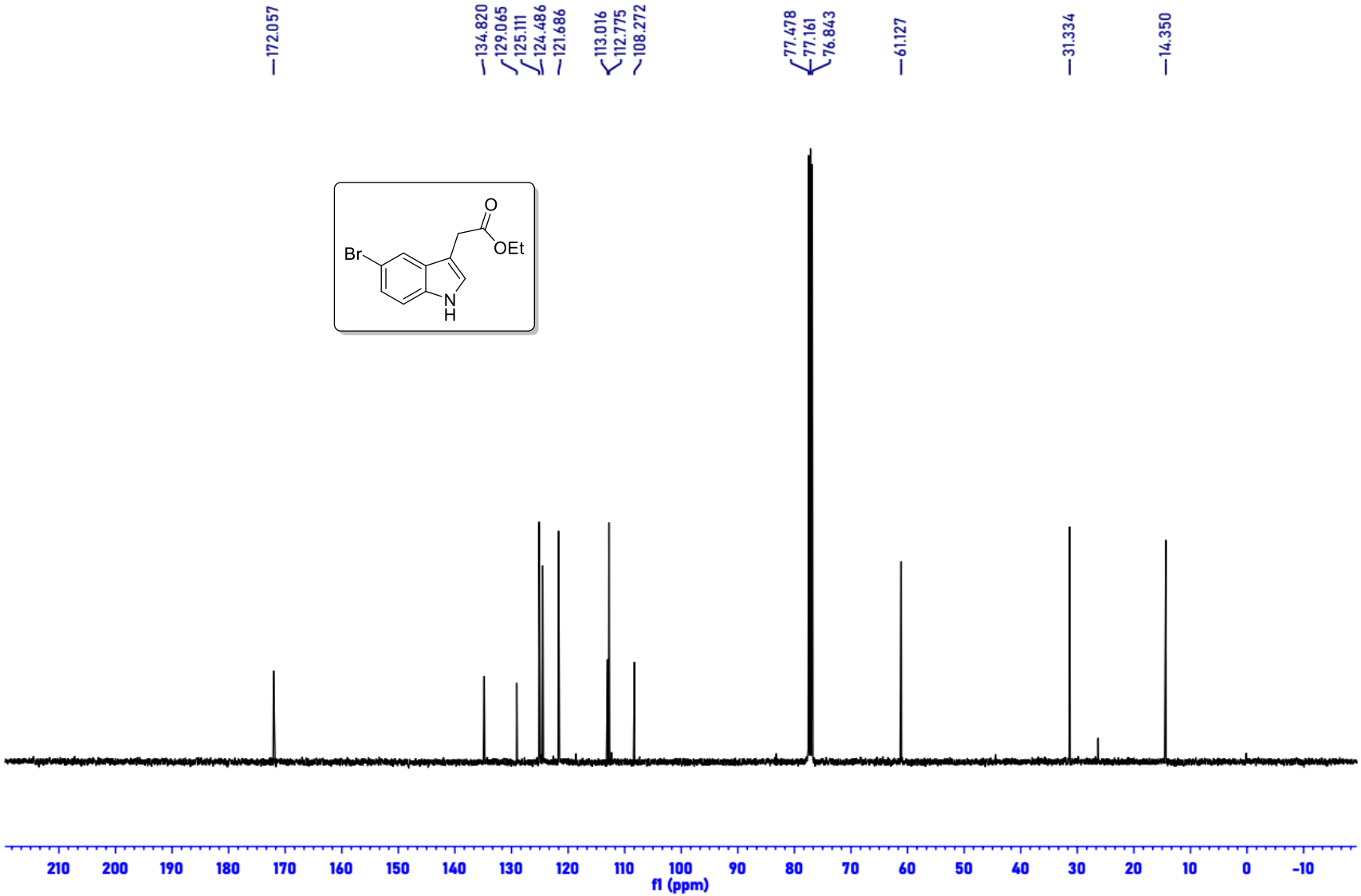
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2da



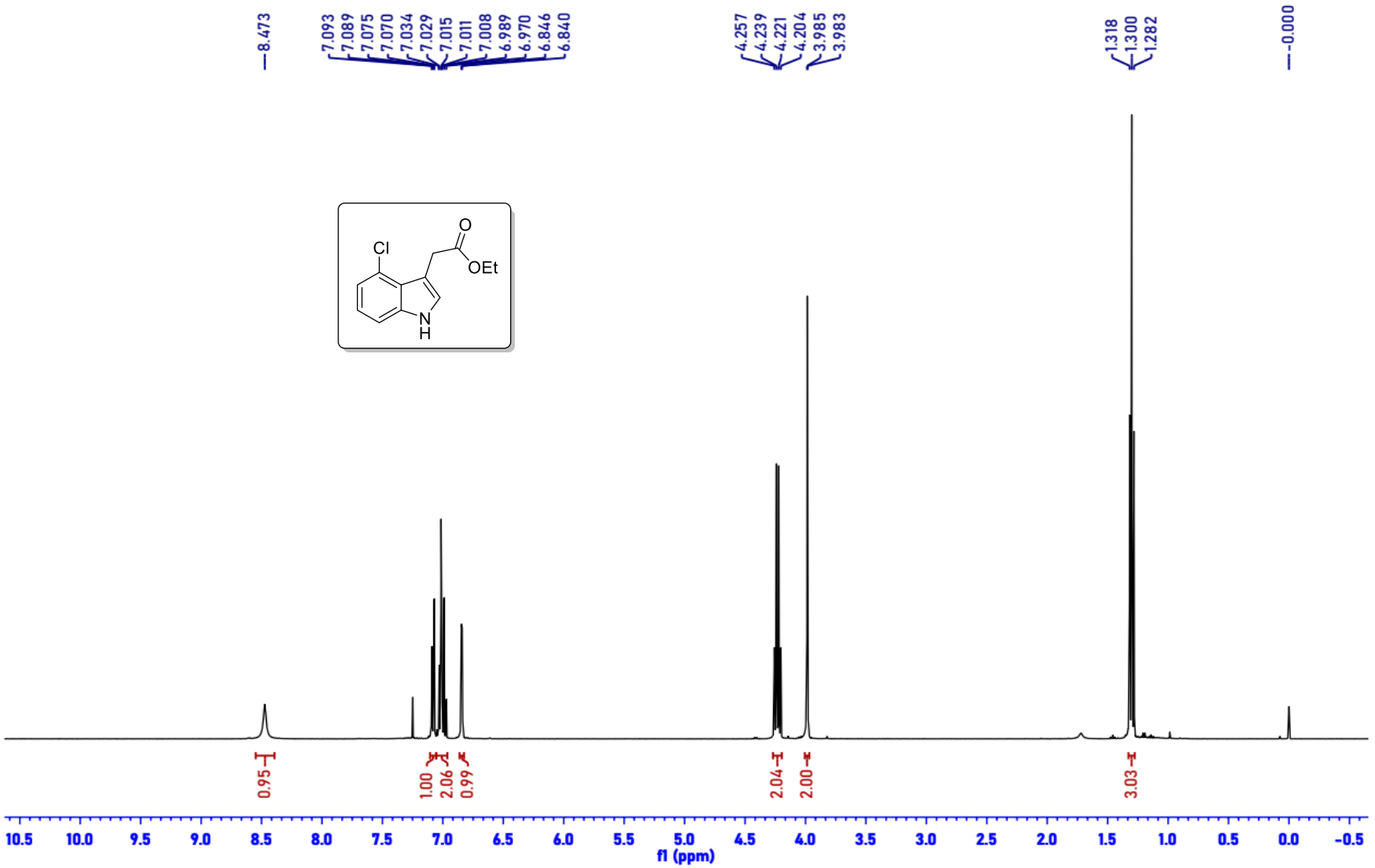
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ea



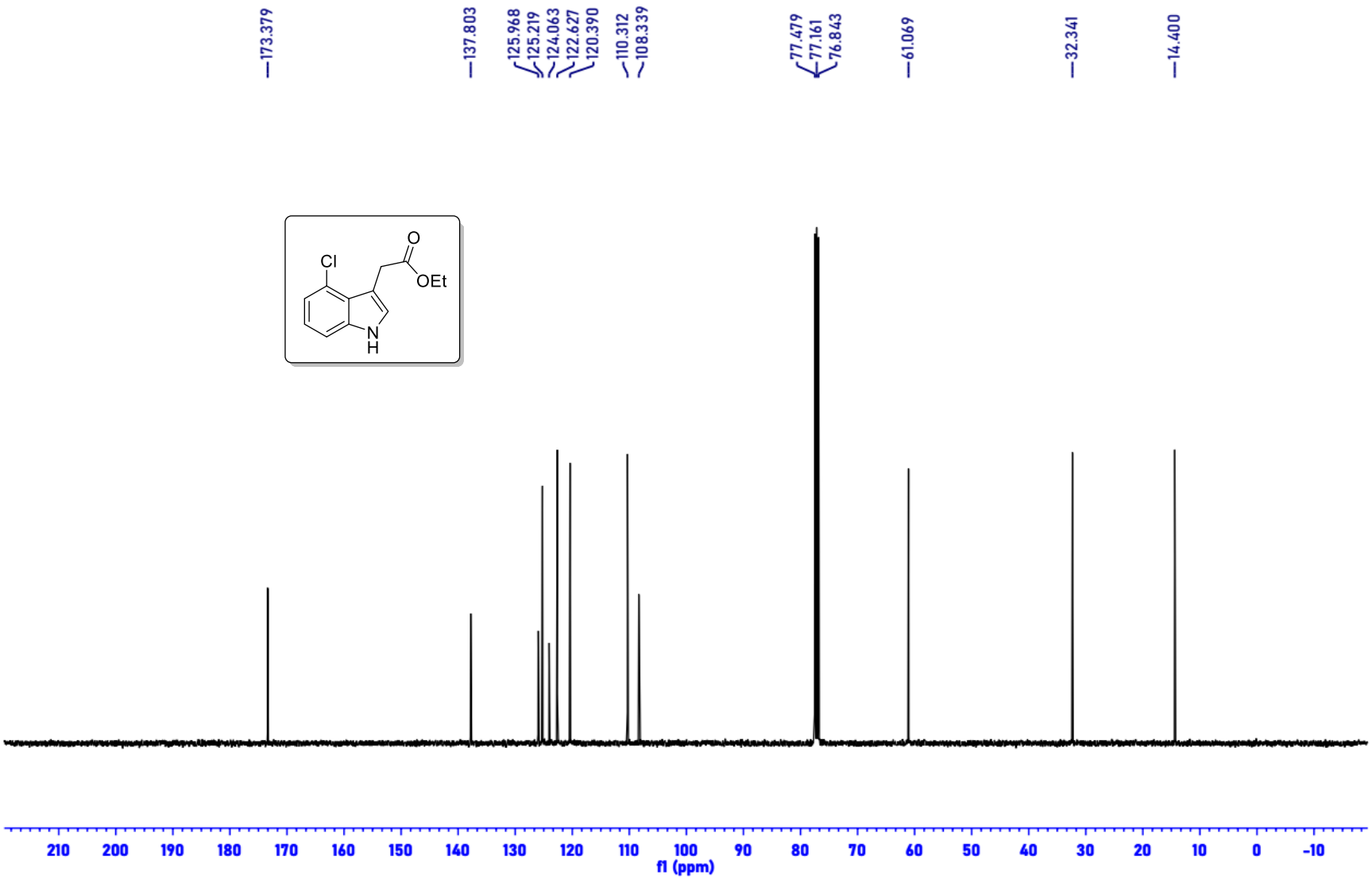
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ea



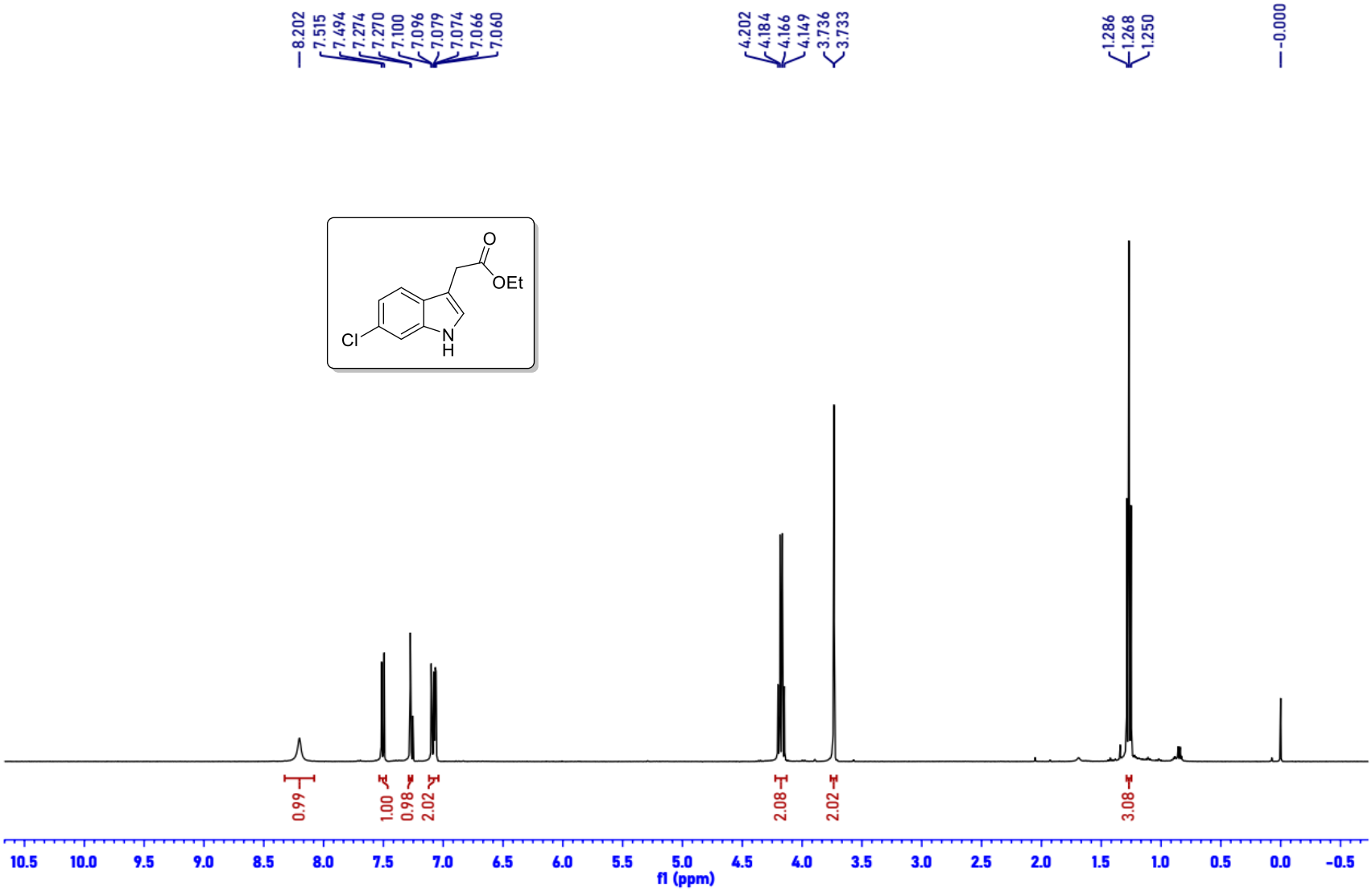
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2fa



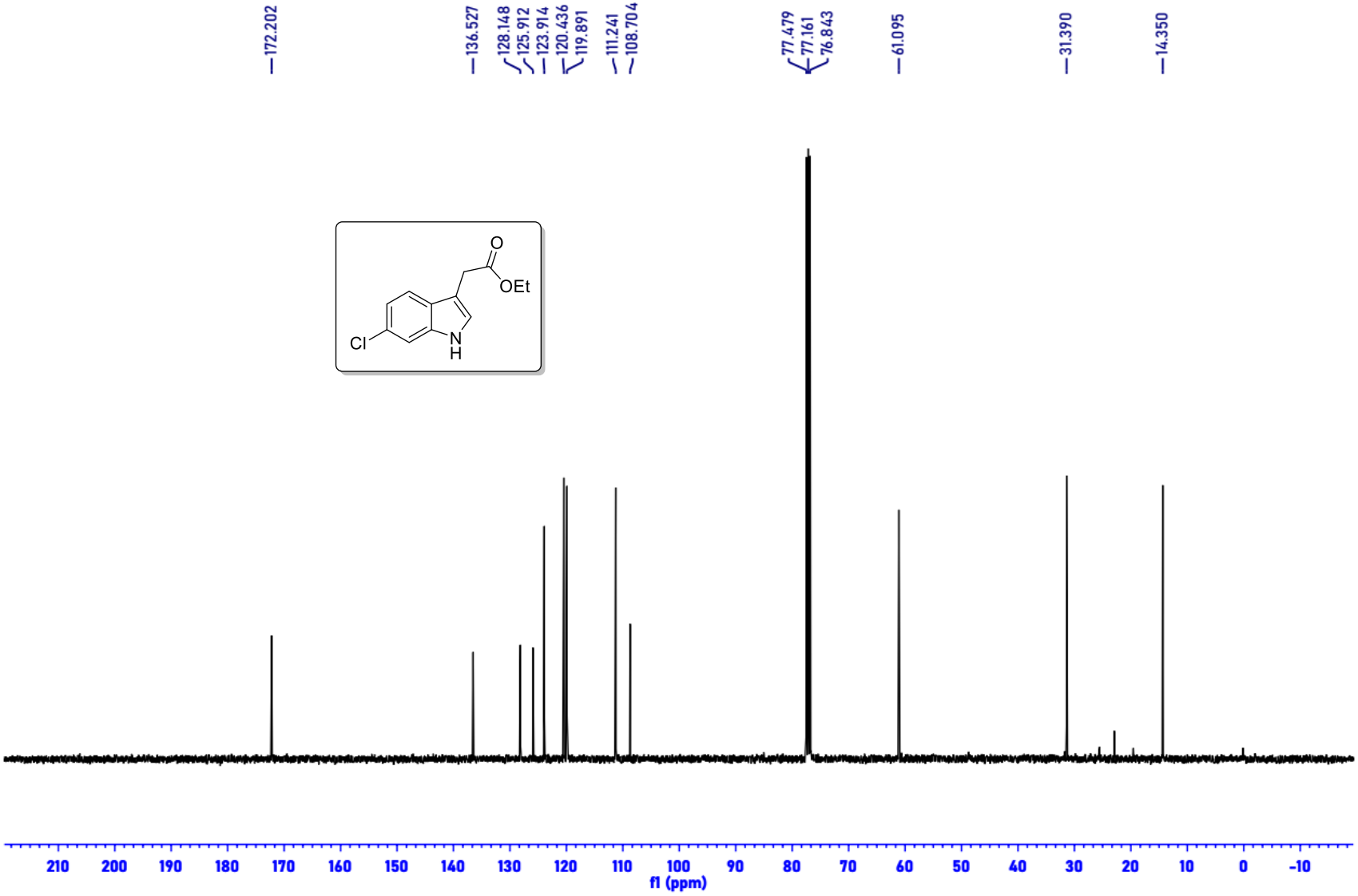
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2fa



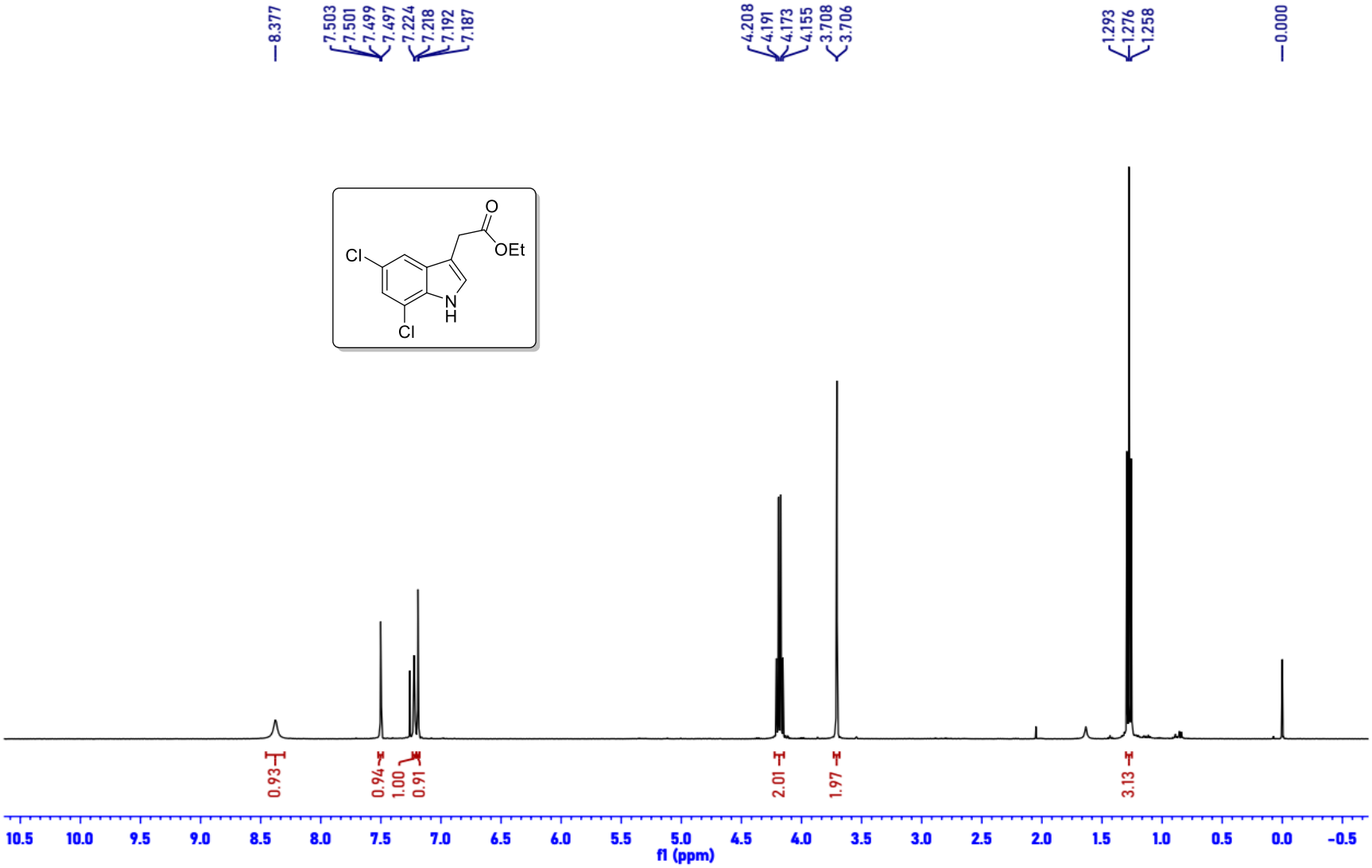
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ga



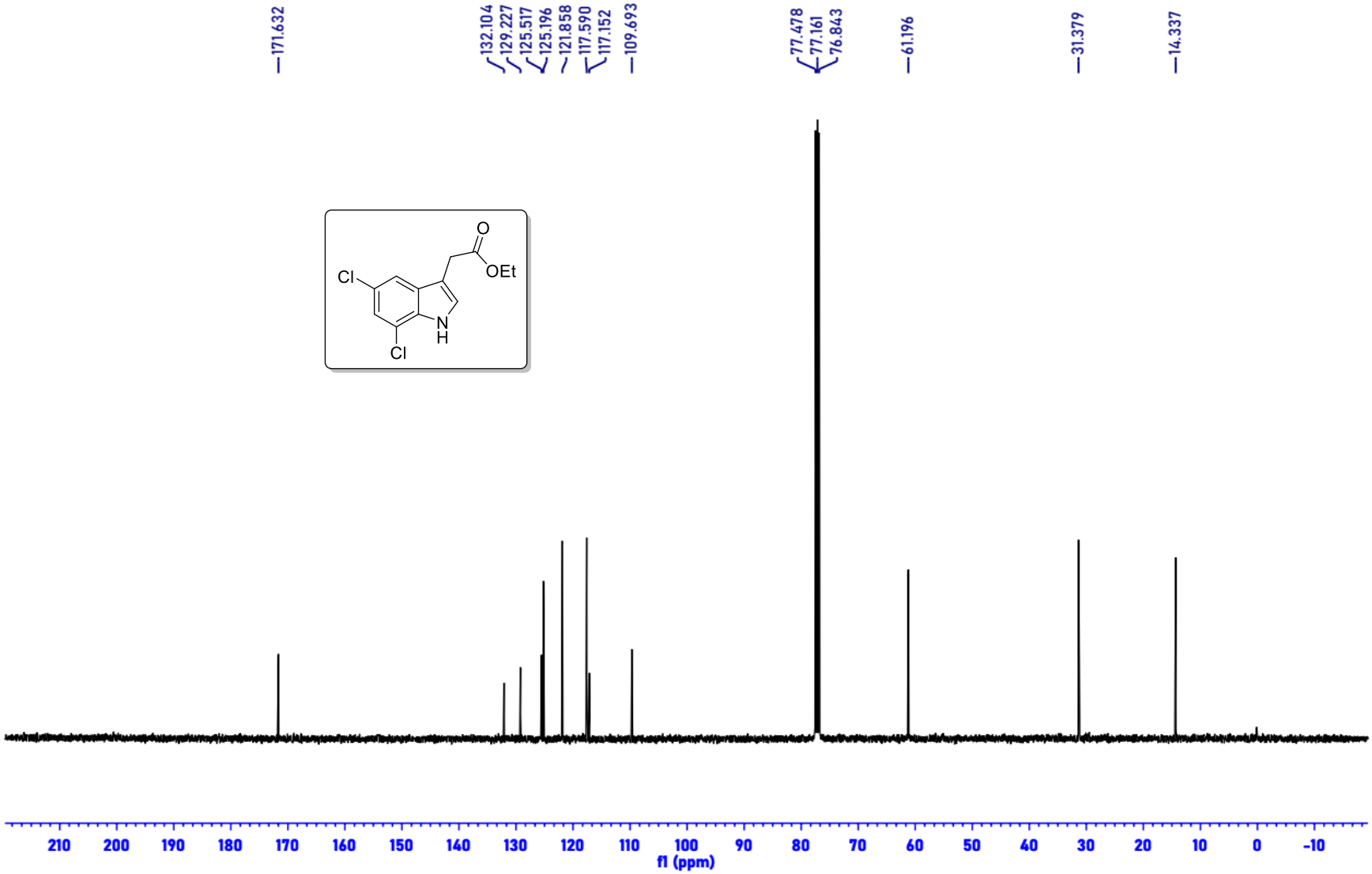
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ga



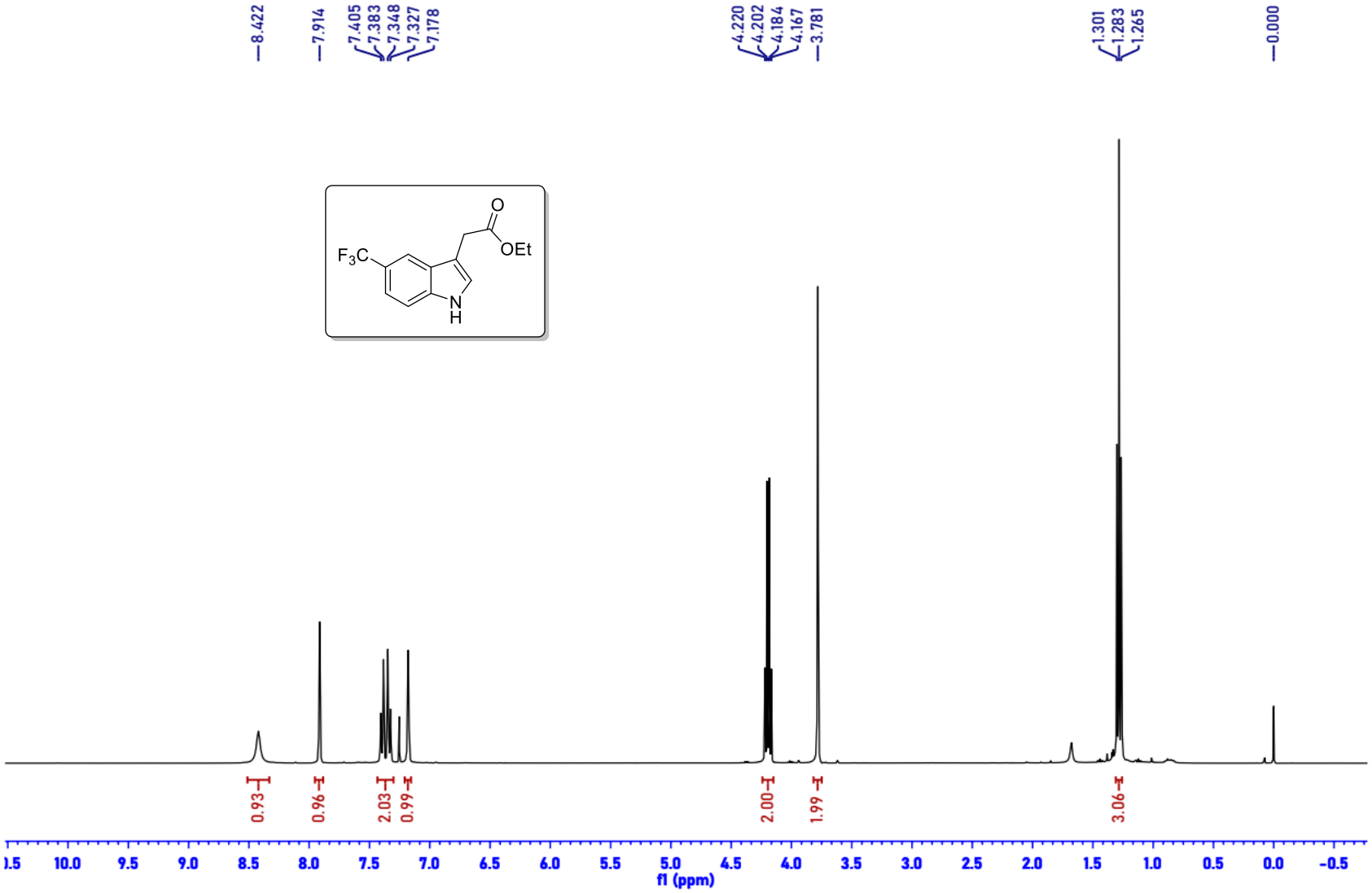
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ha



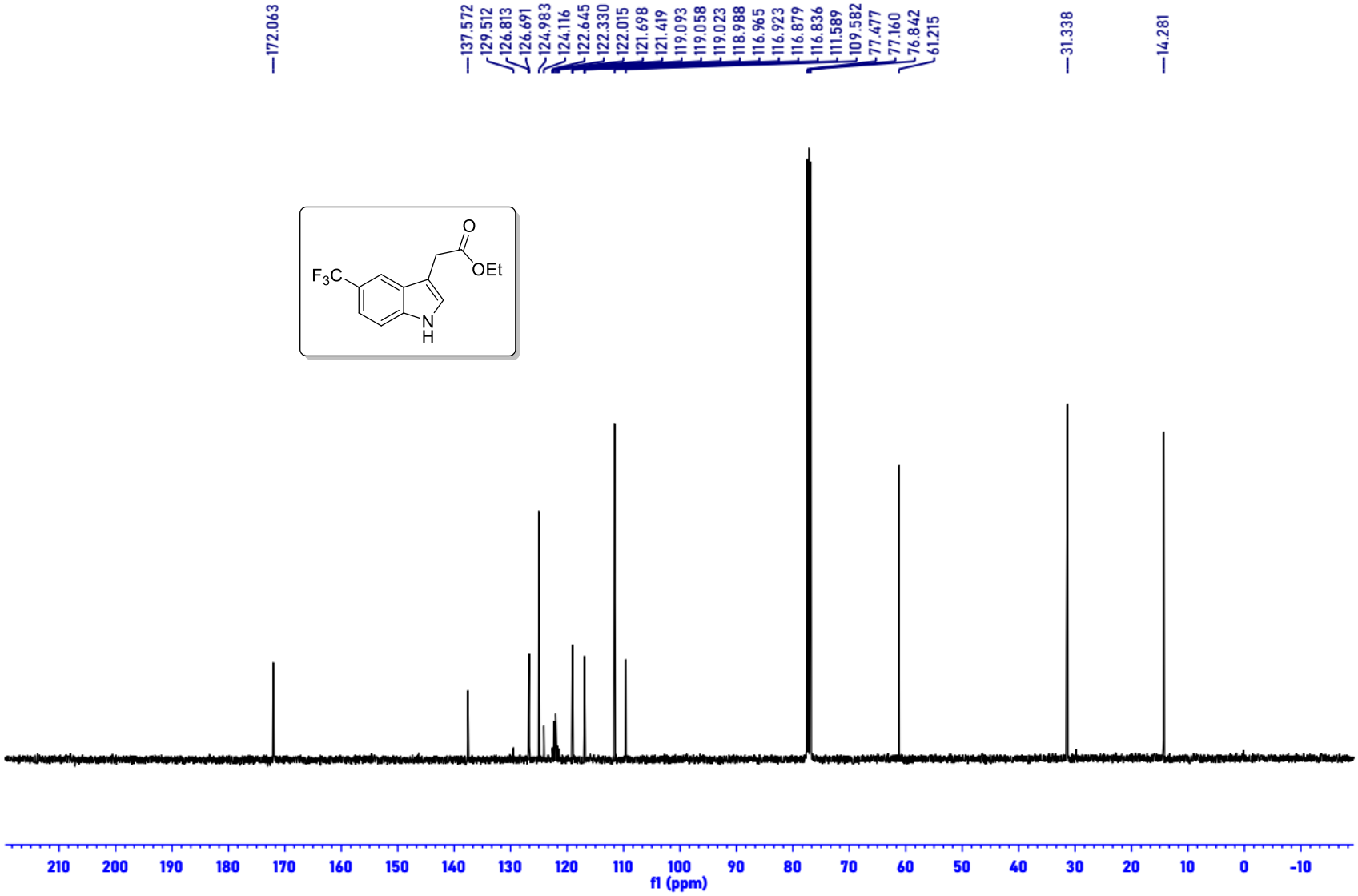
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ha



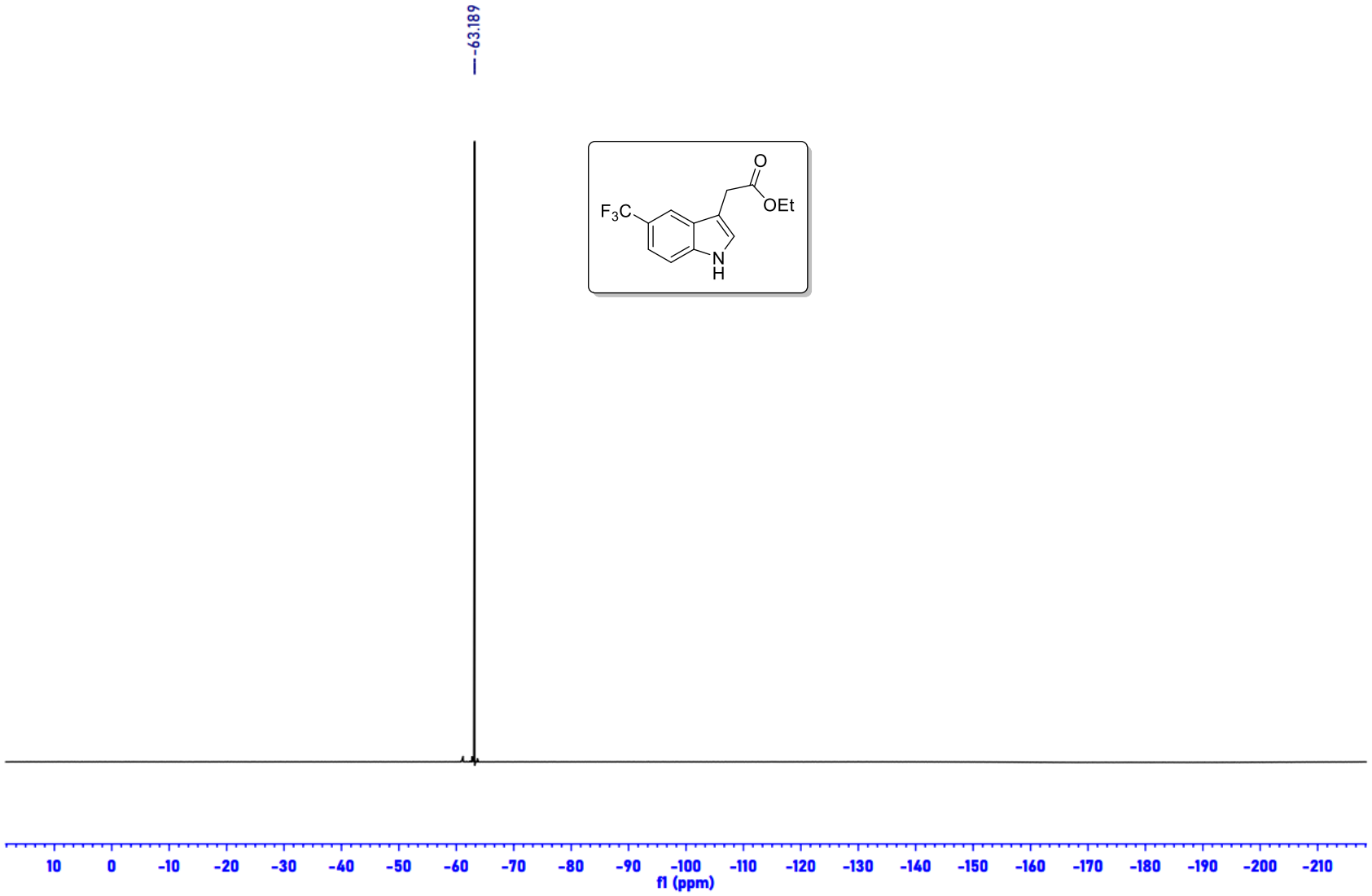
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ia



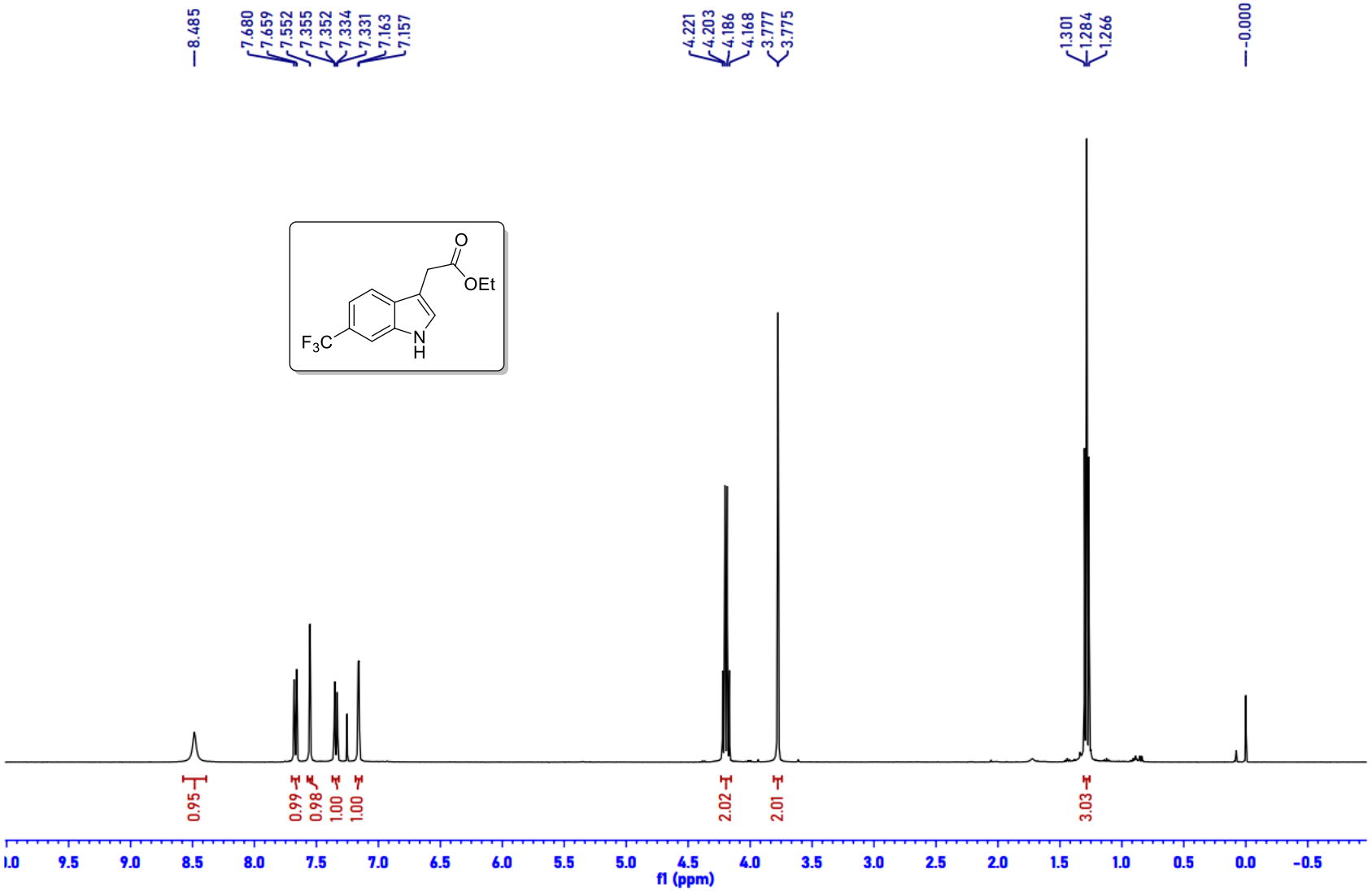
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ia



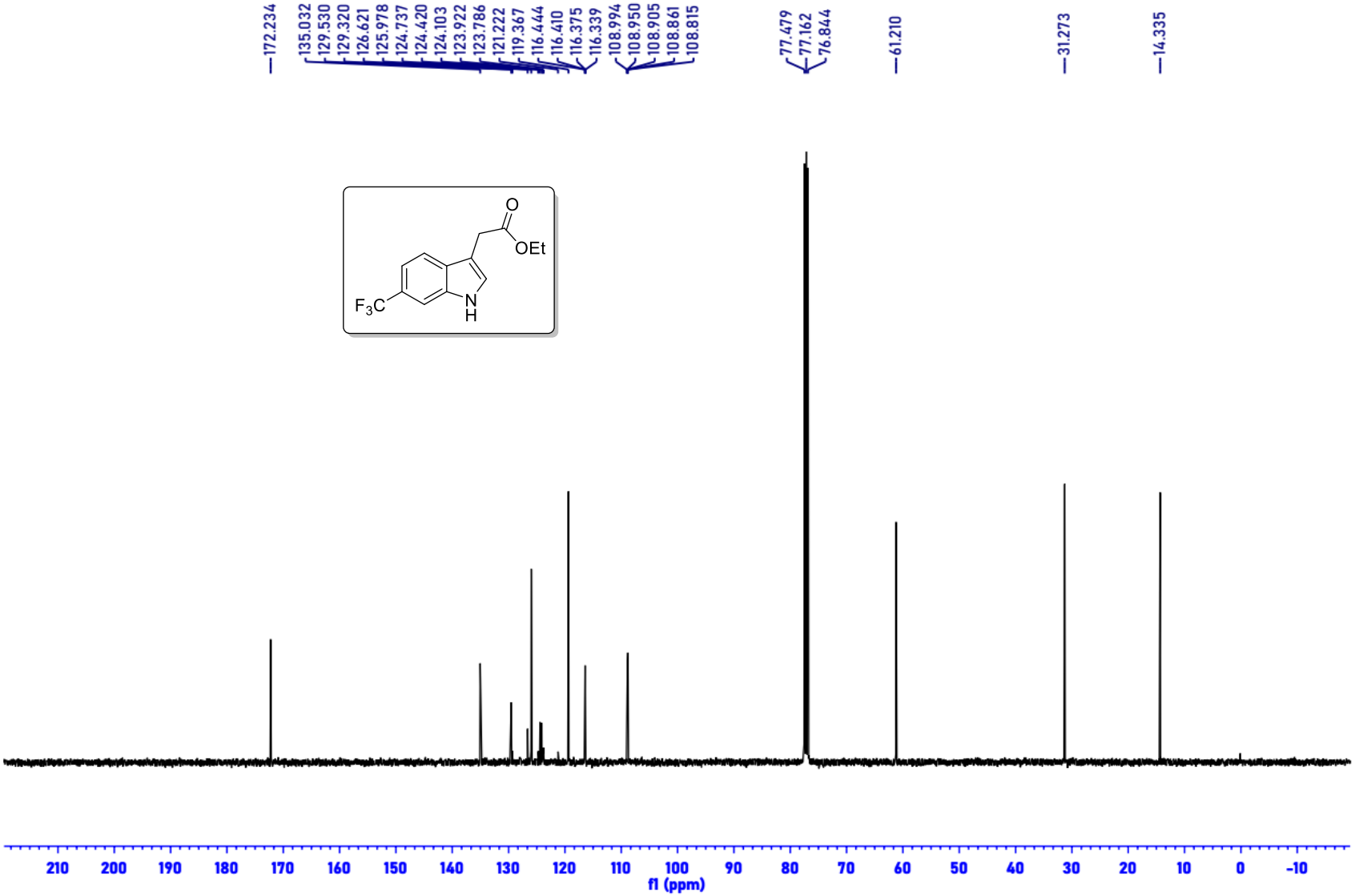
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 2ia



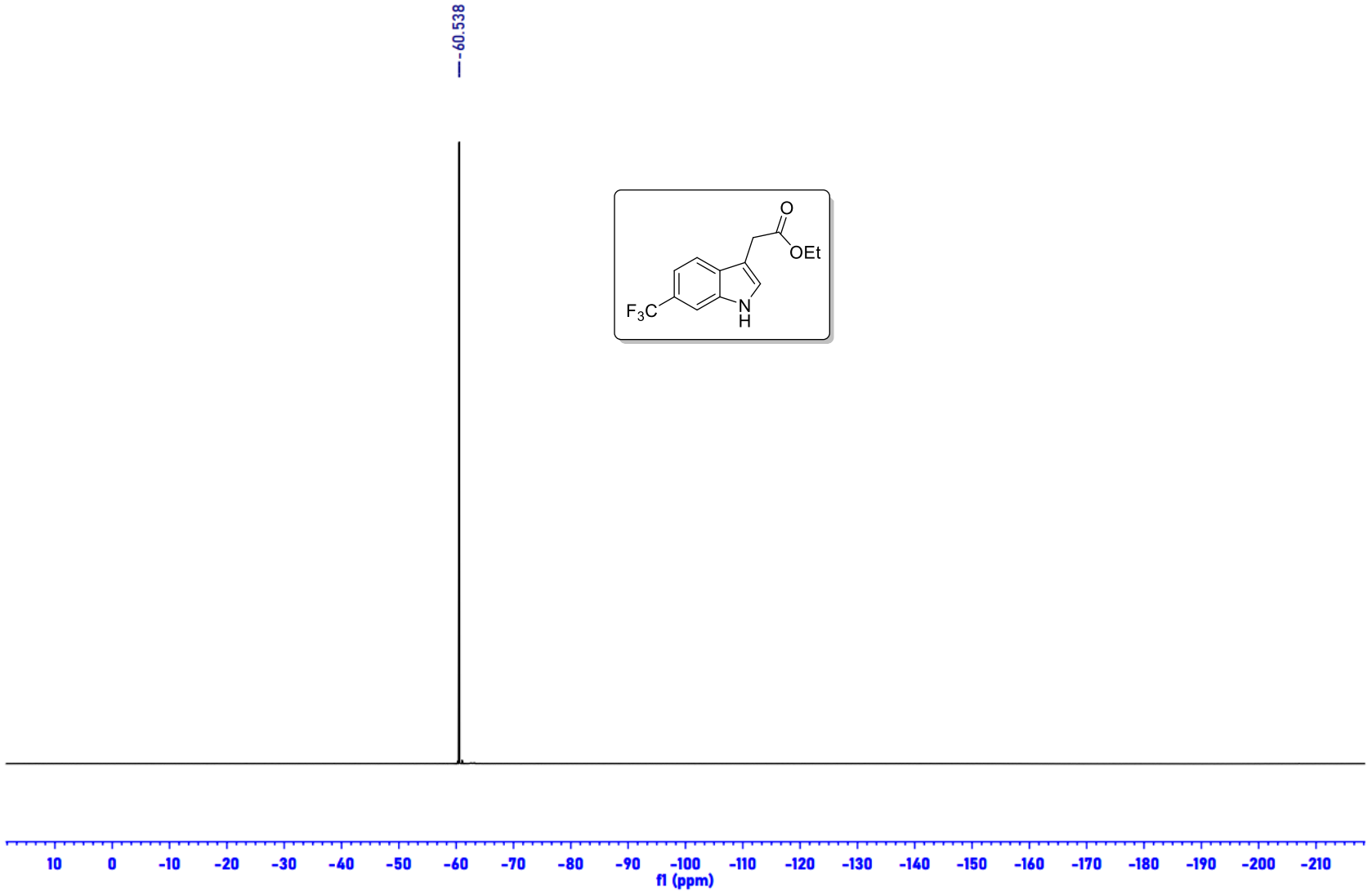
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ja



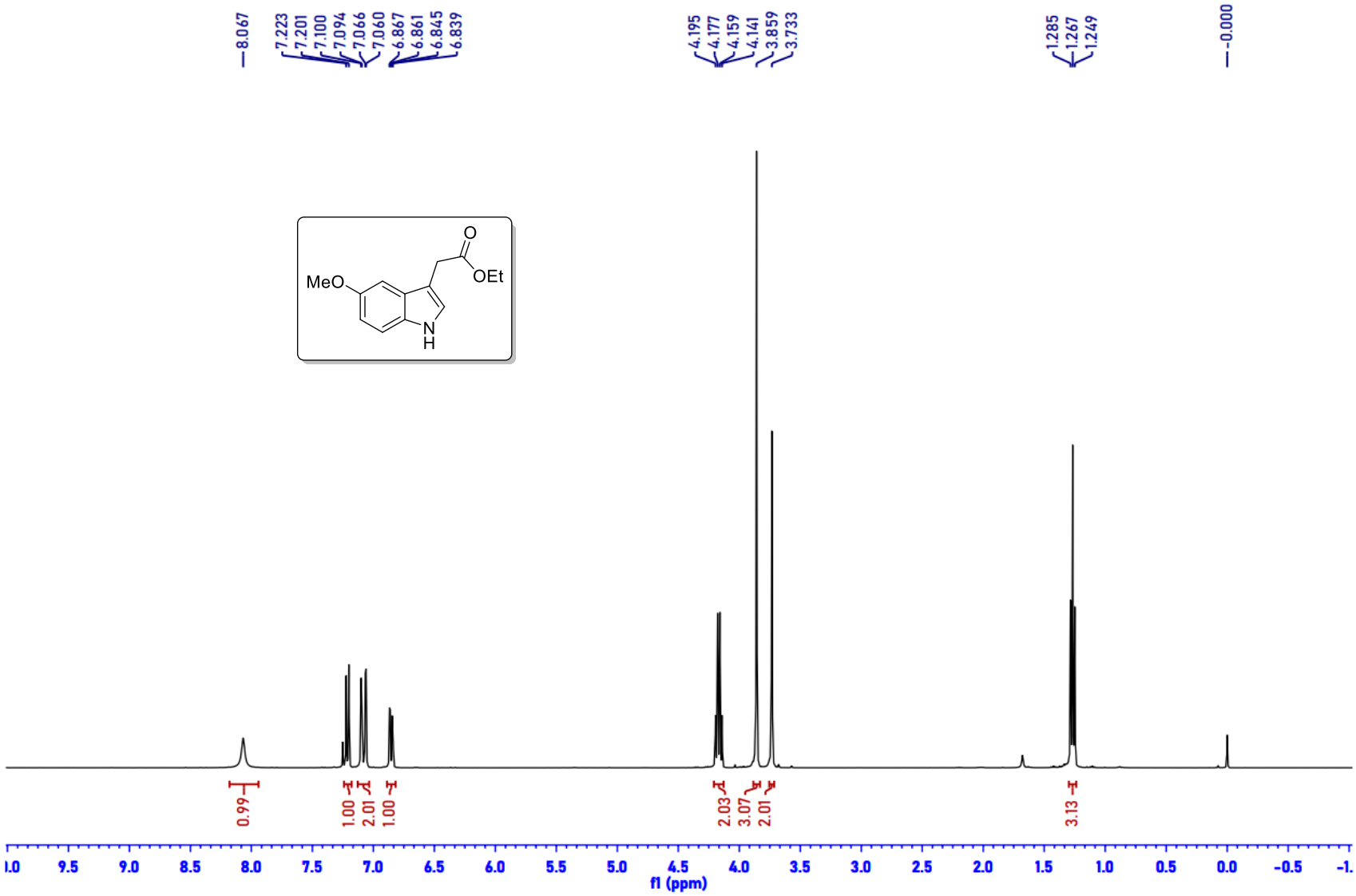
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ja



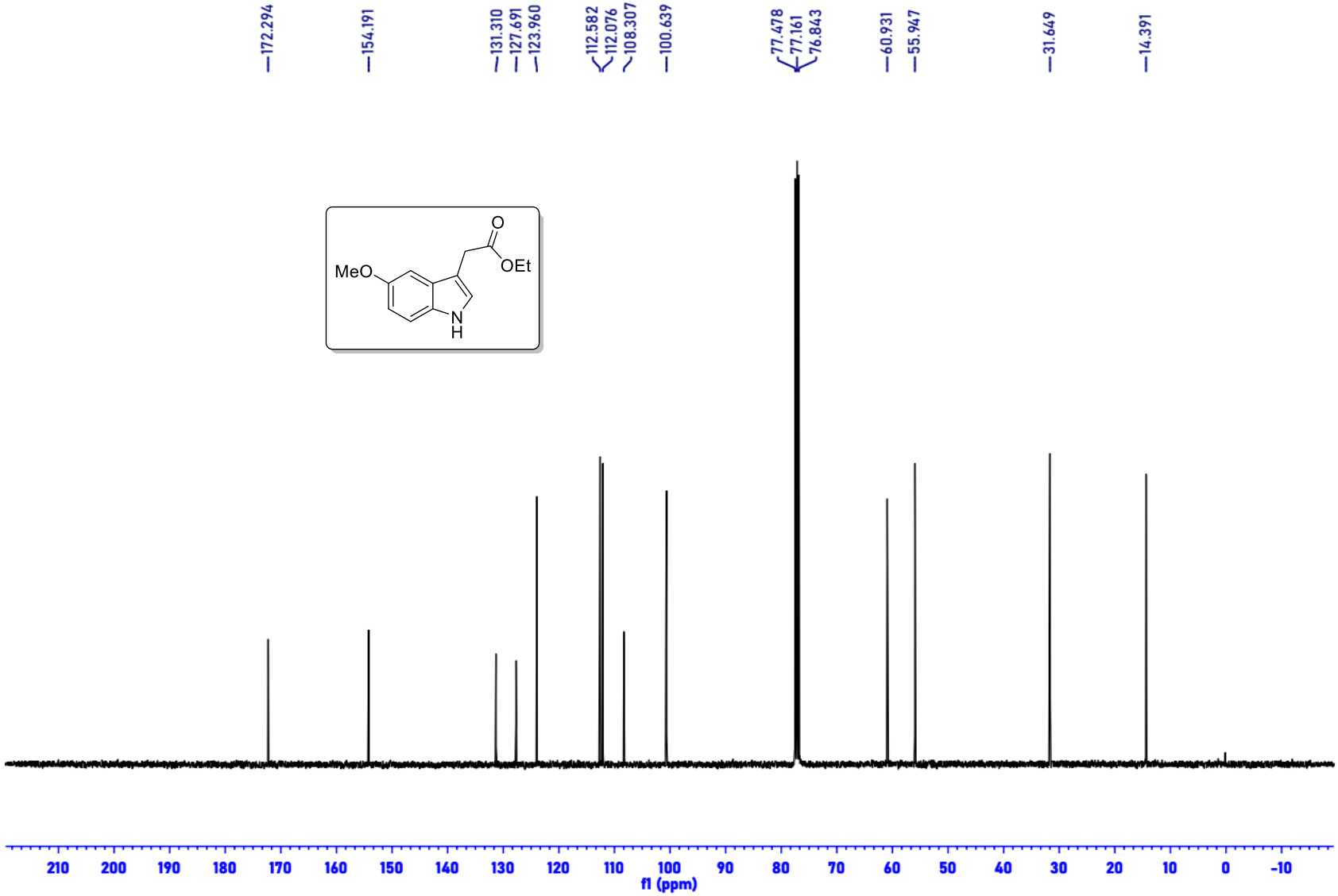
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 2ja



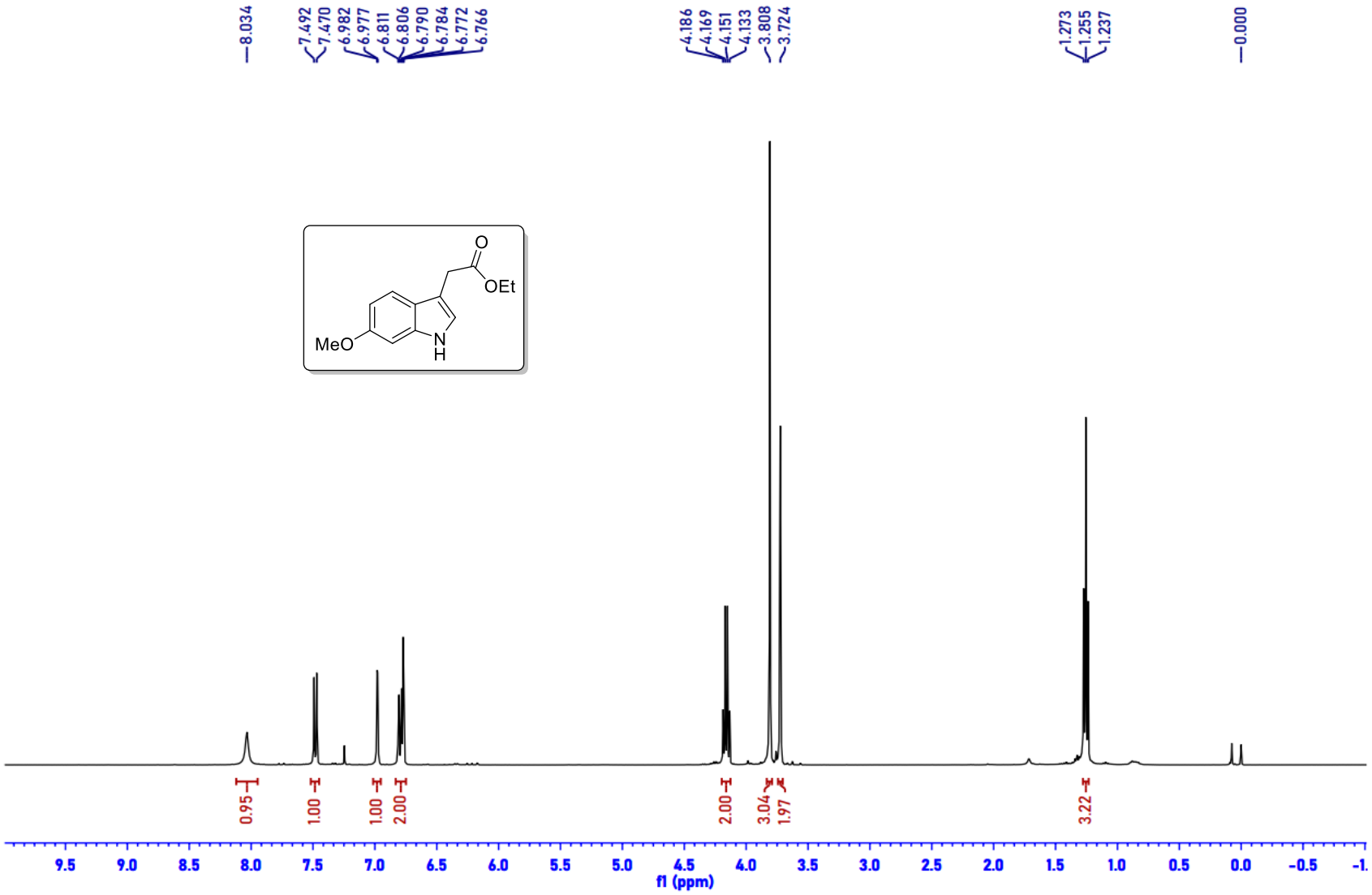
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ka



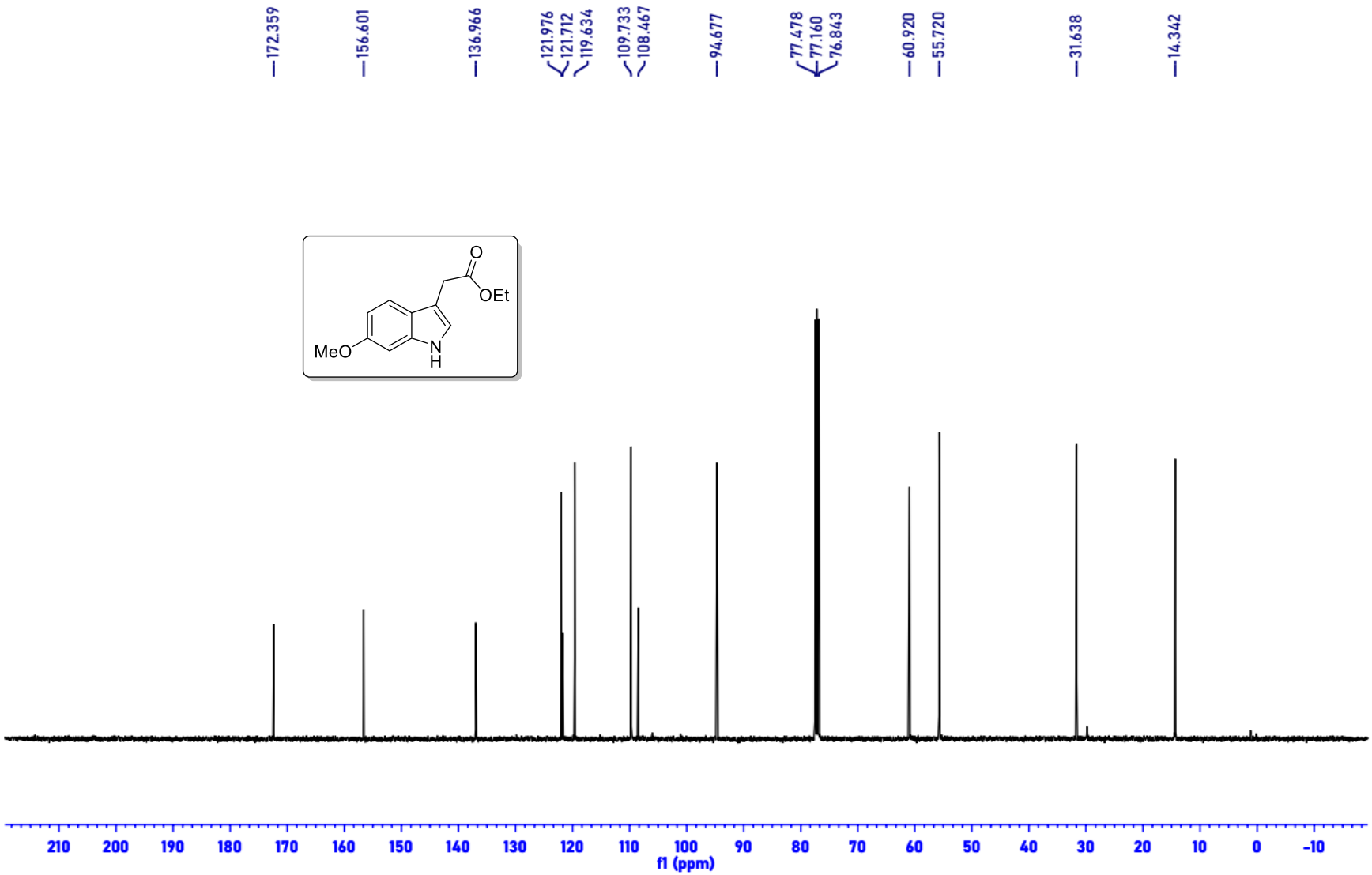
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ka



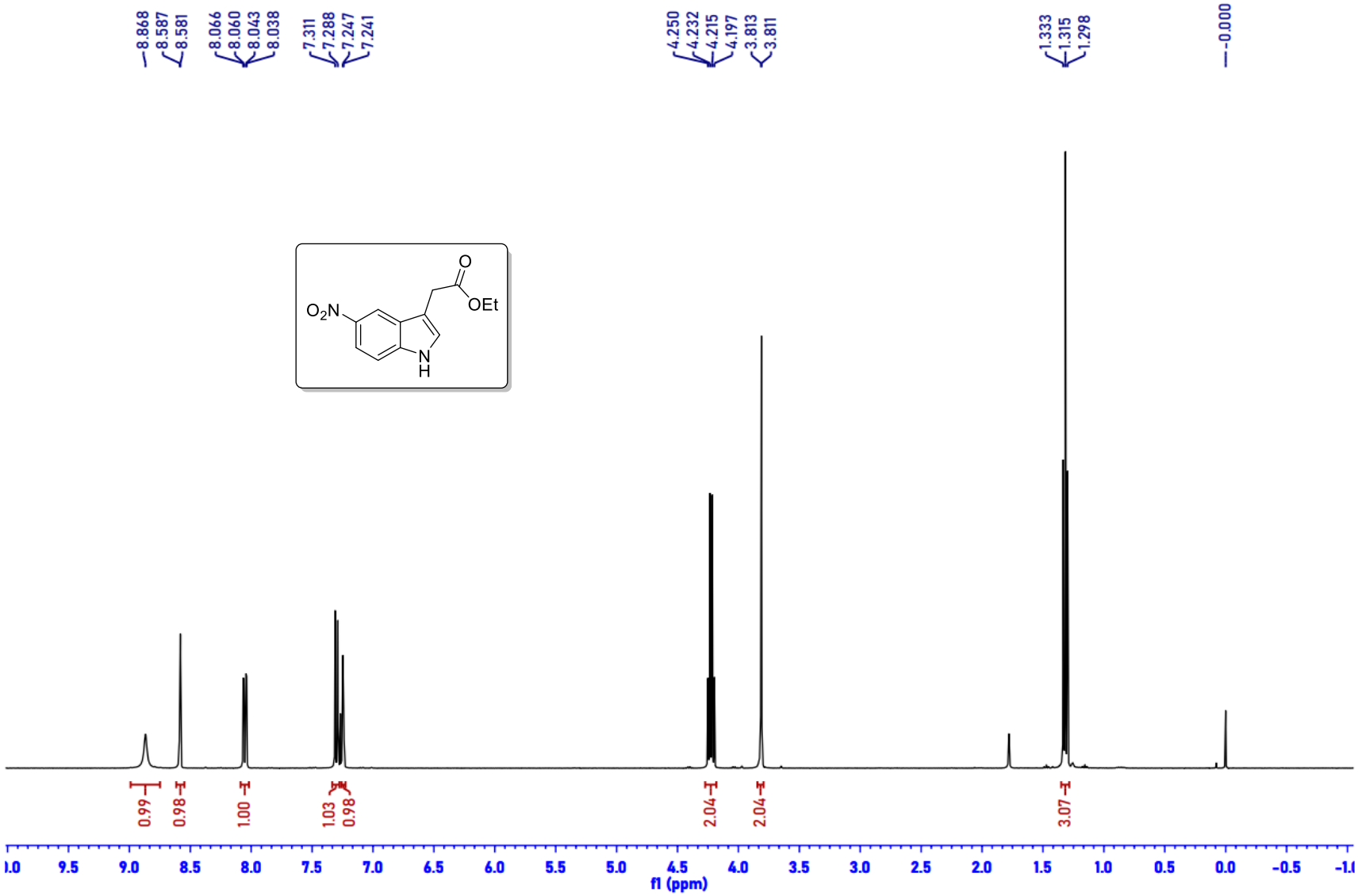
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2la



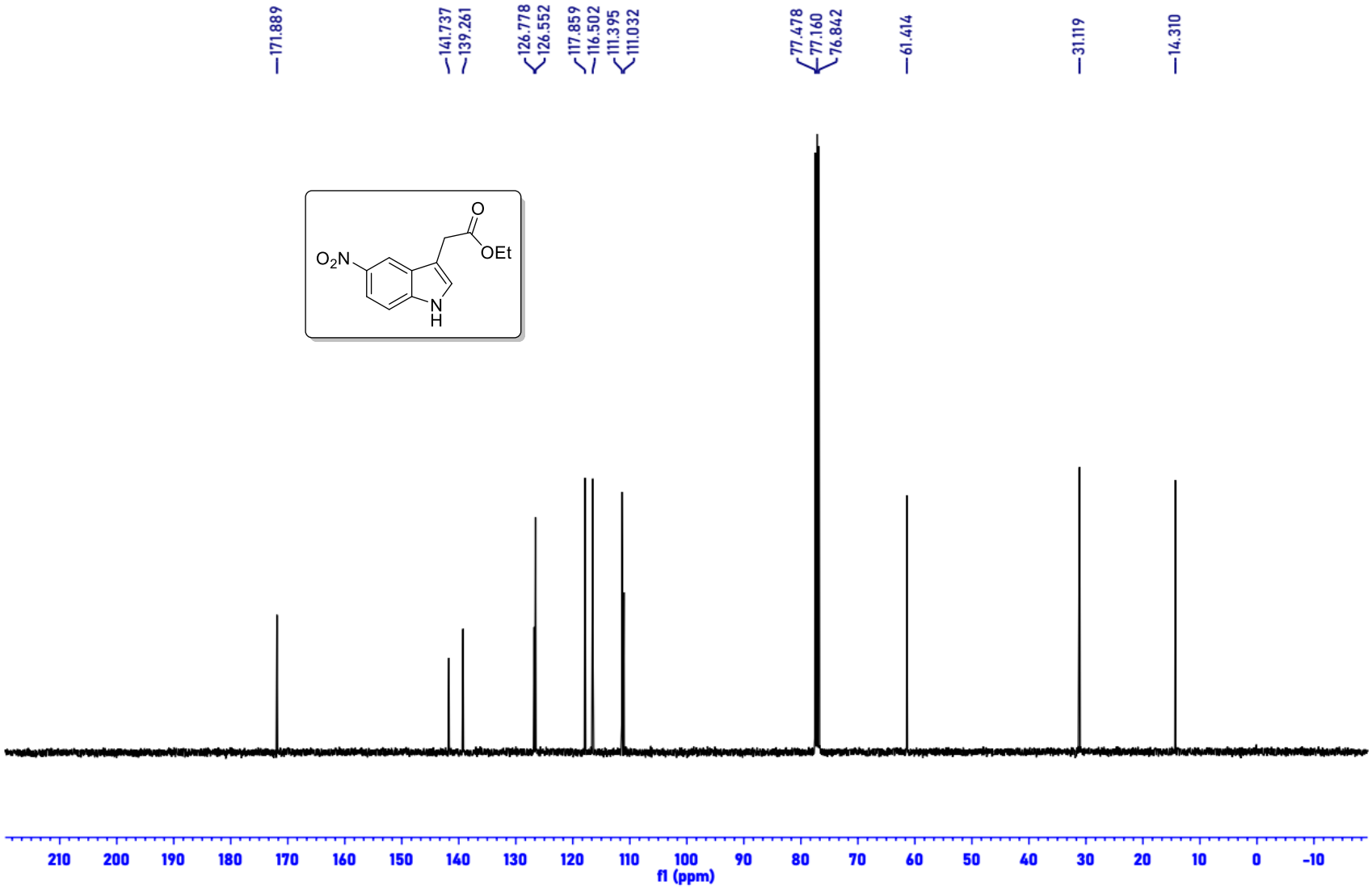
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2la



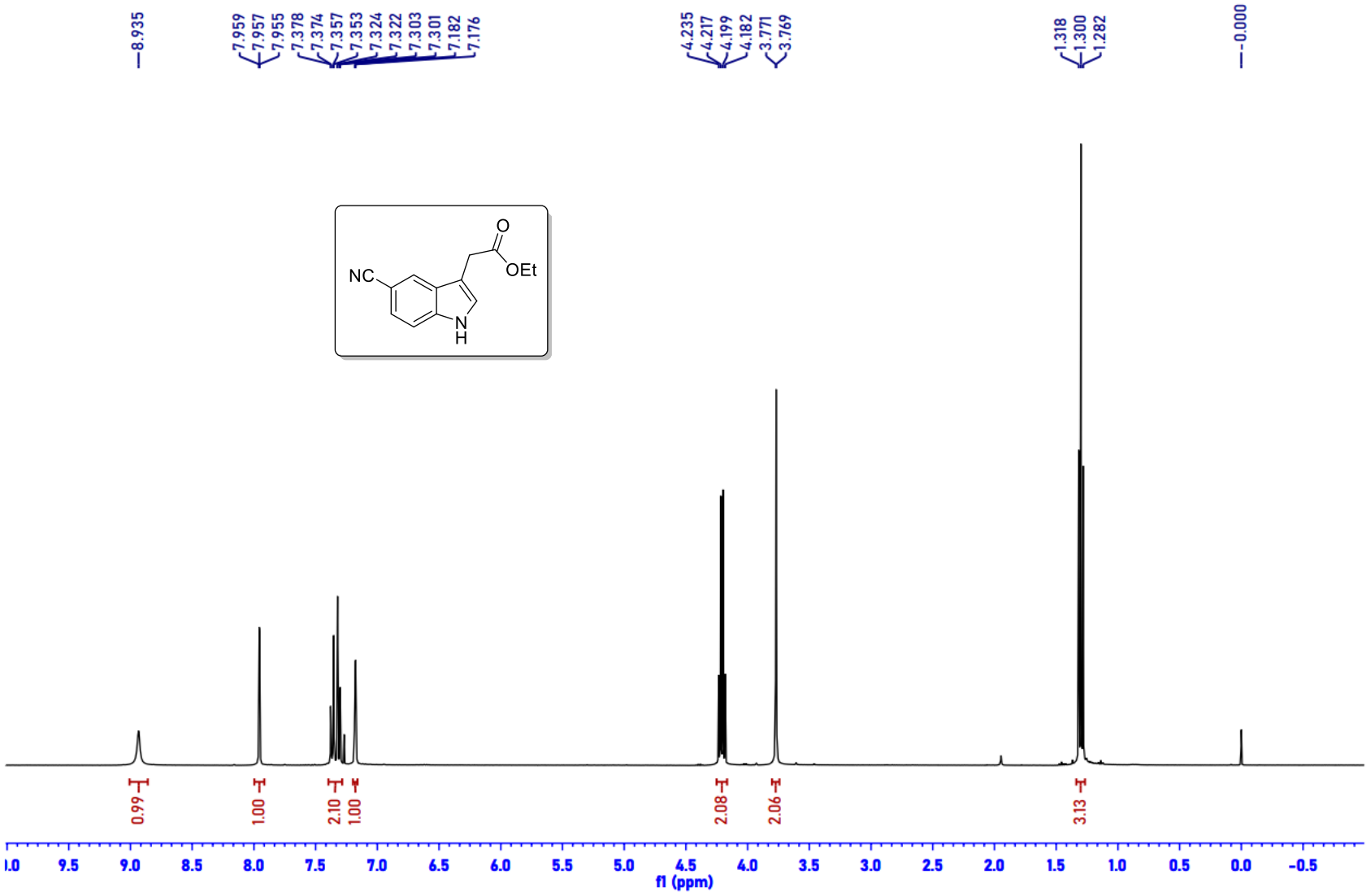
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2ma



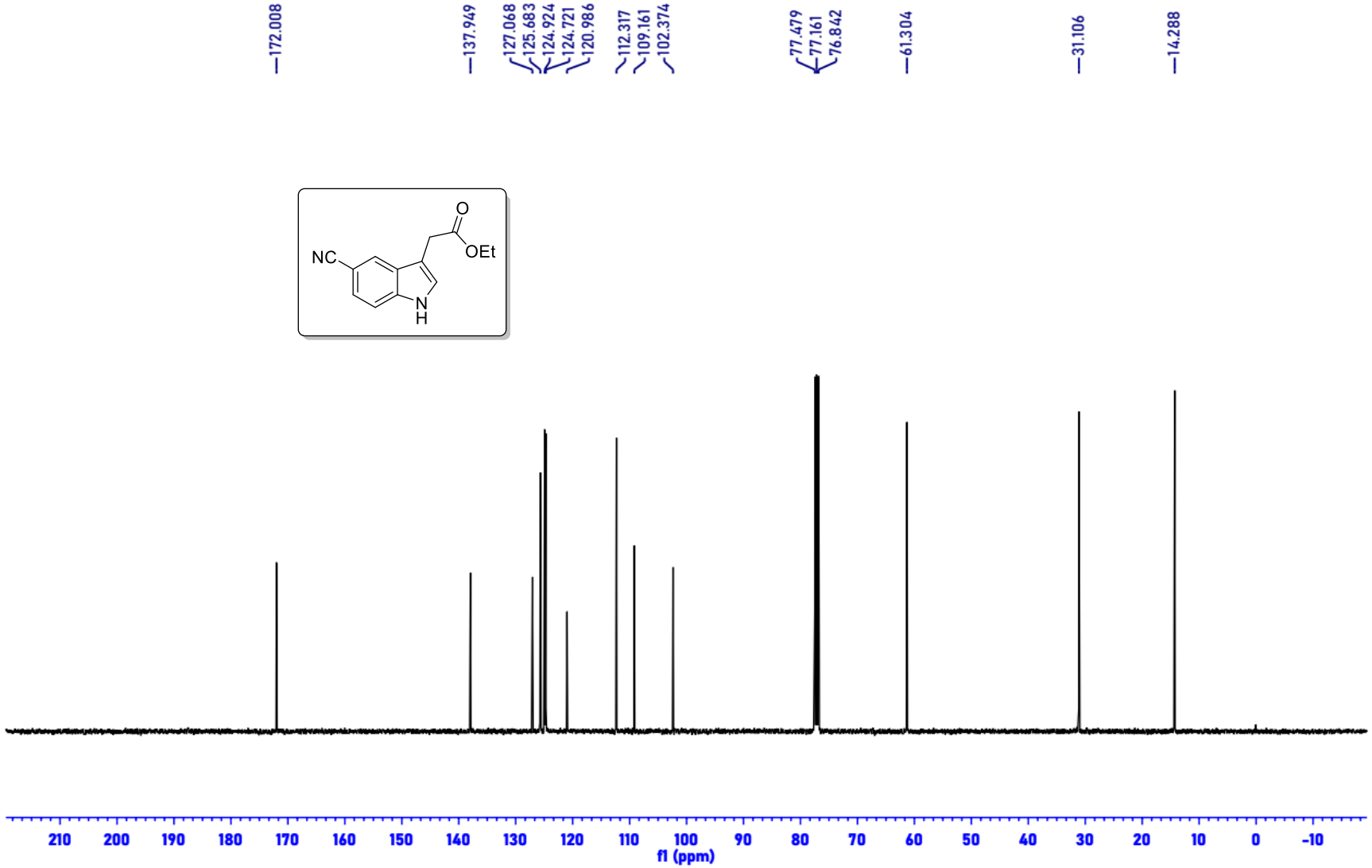
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2ma



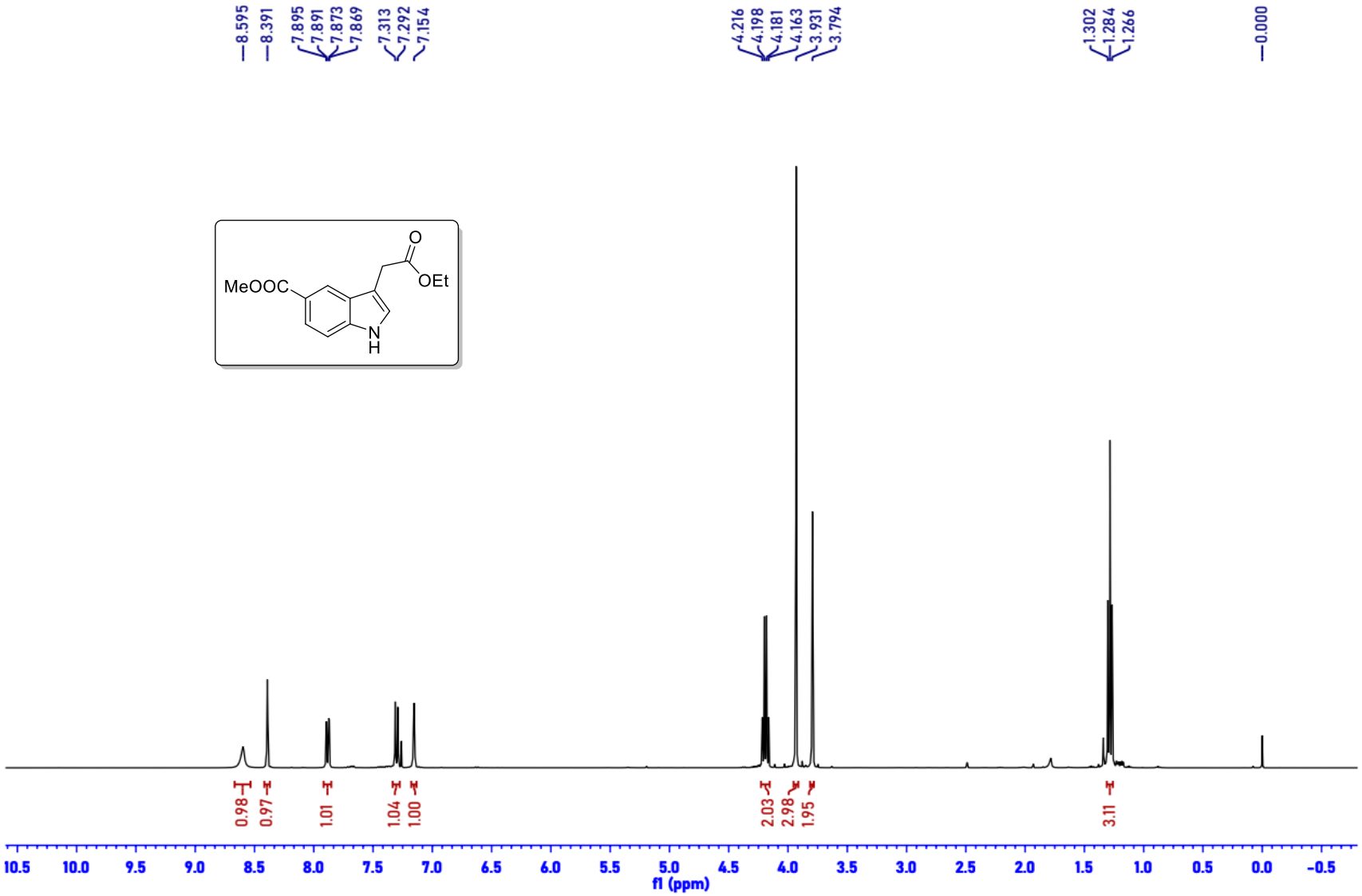
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2na



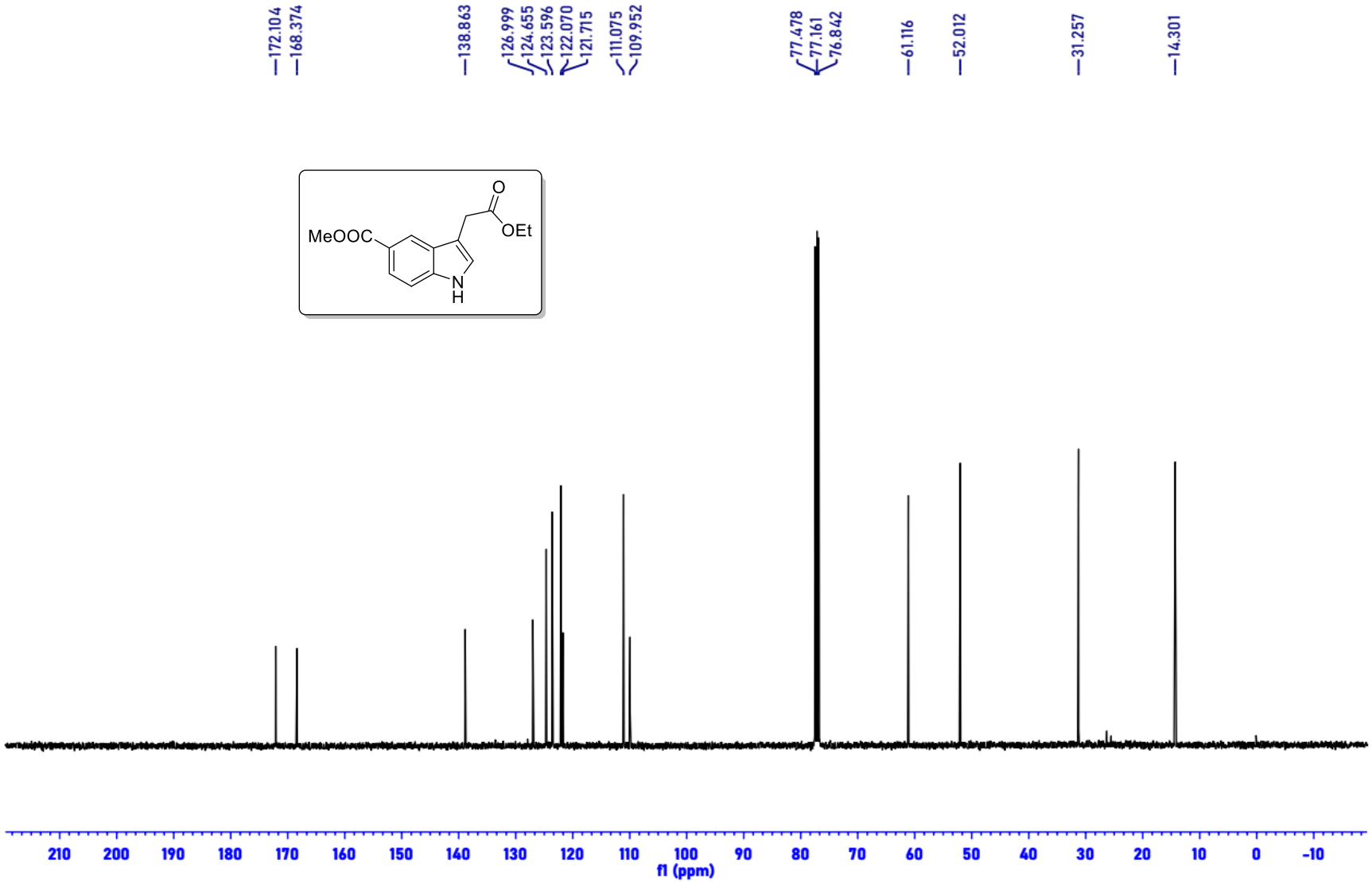
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2na



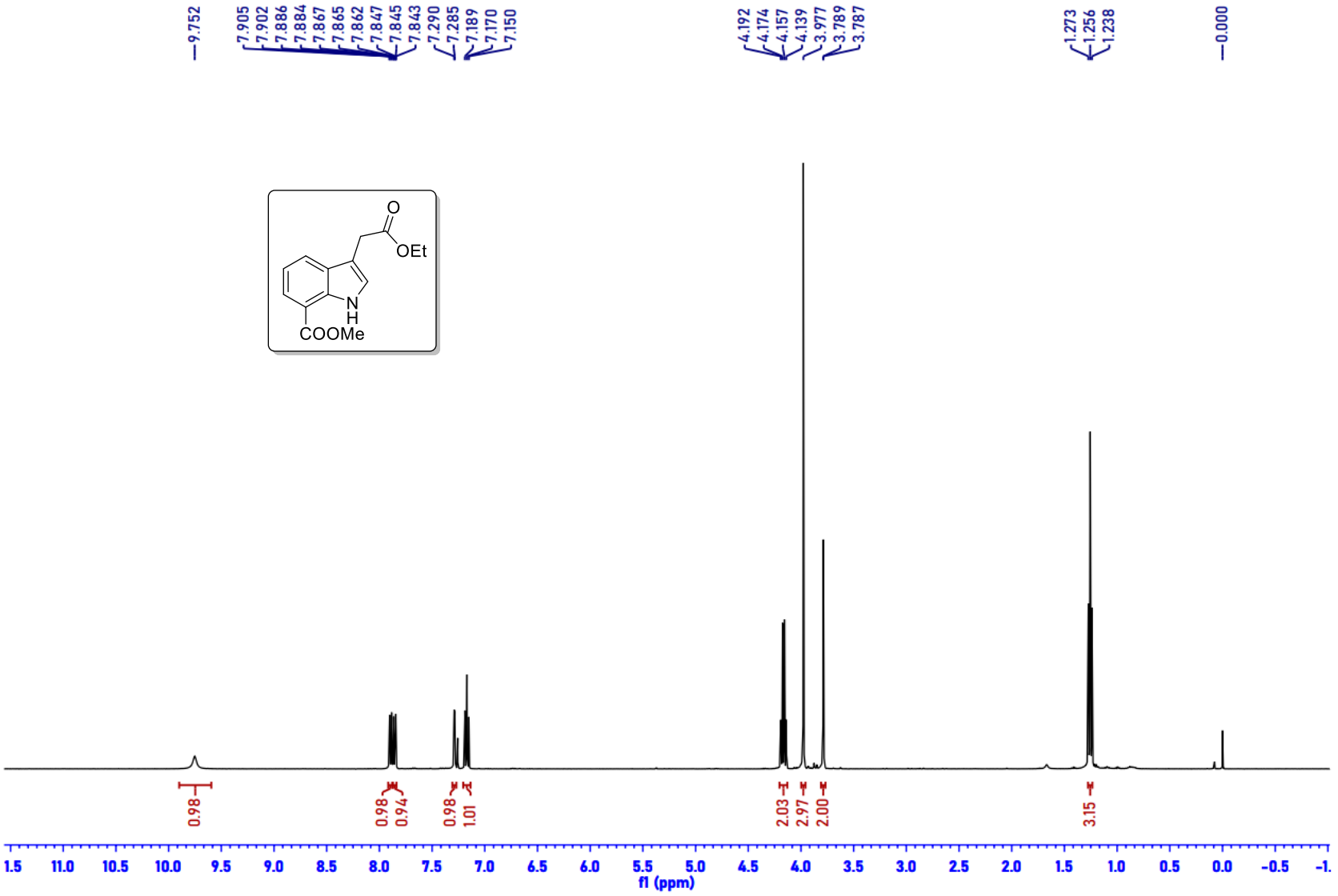
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2oa



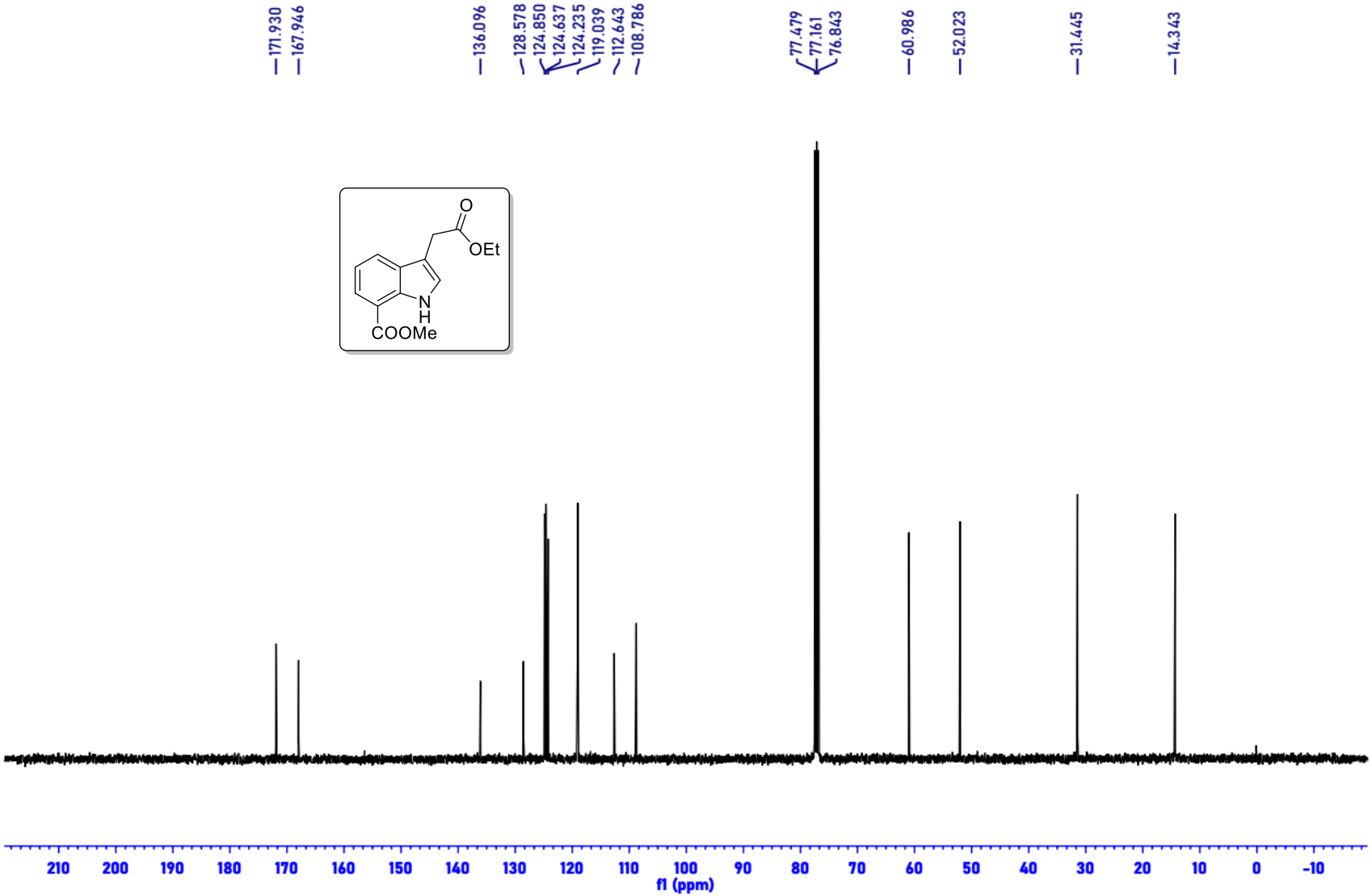
^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2oa



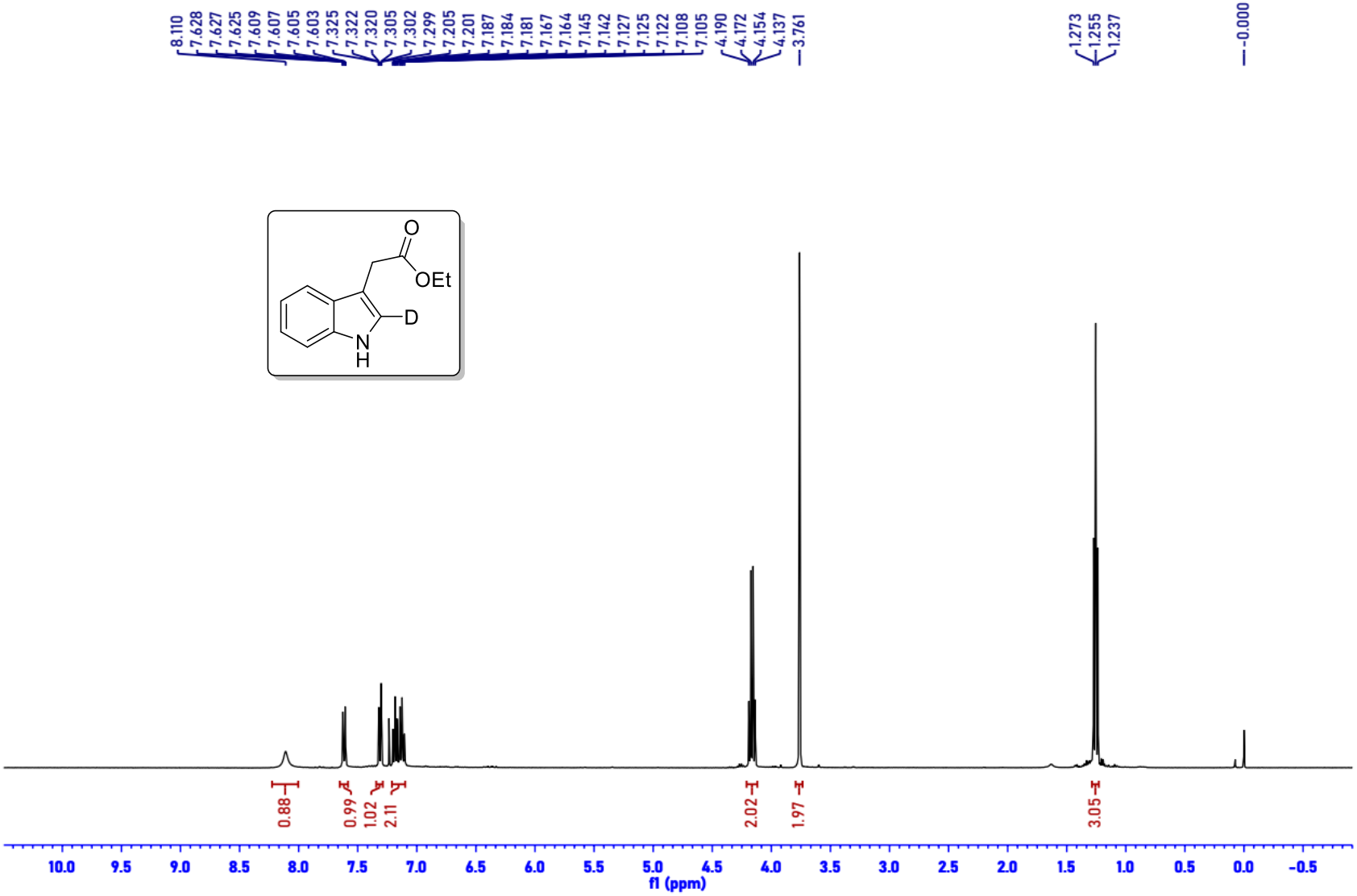
^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2pa



^{13}C NMR (100 MHz, $CDCl_3$) spectra for 2pa



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aa-1



^{1}H NMR (400 MHz, $CDCl_3$) spectra for 2aa-2