Electronic Supplementary Information

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1 General

1.1 Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR (400 or 500 MHz) and ^{13}C NMR (100 or 125 MHz) spectra were recorded on Bruker Avance 400 or 500 spectrometers in $CDCl_3$ [using TMS ($\delta = 0.00$) for ^{1}H and CDCl3 ($\delta = 77.00$) for ^{13}C as internal standard] and CD_3CN [CD_3CN ($\delta = 1.94$) for ^{1}H as internal standard]. ^{11}B NMR (128 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Bruker Avance 400 spectrometers in $CDCl_3$. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. ^{1}H NMR yields were measured using 1,1,2,2-tetrachloroethane (purchased from Sigma-Aldrich, product number: 185434) as an internal standard.

1.2 Mass spectroscopy

High-resolution mass (HRMS) spectra were obtained with a Waters Q-Tof Premier mass spectrometer.

1.3 Melting points

Melting points (MP) are uncorrected and were recorded on an MPA 100 OptiMelt Automated Melting Point System.

1.4 Purification methods

Flash chromatography was performed using Merck silica gel 60 with distilled solvents.

1.5 Catalysts, reagents, and solvents

Catalysts: Potassium polysulfide (K_2S_x) was purchased from Sigma-Aldrich (product number: 12665) and the composition of sulfur (S) in K_2S_x (36.3 wt%) was determined by inductively coupled prasma-optical emission spectrometry (ICP-OES) analysis with a Thermo Fischer iCAP6000 inductively coupled plasma – optical emission spectrometer. Lithium sulfide (Li_2S, product number: 213241) and triisopropylsilanethiol (i-Pr_3SiSH, product number: 429937) were purchased from Sigma-Aldrich and used as received.

Solvents: Acetonitrile (CH_3CN) was taken from a solvent purification system (PS-400-5, innovative technology Inc.). Dimethyl sulfoxide (DMSO, anhydrous, product number: 276855) was purchased from Sigma-Aldrich and used as received. Acetone (product number: MFCD00008765) was purchased from VWR and used as received.

Bases: Potassium carbonate (K_2CO_3, product number: 209619), potassium acetate (KOAc, product number 236497), 1,1,3,3-tetramethylguanidine (TMG, product number: 690953), and 1,4-diazabicyclo[2.2.2]octane (DABCO, product number: D27802) were purchased from Sigma-Aldrich. *N,N*-diisopropylethylamine (i-Pr_2NEt, product number: D1599) was purchased from Tokyo Chemical Industry (TCI). They were used as received.

Aryl halides, alkenes, and other reagents: Commercially available reagents were purchased from Sigma-Aldrich, Fluorochem, TCI, Cambridge Isotope Laboratories (CIL) or Leyan and were used as received unless otherwise noted.

1.6 Light sources

The Kessil PR160 lamp (λ_{max} = 440 nm) was used as the LED light source for the reactions (https://www.kessil.com/science/PR160L.php). The emission spectrum (Figure S1) was measured using an Avantes AvaSpec-ULS2048 detector.

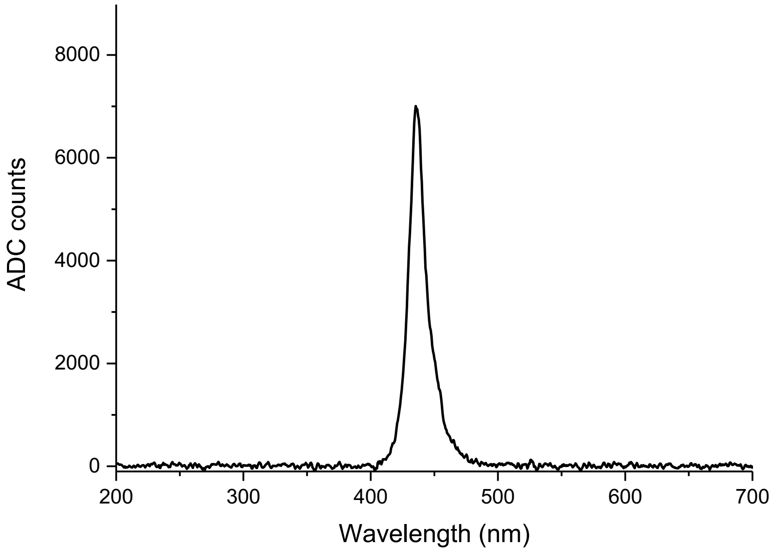


Figure S1 Emission spectrum of Kessil lamp (λ_{max} = 440 nm).

2 Reaction set-up

The reaction setup is displayed in Figure S2. The PR160 Kessil lamp (the light intensity was set 20 W) were used as the light source. All the reactions were run in a 25 mL sealed-tube equipped with an oval shaped stir bar. The distance between the lamp and the sealed tube was set 3.5 cm. All the reactions were stirred at the speed of 500 rpm with external fan cooling so that the ambient temperature of the reaction vessel did not exceed 30 °C.

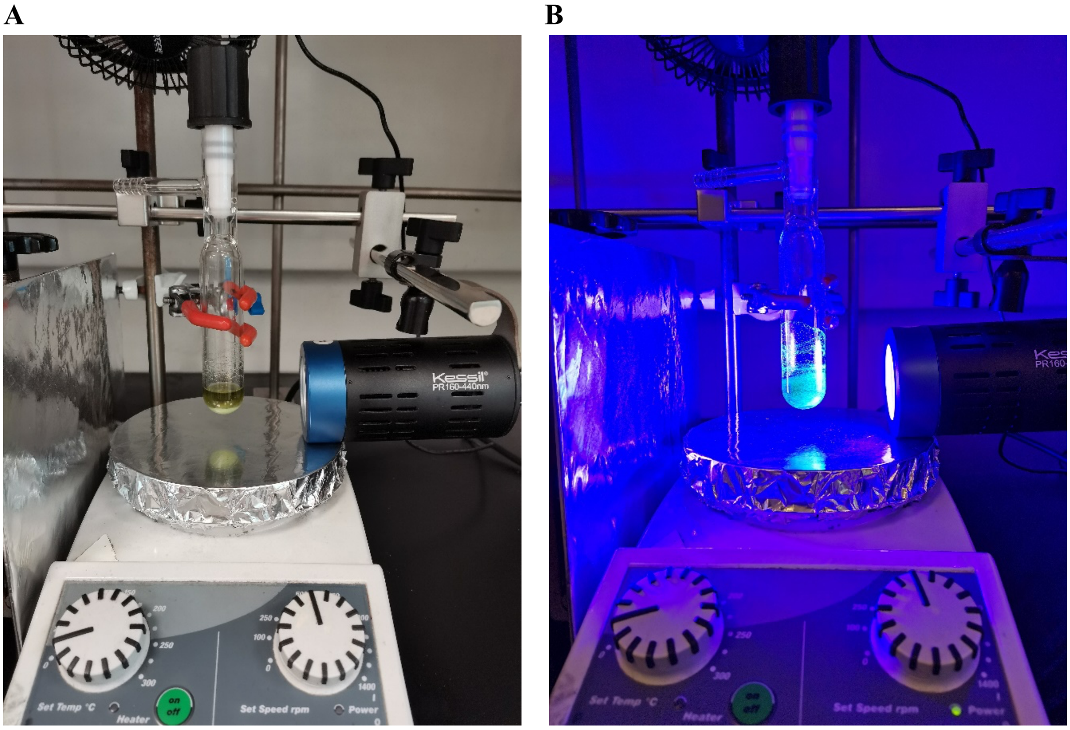
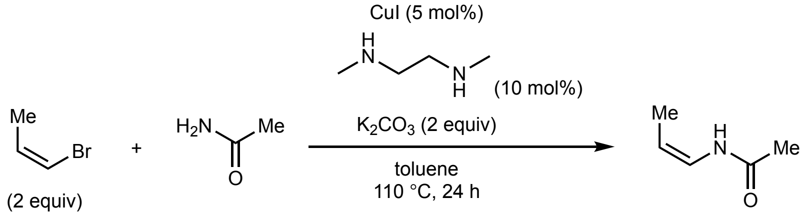


Figure S2 Reaction set-up. (A) The reaction setup. (B) The reaction set up with light irradiation.

3. Synthesis and characterization of starting materials

3.1 Synthesis of (*Z*)-*N*-(prop-1-en-1-yl)acetamide (7)

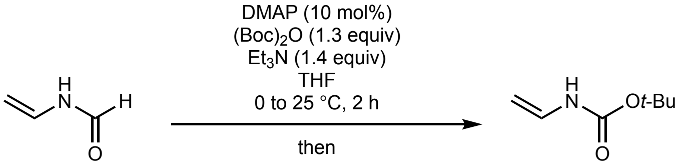


7 79%

To a 100 mL Schlenk flask with a magnetic stir bar was added acetamide (Sigma-Aldrich 00160) (1.49 g, 25.2 mmol), CuI (Sigma-Aldrich 03140) (238 mg, 1.25 mmol), K_2CO_3 (6.91 g, 50.0 mmol). A vacuum-refill cycle was performed thrice under an Ar atmosphere. The Schlenk flask was then charged with degassed anhydrous toluene (35 mL), *N*,*N'*-dimethylethylenediamine (Sigma-Aldrich D157805) (269 µL, 2.50 mmol), and (*Z*)-1-propenyl bromide (Sigma-Aldrich 368679) (4.3 mL, 50.6 mmol). The reaction mixture was stirred at 110 °C with an oil bath for 24 h. After being cooled to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo. The resulting crude residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 70:30) to give (*Z*)-*N*-(prop-1-en-1-yl)acetamide (**7**) (2.25 g, 19.9 mmol) in 79% yield as a white solid. The spectral data matched those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) (major rotamer) δ 7.21 (br, 1H), 6.78 – 6.62 (m, 1H), 4.86 – 4.69 (m, 1H), 2.08 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 3H).
(minor rotamer) δ 7.21 (br, 1H), 6.26 – 6.19 (m, 1H), 4.86 – 4.69 (m, 1H), 2.08 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) (major rotamer) δ 167.3, 121.9, 105.0, 23.3, 10.8.

3.2 Synthesis of *tert*-butyl vinylcarbamate (8)

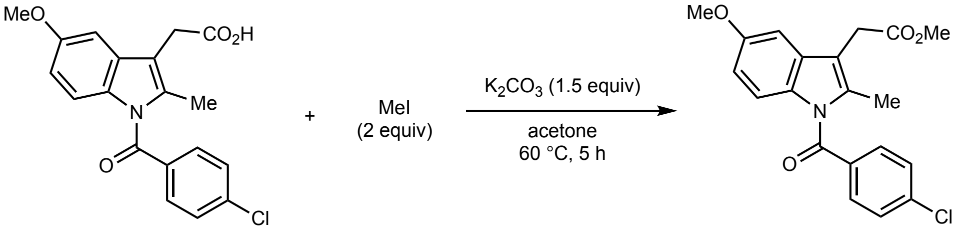


8 82%

To a 250 mL Schlenk flask equipped with a stir bar was added *N*-vinyl formamide (Sigma-Aldrich 447331) (7.0 mL, 100 mmol), anhydrous THF (100 mL, 1 M), triethylamine (19.5 mL, 140 mmol, 1.4 equiv), di-*tert*-butyl dicarbonate (Sigma-Aldrich 205249) [$(Boc)_2O$, 28.4 g, 130 mmol, 1.3 equiv], and 4-dimethylaminopyridine (Sigma-Aldrich 107700) (DMAP, 1.22 g, 10.0 mmol) consecutively under an Ar atmosphere at 0 °C. The reaction was warmed to room temperature and stirred for 2 h. LiOH (5 M in 70 mL H_2O, 350 mmol, 3.5 equiv) was then added to the reaction mixture, and continuously stirred at 50 ºC with an oil bath for 4 h. The mixture was cooled to room temperature and diluted with H_2O (100 mL). The aqueous layer was separated and extracted with Et_2O (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting crude residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 20:80) to give solid materials, recrystallization of which in pentane at –30 ºC afforded *tert*-butyl vinylcarbamate (**8**) (11.7 g, 81.7 mmol) in 82% yield as a white solid. The spectral data matched those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.48 (m, 1H), 6.57 – 6.30 (m, 1H), 4.40 (d, *J* = 15.7 Hz, 1H), 4.30 – 3.95 (br d, *J* = 8.8 Hz, 1H), 1.47 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 123.1, 84.9, 73.4, 21.2.

3.3 Synthesis of indomethacin methyl ester (39)



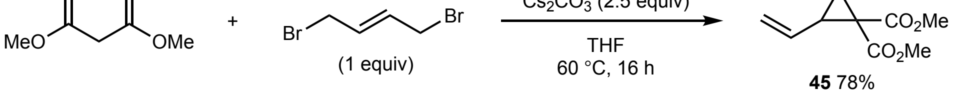
indomethacin

39 92%

To a 100 mL round bottom flask equipped with a stir bar was added indomethacin (Sigma-Aldrich I7378) (3.57 g, 10.0 mmol) and K_2CO_3 (2.04 g, 14.8 mmol, 1.5 equiv), and acetone (20 mL). Iodomethane (TCI 10060) (1.3 mL, 20.8 mmol, 2 equiv) was then added at 0 °C. The reaction mixture was warmed at 60 °C with an oil bath and stirred for 5 h. After being cooled to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated *in vacuo*. The resulting crude residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 80:20) to give **39** (3.43 g, 9.22 mmol) in 92% yield as a white solid. The spectral data matched those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.3, 156.0, 139.2, 135.9, 133.9, 131.2, 130.8, 130.6, 129.1, 114.9, 112.5, 111.6, 101.3, 55.7, 52.1, 30.1, 13.3.

3.4 Synthesis of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (45)

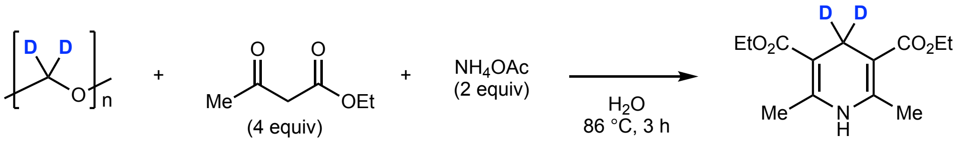


45 78%

To a 100 mL two-neck round bottom flask equipped with a condenser and a stir bar was added dimethyl malonate (1.2 mL, 10.5 mmol) (Sigma-Aldrich 136441), *trans*-1,4-dibromo-2-butene (1.2 mL, 10.7 mmol, 1 equiv) (Sigma-Aldrich D39207), Cs_2CO_3 (8.22 g, 25.2 mmol, 2.5 equiv) and THF (50 mL). The reaction mixture was warmed at 60 °C with an oil bath and stirred for 16 h. After being cooled to room temperature, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated *in vacuo*. The resulting crude residue was purified by flash column chromatography (silica gel, hexane:diethyl ether = 85:15) to give vinyl cyclopropane **45** (1.51 g, 8.20 mmol) in 78% yield as a colorless oil. The spectral data matched those reported in the literature.[4]

^{1}H NMR (500 MHz, CDCl$_3$): δ 5.50 – 5.38 (ddd, *J* = 17.0, 10.2, 8.3 Hz, 1H), 5.30 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.15 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.74 (s, 6H), 2.62 – 2.54 (ddd, *J* = 9.0, 8.3, 7.6 Hz, 1H), 1.72 (dd, *J* = 7.6, 5.0 Hz, 1H), 1.59 (dd, *J* = 9.0, 5.0 Hz, 1H).
^{13}C NMR (125 MHz, CDCl$_3$): δ 169.9, 167.7, 132.9, 118.6, 52.7, 52.5, 35.7, 31.4, 20.5.

3.5 Synthesis of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-*d*$_2$ (3-*d*$_2$)

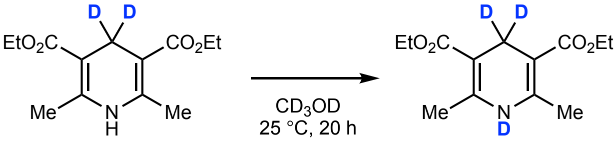


3-*d*$_2$ 97%

To a 100 mL two-neck round bottom flask equipped with a stir bar was added paraformaldehyde-*d*$_2$ (CIL DLM-300-PK) (0.963 g, 30.1 mmol / DC(O)D, 1 equiv), ethyl acetoacetate (Sigma-Aldrich 537349) (15.2 mL, 120 mmol, 4 equiv), ammonium acetate (Sigma-Aldrich 238074) (4.64 g, 60.2 mmol, 2 equiv) and water (60 mL, 0.5 M). The reaction mixture was warmed at 86 °C with an oil bath and vigorously stirred for 3 h. The mixture was filtrated and washed with water and cold diethyl ether. The solid was dried under vacuum to afford the Hantzsch ester (**3-*d*$_2$**) (7.47g, 29.3mmol, 97%) as a yellow solid. The spectral data matched those reported in the literature.[5]

^{1}H NMR (400 MHz, CDCl$_3$): δ 5.18 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 168.1, 144.9, 99.2, 59.6, 24.1 (t, $J_{C\text{-}D}$ = 20.3 Hz), 19.0, 14.4.

3.6 Synthesis of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-1,4,4-*d*$_3$ (3-*d*$_3$)



3-*d*$_2$ **3-*d*$_3$** 99%

To a 50 mL Schlenk flask equipped with a stir bar was added Hantzsch ester (**3-*d*$_2$**) (1.02 g, 4.00 mmol, 1 equiv). A vacuum-refill cycle was performed thrice under an Ar atmosphere. The Schlenk flask was then charged with CD$_3$OD (CIL DLM-24-10) (10 mL, 0.4 M). The reaction mixture was stirred at 25 °C for 20 h. Then the reaction mixture was concentrated *in vacuo* to afford the

Hantzsch ester (**3-*d*$_3$**) (1.02g, 3.98 mmol, 99%) as a yellow solid. The spectral data matched those reported in the literature.[5]

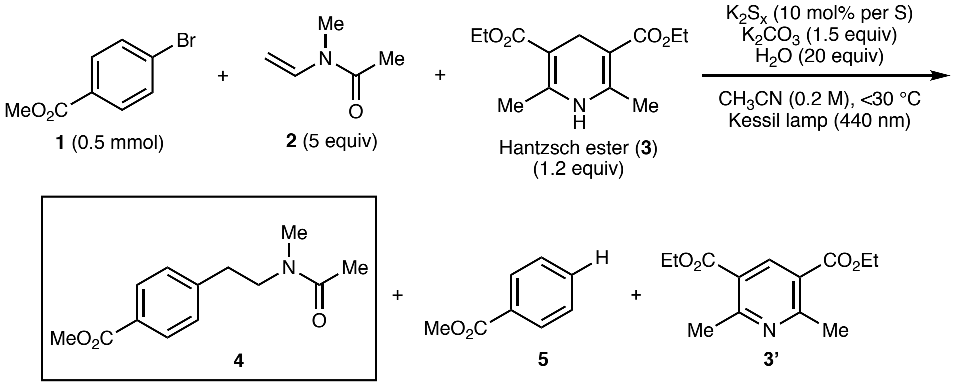
<u>^{1}H NMR (500 MHz, CDCl$_3$):</u> δ 4.17 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 6H).
<u>^{13}C NMR (125 MHz, CDCl$_3$):</u> δ 168.1, 144.8, 99.2, 59.6, 19.0, 14.4. (The deuterium-bounded carbon was not detected)

4 Hydroarylation of alkenes

4.1 Reaction optimization for hydroarylation of 2 with methyl 4-bromobenzoate (1)

The details on the reaction optimization for the hydroarylation of *N*-methyl-*N*-vinylacetamide (**2**) with methyl 4-bromobenzoate (**1**) were summarized in Table S1. Irradiation with visible light (Kessil lamp, λ_{max} = 440 nm) to the mixture of **1**, **2** (5 equiv) and the Hantzsch ester (**3**) (1.2 equiv) (TCI D3775) in the presence of K_2S_x (10 mol% per S atom), potassium carbonate (K_2CO_3, 1.5 equiv) and water (H_2O, 20 equiv) in acetonitrile (CH_3CN, 0.2 M) for 16 h gave arylethylacetamide **4** as the hydroarylation product in 76% yield along with the formation of methyl benzoate (**5**) via hydrodebromination in 16% yield (entry 1). The control experiments indicated that the presence of K_2S_x, irradiation with visible light, base (K_2CO_3), and H_2O are all essential for the process (entries 2-5), and the reaction was hampered under an air atmosphere (entry 6). The yield of **4** decreased approximately 10% when the amount of alkene (**2**) was reduced to 2.5 equiv (entry 7). The use of *i*-Pr_3SiSH or Li_2S, identified as the potential precatalysts for the polysulfide anions, performed comparably (entries 8 and 9). The yield of **4** was slightly reduced when the reaction was conducted in 0.1 M concentration (entry 10) or when acetone was the solvent (entry 11). It should be noted that the reaction in DMSO gave full conversion of **1** within 4 h, while the yield of **4** fallen down by about 10% (entry 12). Using other stoichiometric reductant like HCO_2Na or *i*-Pr_2NEt was detrimental (entries 13 and 14). Use of the Hantzsch ester (**3**) in 2 equivalents did not improve the yield (entry 15). Use of organic bases such as *i*-Pr_2NEt, 1,4-diazabicyclo[2.2.2]octane (DABCO), tetramethylguanidine (TMG) were not optimal for the hydroarylation (entries 16-18).

Table S1 Reaction optimization[a]



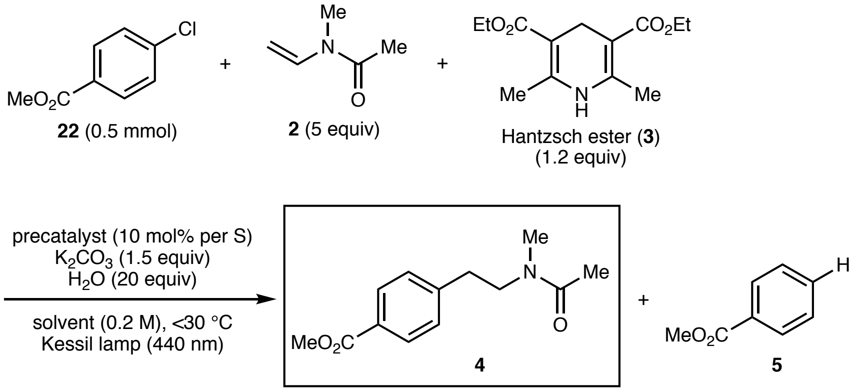
Entry	Variation from "the standard conditions"	Time (h)	Conversion of **1** (%)	Yield of **4** (%)[b]	Yield of **5** (%)[b]	Yield of **3'** (%)[b]
1	none	16	>99	76 (75)	16	85
2	no K_2S_x	16	4	0	trace	13
3	no irradiation with light	16	0	0	0	0
4	no K_2CO_3	16	2	trace	trace	22
5	no H_2O	16	60	38	8	51
6	under an air atmosphere	16	8	0	trace	72
7	alkene (**2**) (2.5 equiv)	16	87	62	20	77
8	*i*-Pr_3SiSH (10 mol%) instead of K_2S_x	16	>99	74	20	87
9	Li_2S (10 mol%) instead of K_2S_x	16	>99	73	21	86
10	CH_3CN (5 mL)	20	>99	69	16	87
11	acetone as a solvent instead of CH_3CN	16	>99	72	25	88
12	DMSO as a solvent instead of CH_3CN	4	>99	64	21	77
13	HCOONa instead of Hantzsch ester (**3**)	16	0	0	0	0
14	*i*-Pr_2NEt instead of Hantzsch ester (**3**)	16	3	2	trace	0
15	Hantzsch ester (**3**) (2 equiv)	20	>99	71	17	51
16[c]	*i*-Pr_2NEt instead of K_2CO_3	16	53	29	19	43
17[c]	DABCO instead of K_2CO_3	16	18	13	5	23
18[c]	TMG instead of K_2CO_3	14	>99	55	32	93

[a] Standard conditions: **1** (0.5 mmol), **2** (5 equiv), **3** (1.2 equiv), K_2S_x (10 mol% per S), K_2CO_3 (1.5 equiv), H_2O (20 equiv), CH_3CN (2.5 mL, 0.2 M), 440 nm light (Kessil lamp), <30 °C. [b] Yields determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard (isolated yield in parenthesis). [c] CH_3CN (5 mL) was used.

4.2 Reaction optimization for hydroarylation of 2 with methyl 4-chlorobenzoate (22)

We also conducted optimization of the reaction conditions for the hydroarylation of **2** with methyl 4-chlorobenzoate (**22**) (Table S2). The reactions in CH_3CN resulted in incomplete conversion of **22** (entries 1-3), whereas that in DMSO led full conversion within 6 h, affording **4** in 67% yield (entry 4).

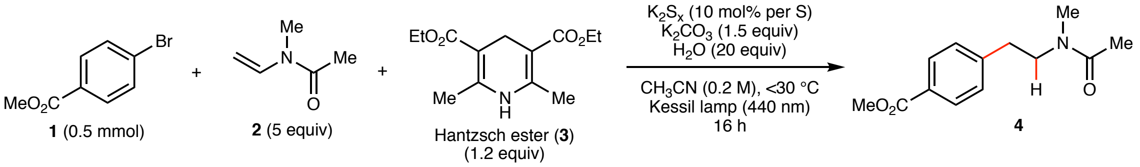
Table S2 Reaction optimization for methyl 4-chlorobenzoate (**22**)[a]



Entry	Precatalyst	Solvent	Time (h)	Conversion of **22** (%)	Yield of **4** (%)[b]	Yield of **5** (%)[b]
1	K_2S_x	CH_3CN	24	72	53	13
2	*i*-Pr_3SiSH	CH_3CN	24	77	61	14
3	Li_2S	CH_3CN	24	84	66	14
4	K_2S_x	DMSO	6	>99	71 (67)[c]	20

[a] Reaction conditions: **22** (0.5 mmol), **2** (5 equiv), **3** (1.2 equiv), precatalyst (10 mol% per S), K_2CO_3 (1.5 equiv), H_2O (20 equiv), solvent (2.5 mL, 0.2 M), 440 nm light (Kessil lamp), <30 °C. [b] Yields determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield.

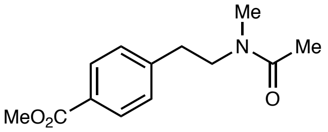
4.3 Experimental protocol



To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (Sigma-Aldrich 407593) (107.7 mg, 0.501 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (Sigma-Aldrich 255130) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.1 mg, 10 mol% per S), the Hantzsch ester (TCI D3775) (**3**) (152.2 mg, 0.601 mmol, 1.2 equiv), K_2CO_3 (103.7 mg, 0.750 mmol), H_2O (180 µL, 10 mmol, 20 equiv) and CH_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of visible light (Kessil lamp, λ_{max} = 440 nm, 20 W) for 16 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting crude residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (88.7 mg, 0.377 mmol) in 75% yield as a colorless oil.

4.4 Characterization of products

4.4.1 Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)



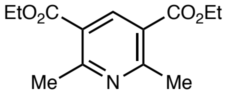
Prepared using methyl 4-bromobenzoate (**1**) (Sigma-Aldrich 407593) (107.7 mg, 0.501 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (Sigma-Aldrich 255130) (258 µL, 5 equiv) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 75% yield (88.7 mg, 0.377 mmol, 16 h) as a colorless oil.

Prepared using methyl 4-chlorobenzoate (**22**) (Sigma-Aldrich 216089) (85.7 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 67% yield (78.6 mg, 0.334 mmol, 6 h) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) (major rotamer) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.60 (t, *J* = 7.4 Hz, 2H), 2.93 – 2.89 (m, 2H), 2.87 (s, 3H), 2.06 (s, 3H).
(minor rotamer) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 3.54 (t, *J* = 7.2 Hz, 2H), 2.94 (s, 3H), 2.93 – 2.89 (m, 2H), 1.87 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) (mixture of rotamers) δ 170.4, 170.3, 166.9, 166.7, 144.6, 143.5, 130.0, 129.7, 128.7, 128.7, 128.7, 128.2, 52.1, 52.0, 51.9, 49.2, 36.8, 34.7, 33.7, 33.3, 21.8, 20.9.

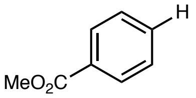
ESIHRMS Found: m/z 258.1105; Calcd for $C_{13}H_{17}NO_3Na$ $(M+Na)^+$ 258.1106.
IR (neat, cm^{-1}) 2953, 1713 [ν(C=O)], 1632, 1614, 1558, 1435, 1413, 1362, 1281, 1113.

Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (3')[6]



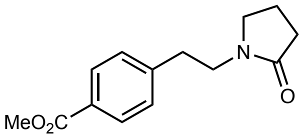
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 4H), 2.85 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 162.2, 140.8, 123.0, 61.3, 24.9, 14.2.

Methyl benzoate (5)[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 7.8, 7.4 Hz, 2H), 3.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 132.9, 130.2, 129.6, 128.3, 52.1.

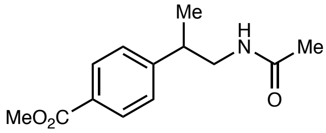
4.4.2 Methyl 4-(2-(2-oxopyrrolidin-1-yl)ethyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (108.2 mg, 0.503 mmol) and 1-vinyl-2-pyrrolidinone (**6**) (Sigma-Aldrich V3409) (267 μL, 2.50 mmol) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 72% yield (89.0 mg, 0.360 mmol, 20 h) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.55 (t, *J* = 7.4 Hz, 2H), 3.24 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.34 (t, *J* = 8.1 Hz, 2H), 2.02 – 1.87 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 166.9, 144.2, 129.7, 128.6, 128.4, 51.9, 47.6, 43.5, 33.7, 30.8, 17.9.
ESIHRMS Found: m/z 248.1285; Calcd for $C_{14}H_{18}NO_3$ $(M+H)^+$ 248.1287.
IR (neat, cm^{-1}) 2984, 2941, 1713 [ν(C=O)], 1680 [ν(C=O)], 1427, 1373, 1242, 1105, 1047.

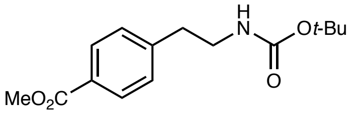
4.4.3 Methyl 4-(1-acetamidopropan-2-yl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.2 mg, 0.499 mmol) and (*Z*)-*N*-(prop-1-en-1-yl)acetamide (**7**) (285.4, 2.52 mmol) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 30:70)
Yield: 53% yield (65.6 mg, 0.263 mmol, 20 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.41 (br, 1H), 3.91 (s, 3H), 3.62 (ddd, *J* = 13.7, 6.6, 6.6 Hz, 1H), 3.27 (ddd, *J* = 13.7, 8.6, 5.3 Hz, 1H), 3.03 (ddq, *J* = 8.6, 6.6, 7.0 Hz, 1H), 1.89 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 170.1, 166.9, 149.6, 129.9, 128.5, 127.2, 52.0, 45.9, 39.7, 23.1, 19.1.
ESIHRMS Found: m/z 236.1285; Calcd for $C_{13}H_{18}NO_3$ $(M+H)^+$ 236.1287.
IR (neat, cm^{-1}) 3449, 3321, 3053, 2972, 1713 [ν(C=O)], 1667 [ν(C=O)], 1515, 1437, 1265, 1194, 1117.

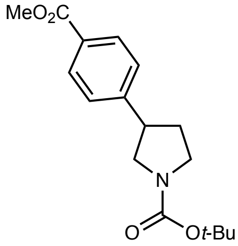
4.4.4 Methyl 4-(2-((*tert*-butoxycarbonyl)amino)ethyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.5 mg, 0.500 mmol) and *tert*-butyl vinylcarbamate (**8**) (359.2 mg, 2.51 mmol) with *i*-Pr_3SiSH (11 μL, 0.0512 mmol, 10 mol%) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 80% yield (111.9 mg, 0.401 mmol, 16 h) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.54 (br, 1H), 3.90 (s, 3H), 3.39 (dt, *J* = 7.0, 6.8 Hz, 2H), 2.86 (t, *J* = 7.0 Hz, 2H), 1.43 (s, 9H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 166.9, 155.8, 144.5, 129.8, 128.8, 128.4, 79.3, 52.0, 41.4, 36.2, 28.3.
ESIHRMS Found: m/z 280.1547; Calcd for $C_{15}H_{22}NO_4$ $(M+H)^+$ 280.1549.
IR (neat, cm^{-1}) 3447, 3053, 2982, 1709 [ν(C=O)], 1697 [ν(C=O)], 1611, 1503, 1437, 1367, 1265, 1169, 1113.
MP: 100-102 °C.

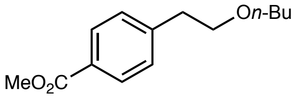
4.4.5 *tert*-Butyl 3-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate



Prepared using methyl 4-bromobenzoate (**1**) (108.0 mg, 0.502 mmol) and 1-(*tert*-butoxycarbonyl)-2,3-dihydro-1*H*-pyrrole (**9**) (Sigma-Aldrich 709972) (432 µL, 2.50 mmol) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 88:12)
Yield: 50% yield (83.8 mg, 0.274 mmol, 7 h) as a colorless oil.
The spectral data matched those reported in the literature.[8]

^{1}H NMR (500 MHz, CDCl$_3$) (mixture of rotamers) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 3.87 (dd, *J* = 8.9, 8.9 Hz, 0.5H), 3.80 (dd, *J* = 9.1, 9.1 Hz, 0.5H), 3.65 (dd, *J* = 9.5, 9.5 Hz, 0.5H), 3.56 (dd, *J* = 9.5, 9.5 Hz, 0.5H), 3.48 – 3.38 (m, 2H), 3.38 – 3.33 (m, 0.5H), 3.33 – 3.26 (m, 0.5H), 2.35 – 2.22 (m, 1H), 2.05 – 1.92 (m, 1H), 1.48 (s, 9H).
^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 166.9 (overlapped with 2C), 154.4 (overlapped with 2C), 146.9, 146.8, 129.9 (overlapped with 2C), 128.7 (overlapped with 2C), 127.1 (overlapped with 2C), 79.4 (overlapped with 2C), 52.2, 52.0 (overlapped with 2C), 51.5, 45.8, 45.5, 44.2, 43.3, 33.2, 32.3, 28.5 (overlapped with 2C).

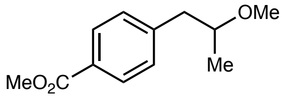
4.4.6 Methyl 4-(2-butoxyethyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.9 mg, 0.502 mmol) and butyl vinyl ether (**10**) (Sigma-Aldrich 110299) (324 µL, 2.50 mmol) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 97:3)
Yield: 56% yield (66.5 mg, 0.281 mmol, 5 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 1.59 – 1.48 (m, 2H), 1.43 – 1.27 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.1, 144.8, 129.6, 128.9, 128.1, 71.1, 70.8, 51.9, 36.4, 31.7, 19.3, 13.8.
ESIHRMS Found: m/z 237.1494; Calcd for $C_{14}H_{21}O_3$ $(M+H)^+$ 237.1491.
IR (neat, cm^{-1}) 2957, 2868, 1713 [ν(C=O)], 1612, 1435, 1282, 1180, 1111.

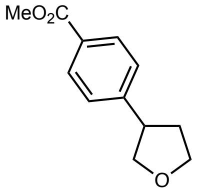
4.4.7 Methyl 4-(2-methoxypropyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.3 mg, 0.499 mmol) and 2-methoxypropene (**11**) (Sigma-Aldrich 174645) (239 μL, 2.50 mmol) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 92:8)
Yield: 63% yield (65.1 mg, 0.313 mmol, 24 h) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.55 (ddq, *J* = 6.4, 6.2, 6.1 Hz, 1H), 3.32 (s, 3H), 2.93 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.2 Hz, 1H), 1.13 (d, *J* = 6.1 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 144.8, 135.2, 129.6, 128.3, 77.5, 56.3, 42.7, 26.5, 18.9.
ESIHRMS Found: m/z 209.1178; Calcd for $C_{12}H_{17}O_3$ $(M+H)^+$ 209.1178.
IR (neat, cm^{-1}) 2976, 2942, 1713 [ν(C=O)], 1612, 1435, 1281, 1180, 1109.

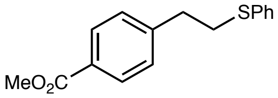
4.4.8 Methyl 4-(tetrahydrofuran-3-yl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.4 mg, 0.500 mmol) and 2,3-dihydrofuran (**12**) (Sigma-Aldrich 200018) (189 μL, 2.50 mmol) with K_2S_x (4.0 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 92:8)
Yield: 43% yield (44.2 mg, 0.214 mmol, 4 h) as a colorless oil.
The spectral data matched those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.14 (dd, *J* = 8.6, 7.6 Hz, 1H), 4.09 (ddd, *J* = 8.4, 8.4, 4.6 Hz, 1H), 3.92 (ddd, *J* = 8.4, 7.6, 7.6 Hz, 1H), 3.91 (s, 3H), 3.76 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.46 (dddd, *J* = 7.6, 7.6, 7.6, 7.0 Hz, 1H), 2.40 (dddd, *J* = 12.4, 7.6, 7.6, 4.6 Hz, 1H), 2.00 (dddd, *J* = 12.4, 8.4, 7.6, 7.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.4, 129.9, 128.4, 127.2, 74.4, 68.4, 52.0, 44.9, 34.6.

4.4.9 Methyl 4-(2-(phenylthio)ethyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.6 mg, 0.500 mmol) and phenyl vinyl sulfide (**13**) (TCI P1287) (327 μL, 2.50 mmol) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).

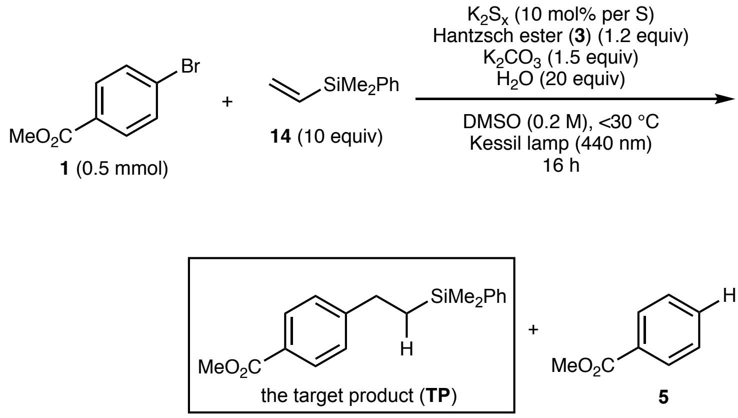
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 98:2)
Yield: 73% yield (99.5 mg, 0.365 mmol, 20 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.17 (m, 1H), 3.91 (s, 3H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 166.9, 145.4, 135.9, 129.8, 129.5, 128.9, 128.5, 128.4, 126.2, 52.0, 35.5, 34.7.
ESIHRMS Found: m/z 273.0948; Calcd for $C_{16}H_{17}O_2S$ $(M+H)^+$ 273.0949.
IR (neat, cm^{-1}) 3059, 3001, 2843, 1932, 1712 [ν(C=O)], 1610, 1583, 1481, 1435, 1280, 1179, 1111, 1020.

4.4.10 Methyl 4-(2-(dimethyl(phenyl)silyl)ethyl)benzoate

We found that use of 10 equivalents of alkenylsilane **14** is required to achieve the full conversion of **1** (Table S3).

Table S3 Optimization of the reaction conditions for hydroarylation of **14**



Entry	Variation from “the standard conditions”	Time (h)	Conversion of **1** (%)	Yield of **TP** (%)^a	Yield of **5** (%)^a
1	none	6	>99	59 (55)	17
2	alkene (**14**) (5 equiv)	4	97	48	31
3	alkene (**14**) (5 equiv), CH_3CN as the solvent	20	54	28	13

[a] ^{1}H NMR yields were given (isolated yield in parenthesis).

Prepared using methyl 4-bromobenzoate (**1**) (107.6 mg, 0.500 mmol) and dimethylphenylvinylsilane (**14**) (Sigma-Aldrich 483435) (910 μL, 5.00 mmol) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 99:1)

Yield: 55% yield (81.6 mg, 0.273 mmol, 6 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.42 – 7.34 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 2.67 (ddd, *J* = 14.7, 12.4, 5.0 Hz, 2H), 1.12 (ddd, *J* = 14.7, 12.4, 5.0 Hz, 2H), 0.29 (s, 6H).
^{13}C NMR (125 MHz, CDCl$_3$) δ 167.1, 150.5, 138.6, 133.5, 129.7, 129.0, 127.8, 127.8, 127.5, 51.9, 30.1, 17.5, -3.2.
ESIHRMS Found: m/z 299.1466; Calcd for $C_{18}H_{23}O_2Si$ $(M+H)^+$ 299.1467.
IR (neat, cm^{-1}) 3069, 2999, 2951, 2843, 1721 [ν(C=O)], 1608, 1423, 1278, 1179, 1111.

Interpretation of AA’BB’ couplings on the methylene protons
The assignment indicates that all 4 protons are not magnetically equivalent (AA’BB’ coupling). The set of peaks at 2.67 ppm and 1.12 ppm are mirror image of each other. Figure S3 showed interpretation of AA’BB’ coupling of the methylene protons at 2.67 ppm.

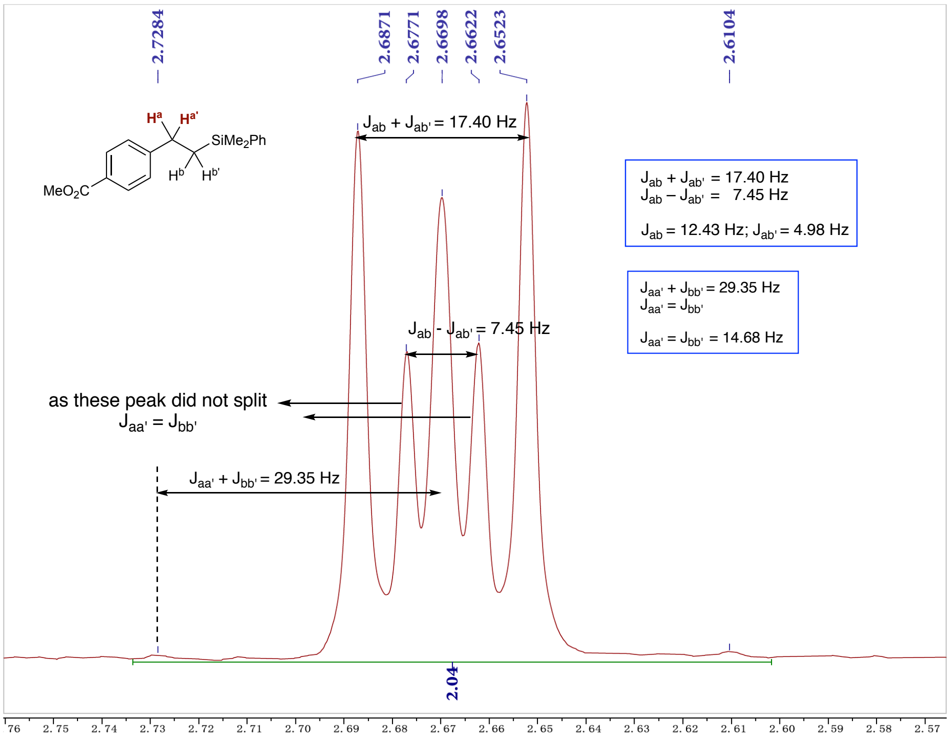
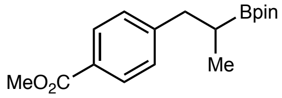


Figure S3 Interpretation of AA’BB’ coupling of the methylene protons at 2.67 ppm.

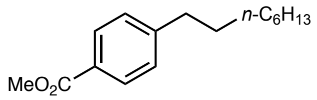
4.4.11 Methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.7 mg, 0.501 mmol) and 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (**15**) (Leyan 1019073) (470 µL, 2.50 mmol) with K$_2$S$_x$ (4.1 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 96:4)
Yield: 27% yield (41.3 mg, 0.136 mmol, 6 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H), 2.85 (dd, J = 13.6, 7.7 Hz, 1H), 2.60 (dd, J = 13.6, 8.1 Hz, 1H), 1.38 (ddq, J = 8.1, 7.7, 7.4 Hz, 1H), 1.18 (s, 12H), 0.97 (d, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.3, 148.1, 129.4, 128.9, 127.6, 83.1, 51.9, 39.0, 24.7, 15.2. (The boron-bound carbon was not detected)
^{11}B NMR (128 MHz, CDCl$_3$) δ 34.84.
ESIHRMS Found: m/z 305.1927; Calcd for C$_{17}$H$_{26}$O$_4$B (M+H)$^+$ 305.1924.
IR (neat, cm^{-1}) 2980, 1719 [ν(C=O)], 1647, 1564, 1437, 1319, 1283, 1142, 1111.

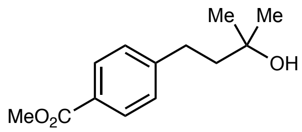
4.4.12 Methyl 4-octylbenzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.8 mg, 0.501 mmol) and 1-octene (**16**) (Sigma-Aldrich O4806) (392 µL, 2.50 mmol) with *i*-Pr$_3$SiSH (11 µL, 0.0512 mmol, 10 mol%) as the precatalyst in CH$_3$CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 99:1)
Yield: 42% yield (51.9 mg, 0.209 mmol, 24 h) as a colorless oil.
The spectral data matched those reported in the literature.[9]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 3.90 (s, 3H), 2.65 (t, J = 7.7 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.35 – 1.21 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.2, 148.5, 129.6, 128.4, 127.6, 51.9, 36.0, 31.8, 31.1, 29.4, 29.2, 29.2, 22.6, 14.1.

4.4.13 Methyl 4-(3-hydroxy-3-methylbutyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.6 mg, 0.500 mmol) and 2-methyl-3-buten-2-ol (**17**) (Sigma-Aldrich 136816) (261 µL, 2.50 mmol) with K$_2$S$_x$ (4.0 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).

Purification: flash column chromatography (silica gel, Hexane:EtOAc = 85:15)
Yield: 55% yield (60.8 mg, 0.274 mmol, 4 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 2.77 (ddd, *J* = 13.8, 12.5, 5.0 Hz, 2H), 1.79 (ddd, *J* = 13.8, 12.5, 5.0 Hz, 2H), 1.30 (s, 6H), 1.28 (s, 1H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 167.1, 148.2, 129.7, 128.3, 127.7, 70.7, 51.9, 45.2, 30.8, 29.3.
ESIHRMS Found: m/z 223.1336; Calcd for $C_{13}H_{19}O_3$ (M+H)$^+$ 223.1334.
IR (neat, cm^{-1}) 3053, 2974, 1713 [ν(C=O)], 1611, 1437, 1275, 1180, 1113.

Interpretation of AA’BB’ couplings on the methylene protons
The assignment indicates that all 4 protons are not magnetically equivalent (AA’BB’ coupling). The set of peaks at 2.77 ppm and 1.79 ppm are mirror image of each other. Figure S4 showed interpretation of AA’BB’ coupling of the methylene protons at 2.77 ppm.

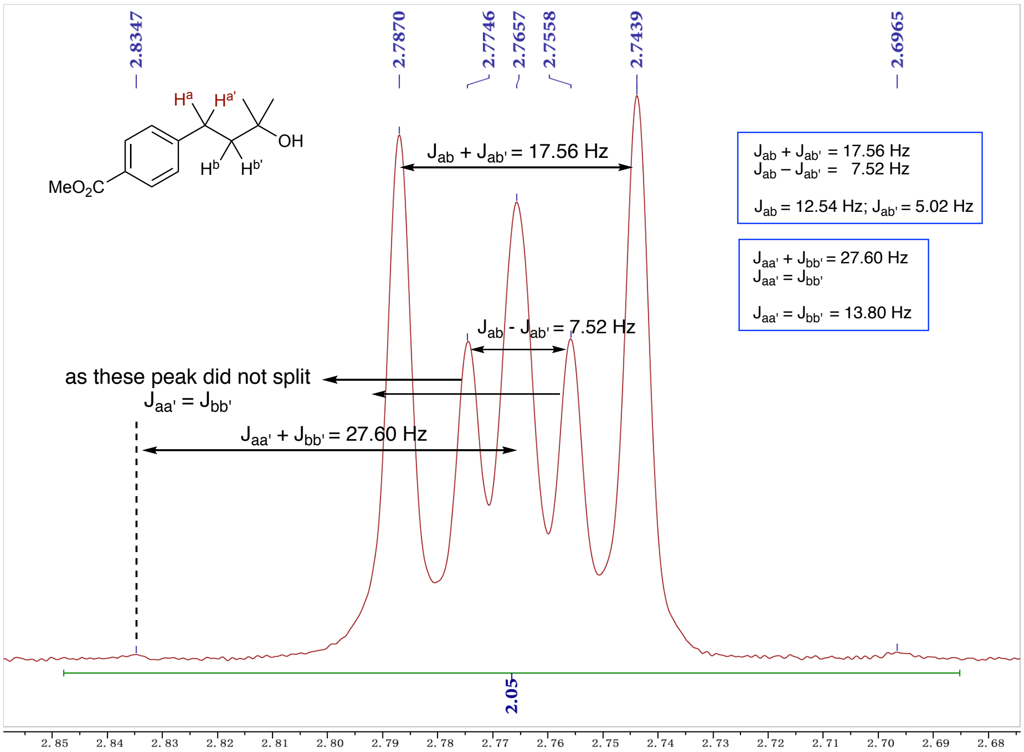
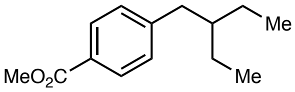


Figure S4 Interpretation of AA’BB’ coupling of the methylene protons at 2.77 ppm.

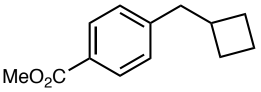
4.4.14 Methyl 4-(2-ethylbutyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.6 mg, 0.500 mmol) and 2-ethyl-1-butene (**18**) (Sigma-Aldrich E14705) (305 μL, 2.50 mmol) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 99:1)
Yield: 40% yield (44.5 mg, 0.202 mmol, 4 h) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 2.58 (d, *J* = 7.1 Hz, 2H), 1.62 – 1.44 (m, 1H), 1.29 (qd, *J* = 7.4, 6.0 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 147.6, 129.4, 129.1, 127.6, 51.9, 42.5, 39.8, 25.0, 10.8.
ESIHRMS Found: m/z 221.1540; Calcd for $C_{14}H_{21}O_2$ $(M+H)^+$ 221.1542.
IR (neat, cm^{-1}) 2964, 2875, 1716 [ν(C=O)], 1611, 1437, 1284, 1180, 1113.

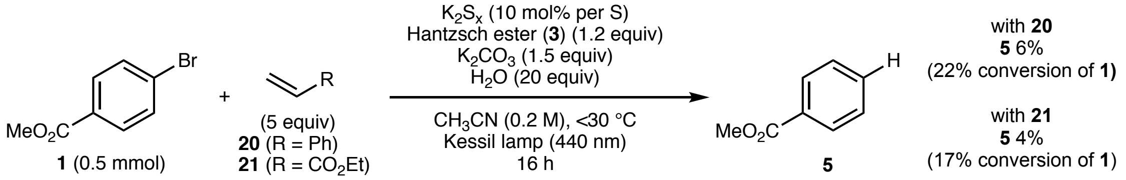
4.4.15 Methyl 4-(cyclobutylmethyl)benzoate



Prepared using methyl 4-bromobenzoate (**1**) (107.8 mg, 0.501 mmol) and methylenecyclobutane (**19**) (Sigma-Aldrich M45008) (231 μL, 2.50 mmol) with *i*-Pr_3SiSH (11 μL, 0.0512 mmol, 10 mol%) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 99:1)
Yield: 54% yield (55.2 mg, 0.270 mmol, 24 h) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 2.74 (d, *J* = 7.6 Hz, 2H), 2.64 – 2.47 (m, 1H), 2.22 – 1.95 (m, 2H), 1.95 – 1.77 (m, 2H), 1.77 – 1.64 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 146.8, 129.5, 128.5, 127.6, 51.9, 42.9, 36.9, 28.2, 18.3.
ESIHRMS Found: m/z 205.1228; Calcd for $C_{13}H_{17}O_2$ $(M+H)^+$ 205.1229.
IR (neat, cm^{-1}) 2953, 1715 [ν(C=O)], 1611, 1435, 1280, 1178, 1111.

4.4.16 The reactions with styrene (20) and ethyl acrylate (21)

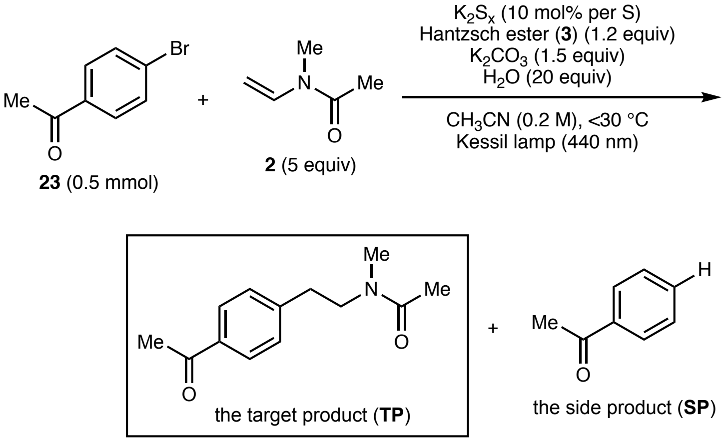


We have tested hydroarylation of styrene (**20**) and ethyl acrylate (**21**), both of which did not give any desired hydroarylation products. In these reactions, majority of methyl 4-bromobenzoate (**1**) was recovered along with formation of methyl benzoate (**5**) in 4-6% yields, indicating that redox catalysis did not function for the desired hydroarylation. We reasoned that in the case of the reaction with styrene (**20**), its polymerization hampers HAT, while ethyl acrylate (**21**) likely quenches the redox properties of polysulfide ions by working as a Michael acceptor.

4.4.17 *N*-(4-Acetylphenethyl)-*N*-methylacetamide

We found that use of *i*-Pr$_2$NEt as the stoichiometric reductant provided better yield of the hydroarylation product (Table S4, entry 2).

Table S4 Optimization of the reaction conditions for the hydroarylation with **23**



Entry	Variation from "the standard conditions"	Time (h)	Conversion of **23** (%)	Yield of **TP** (%)[a]	Yield of **SP** (%)[a]
1	none	3	>99	66 (61)	13
2	*i*-Pr$_2$NEt (2 equiv) instead of **3** in CH$_3$CN (5 mL)	3	>99	80 (72)	15

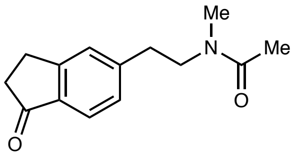
[a] ^{1}H NMR yields were given (isolated yield in parenthesis).

Procedure in entry 1: Prepared using methyl 4′-bromoacetophenone (**23**) (Sigma-Aldrich B56404) (99.1 mg, 0.498 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv) with K$_2$S$_x$ (4.0 mg, 10 mol% per S) as the precatalyst in CH$_3$CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 61% yield (66.6 mg, 0.304 mmol, 3 h) as a colorless oil.

Procedure in entry 2: *N*-(4-Acetylphenethyl)-*N*-methylacetamide can also be synthesized by the following protocol to obtain higher yield. Prepared using methyl 4′-bromoacetophenone (**23**) (99.7 mg, 0.501 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv), *i*-Pr$_2$NEt (174 µL, 1.00 mmol, 2 equiv), and H$_2$O (180 µL, 20 equiv) with K$_2$S$_x$ (4.1 mg, 10 mol% per S) as the precatalyst in CH$_3$CN (5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 72% yield (78.9 mg, 0.360 mmol, 3 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.61 (t, *J* = 7.5 Hz, 2H), 2.94 – 2.90 (m, 2H), 2.90 (s, 3H), 2.58 (s, 3H), 2.06 (s, 3H).
(minor rotamer) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.55 (t, *J* = 7.1 Hz, 2H), 2.95 (s, 3H), 2.94 – 2.90 (m, 2H), 2.59 (s, 3H), 1.86 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 197.7, 197.5, 170.4, 170.4, 144.9, 143.7, 135.7, 135.4, 129.0 (overlapped with 2C), 128.8, 128.5, 52.0, 49.1, 36.8, 34.7, 33.7, 33.3, 26.5 (overlapped with 2C), 21.8, 20.9.
ESIHRMS Found: m/z 220.1335; Calcd for $C_{13}H_{18}NO_2(M+H)^+$ 220.1338.
IR (neat, cm^{-1}) 2934, 1686 [ν(C=O)], 1645 [ν(C=O)], 1489, 1413, 1360, 1269, 1184, 1109.

4.4.18 *N*-Methyl-*N*-(2-(1-oxo-2,3-dihydro-1*H*-inden-5-yl)ethyl)acetamide

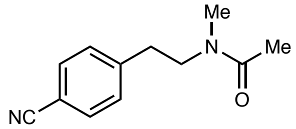


Prepared using 5-bromo-1-indanone (**24**) (Sigma-Aldrich 433098) (105.6 mg, 0.500 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 10:90)
Yield: 82% yield (94.3 mg, 0.408 mmol, 8 h) as a white solid.

Prepared using 5-chloro-1-indanone (**25**) (Sigma-Aldrich 433071) (85.7 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 10:90)
Yield: 65% yield (75.2 mg, 0.325 mmol, 10 h) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.35 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 3.61 (t, *J* = 7.6 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.98 – 2.89 (m, 2H), 2.94 (s, 3H), 2.73 – 2.65 (m, 2H), 2.08 (s, 3H).
(minor rotamer) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 3.56 (t, *J* = 7.2 Hz, 2H), 3.16 – 3.08 (m, 2H), 2.98 – 2.89 (m, 2H), 2.96 (s, 3H), 2.73 – 2.65 (m, 2H), 1.90 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 206.4, 206.2, 170.4, 170.3, 155.8, 155.7, 146.7, 145.6, 135.9, 135.5, 128.2, 128.0, 126.9, 126.9, 124.0, 123.7, 52.1, 49.3, 36.7, 36.3, 36.3, 35.2, 34.1, 33.3, 25.6 (overlapped with 2C), 21.8, 21.0.
ESIHRMS Found: m/z 232.1336; Calcd for $C_{14}H_{18}NO_2$ $(M+H)^+$ 232.1338.
IR (neat, cm^{-1}) 2930, 1703 [ν(C=O)], 1637 [ν(C=O)], 1485, 1435, 1402, 1285, 1103, 1034, 1011.
MP: 133-135 °C.

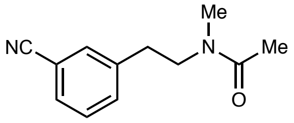
4.4.19 *N*-(4-Cyanophenethyl)-*N*-methylacetamide



Prepared using 4-bromobezonitrile (**26**) (Sigma-Aldrich B58407) (91.4 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 73% yield (73.5 mg, 0.363 mmol, 12 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) (major rotamer) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.60 (t, *J* = 7.5 Hz, 2H), 2.93 – 2.88 (m, 2H), 2.91 (s, 3H), 2.06 (s, 3H).
(minor rotamer) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.54 (t, *J* = 7.2 Hz, 2H), 2.94 (s, 3H), 2.93 – 2.88 (m, 2H), 1.88 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.2, 144.8, 143.7, 132.5, 132.2, 129.5 (overlapped with 2C), 118.8, 118.5, 110.8, 110.2, 51.7, 48.9, 36.7, 34.8, 33.8, 33.3, 21.8, 20.9.
ESIHRMS Found: m/z 225.1006; Calcd for $C_{12}H_{14}N_2ONa$ $(M+Na)^+$ 225.1004.
IR (neat, cm^{-1}) 2936, 2228 [ν(C≡N)], 1630 [ν(C=O)], 1502, 1411, 1362, 1261, 1036, 1009.

4.4.20 *N*-(3-Cyanophenethyl)-*N*-methylacetamide



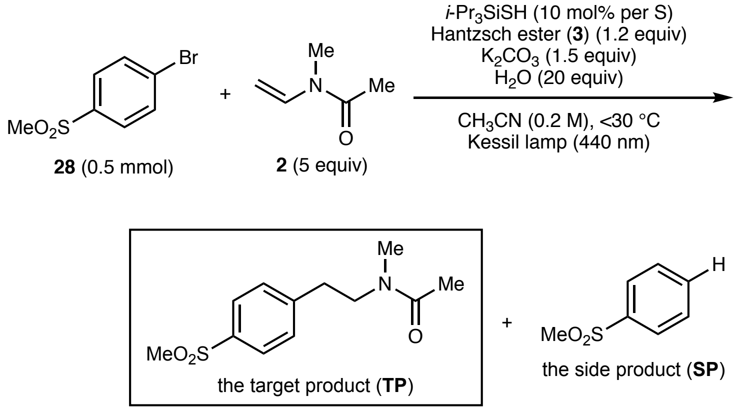
Prepared using 3-bromobezonitrile (**27**) (Sigma-Aldrich B58202) (91.1 mg, 0.500 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 79% yield (80.1 mg, 0.396 mmol, 16 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) (major rotamer) δ 7.59 – 7.39 (m, 4H), 3.58 (t, *J* = 7.5 Hz, 2H), 2.93 (s, 3H), 2.93 – 2.86 (m, 2H), 2.07 (s, 3H).
(minor rotamer) δ 7.59 – 7.39 (m, 4H), 3.54 (t, *J* = 7.3 Hz, 2H), 2.95 (s, 3H), 2.93 – 2.86 (m, 2H), 1.91 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.2, 140.5, 139.6, 133.3, 133.2, 132.2, 132.1, 130.5, 130.1, 129.5, 129.2, 118.7, 118.4, 112.8, 112.4, 51.9, 49.0, 36.7, 34.3, 33.3, 33.2, 21.8, 20.9.
ESIHRMS Found: m/z 225.1004; Calcd for $C_{12}H_{14}N_2ONa$ $(M+Na)^+$ 225.1004.
IR (neat, cm^{-1}) 2936, 2230 [ν(C≡N)], 1632 [ν(C=O)], 1483, 1406, 1364, 1311, 1203, 1037, 1009.

4.4.21 *N*-Methyl-*N*-(4-(methylsulfonyl)phenethyl)acetamide

We observed that *i*-Pr$_3$SiSH serves as the best precatalyst for the hydroarylation with **28** (Table S5).

Table S5 Optimization of the reaction conditions for the hydroarylation with **28**



Entry	Variation from "the standard conditions"	Time (h)	Conversion of **28** (%)	Yield of **TP** (%)[a]	Yield of **SP** (%)[a]
1	none	8	>99	86 (81)	11
2	K$_2$S$_x$ (10 mol% per S) instead of *i*-Pr$_3$SiSH	16	73	53	10
3	K$_2$S$_x$ (10 mol% per S) instead of *i*-Pr$_3$SiSH and DMSO as the solvent	4	>99	55	19

[a] ^{1}H NMR yields were given (isolated yield in parenthesis).

Prepared using 4-bromophenyl methyl sulfone (**28**) (Sigma-Aldrich 556327) (117.1 mg, 0.498 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with *i*-Pr$_3$SiSH (11 μL, 0.0512 mmol, 10 mol%) as the precatalyst in CH$_3$CN (2.5 mL).

Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 10:90)

Yield: 81% yield (103.0 mg, 0.403 mmol, 8 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) (major rotamer) δ 7.87 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 3.61 (t, J = 7.5 Hz, 2H), 3.05 (s, 3H), 3.00 – 2.90 (m, 2H), 2.93 (s, 3H), 2.07 (s, 3H).

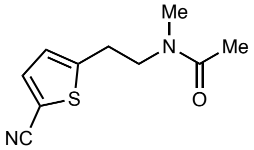
(minor rotamer) δ 7.90 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.57 (t, J = 7.2 Hz, 2H), 3.06 (s, 3H), 3.00 – 2.90 (m, 2H), 2.95 (s, 3H), 1.90 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.2, 145.7, 144.6, 139.1, 138.5, 129.7 (overlapped with 2C), 127.8, 127.5, 51.8, 48.9, 44.5, 44.4, 36.7, 34.6, 33.5, 33.3, 21.8, 20.9.

ESIHRMS Found: m/z 256.1006; Calcd for $C_{12}H_{18}NO_3S$ $(M+H)^+$ 256.1007.

IR (neat, cm^{-1}) 2928, 1616 [ν(C=O)], 1491, 1410, 1296, 1148, 1090, 1009.

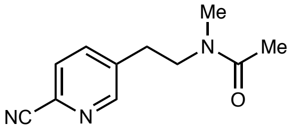
4.4.22 *N*-(2-(5-Cyanothiophen-2-yl)ethyl)-*N*-methylacetamide



Prepared using 5-bromo-2-thiophenecarbonitrile (**29**) (Fluorochem 049323) (94.4 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 10:90)
Yield: 41% yield (42.7 mg, 0.205 mmol, 14 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) (major rotamer) δ 7.48 (d, *J* = 3.7 Hz, 1H), 6.89 (d, *J* = 3.7 Hz, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.15 – 3.08 (m, 2H), 2.95 (s, 3H), 2.09 (s, 3H).
(minor rotamer) δ 7.50 (d, *J* = 3.8 Hz, 1H), 6.86 (d, *J* = 3.8 Hz, 1H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.15 – 3.08 (m, 2H), 2.96 (s, 3H), 1.93 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 170.7, 170.4, 149.8, 148.2, 137.8, 137.7, 126.4, 126.0, 114.3, 113.9, 108.5, 107.8, 51.6, 49.1, 36.9, 33.1, 28.8, 27.9, 21.9, 21.0.
ESIHRMS Found: m/z 231.0566; Calcd for $C_{10}H_{12}N_2OSNa$ $(M+Na)^+$ 231.0568.
IR (neat, cm^{-1}) 2934, 2220 [ν(C≡N)], 1631 [ν(C=O)], 1449, 1406, 1034, 1001.

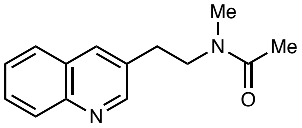
4.4.23 *N*-(2-(6-Cyanopyridin-3-yl)ethyl)-*N*-methylacetamide



Prepared using 2-cyano-5-bromopyridine (**30**) (Fluorochem 045207) (91.5 mg, 0.500 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 10:90)
Yield: 51% yield (51.6 mg, 0.254 mmol, 3 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 8.57 (s, 1H), 7.75 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 3.63 (t, *J* = 7.4 Hz, 2H), 3.01 – 2.91 (m, 2H), 2.97 (s, 3H), 2.07 (s, 3H).
(minor rotamer) δ 8.60 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 3.01 – 2.91 (m, 2H), 2.97 (s, 3H), 1.93 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.7, 170.1, 151.5, 151.4, 138.8, 137.9, 137.1, 137.1, 132.4, 131.9, 128.3, 128.2, 117.2, 117.0, 51.3, 48.4, 36.7, 33.4, 32.1, 30.9, 21.8, 21.0.
ESIHRMS Found: m/z 204.1135; Calcd for $C_{11}H_{14}N_3O$ $(M+H)^+$ 204.1137.
IR (neat, cm^{-1}) 2936, 2236 [ν(C≡N)], 1628 [ν(C=O)], 1568, 1471, 1409, 1362, 1261, 1028, 1009.

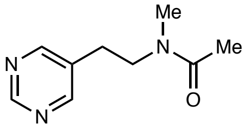
4.4.24 *N*-methyl-*N*-(2-(quinolin-3-yl)ethyl)acetamide



Prepared using 3-bromoquinoline (**31**) (Sigma-Aldrich 124133) (105.0 mg, 0.505 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.0 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 10:90)
Yield: 40% yield (45.8 mg, 0.201 mmol, 3 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 8.79 (s, 1H), 8.20 – 8.05 (m, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.64 (m, 1H), 7.59 – 7.51 (m, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 3.12 – 3.03 (m, 2H), 2.93 (s, 3H), 2.09 (s, 3H).
(minor rotamer) δ 8.79 (s, 1H), 8.20 – 8.05 (m, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.64 (m, 1H), 7.59 – 7.51 (m, 1H), 3.63 (t, *J* = 7.4 Hz, 2H), 3.12 – 3.03 (m, 2H), 2.99 (s, 3H), 1.95 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.6, 170.3, 151.7, 151.3, 147.2, 147.0, 135.1, 135.0, 131.8, 130.7, 129.3, 129.2, 129.1, 128.9, 128.0, 127.8, 127.4, 127.4, 127.0, 126.7, 52.1, 49.3, 37.0, 33.5, 32.2, 31.0, 21.9, 21.1.
ESIHRMS Found: m/z 229.1340; Calcd for $C_{14}H_{17}N_2O$ $(M+H)^+$ 229.1341.
IR (neat, cm^{-1}) 3055, 2936, 1622 [ν(C=O)], 1495, 1404, 1308, 1269, 1128, 1037, 1015.

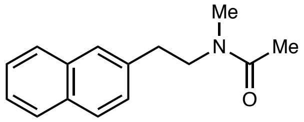
4.4.25 *N*-Methyl-*N*-(2-(pyrimidin-5-yl)ethyl)acetamide



Prepared using 5-bromopyrimidine (**32**) (Sigma-Aldrich 219142) (78.8 mg, 0.496 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 10:90)
Yield: 70% yield (62.2 mg, 0.347 mmol, 6 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 9.10 (s, 1H), 8.63 (s, 2H), 3.61 (t, *J* = 7.1 Hz, 2H), 2.97 (s, 3H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.08 (s, 3H).
(minor rotamer) δ 9.15 (s, 1H), 8.62 (s, 2H), 3.57 (t, *J* = 7.5 Hz, 2H), 2.97 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.98 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.0, 157.4, 157.0, 156.8, 156.7, 132.2, 131.3, 51.3, 48.5, 36.7, 33.2, 29.4, 28.2, 21.7, 21.0.
ESIHRMS Found: m/z 202.0956; Calcd for $C_9H_{13}N_3ONa$ $(M+Na)^+$ 202.0956.
IR (neat, cm^{-1}) 2938, 1609 [ν(C=O)], 1570, 1414, 1364, 1140, 1013.

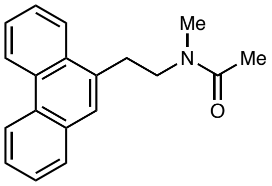
4.4.26 *N*-Methyl-*N*-(2-(naphthalen-2-yl)ethyl)acetamide



Prepared using 2-bromonaphthalene (**33**) (Sigma-Aldrich 183644) (103.3 mg, 0.499 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 60:40 to 40:60)
Yield: 52% yield (59.3 mg, 0.261 mmol, 8 h) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.87 – 7.76 (m, 3H), 7.66 (s, 0.5H), 7.61 (s, 0.5H), 7.52 – 7.40 (m, 2H), 7.37 (dd, *J* = 8.4, 1.8 Hz, 0.5H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 0.5H), 3.67 (t, *J* = 7.3 Hz, 1H), 3.59 (t, *J* = 7.3 Hz, 1H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.97 (s, 1.5H), 2.87 (s, 1.5H), 2.07 (s, 1.5H), 1.90 (s, 1.5H).
^{13}C NMR (100 MHz, $CDCl_3$) (mixture of rotamers) δ 170.5, 170.4, 136.7, 135.6, 133.6, 133.5, 132.2, 132.1, 128.4, 128.0, 127.6, 127.6, 127.4, 127.4, 127.3, 127.2, 127.1, 126.9, 126.3, 126.0, 125.7, 125.3, 52.5, 49.6, 36.9, 35.0, 33.9, 33.4, 21.9, 21.0.
ESIHRMS Found: m/z 250.1209; Calcd for $C_{15}H_{17}NONa$ $(M+Na)^+$ 250.1208.
IR (neat, cm^{-1}) 3053, 2984, 2936, 1632 [ν(C=O)], 1400, 1362, 1265, 1009.

4.4.27 *N*-Methyl-*N*-(2-(phenanthren-9-yl)ethyl)acetamide



Prepared using 9-bromophenanthrene (**34**) (Sigma-Aldrich B75409) (128.0 mg, 0.498 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.0 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 60:40 to 40:60)
Yield: 55% yield (76.6 mg, 0.276 mmol, 10 h) as a colorless oil.

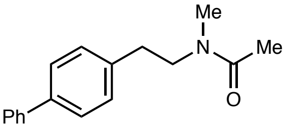
^{1}H NMR (500 MHz, $CDCl_3$) (major rotamer) δ 8.72 – 8.69 (m, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.32 – 8.26 (m, 1H), 7.81 (d, *J* = 7.6, 1H), 7.71 – 7.50 (m, 5H), 3.73 (t, *J* = 7.4 Hz, 2H), 3.38 – 3.28 (m, 2H), 2.85 (s, 3H), 2.08 (s, 3H).
(minor rotamer) δ 8.77 – 8.72 (m, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.81 (d, *J* = 7.6, 1H), 7.71 – 7.50 (m, 5H), 3.67 (t, *J* = 7.4 Hz, 2H), 3.38 – 3.28 (m, 2H), 3.00 (s, 3H), 1.87 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) (mixture of rotamers) δ 170.6, 170.4, 133.6, 132.2, 131.7, 131.4, 131.2, 130.8, 130.6 (overlapped with 2C), 129.8 (overlapped with 2C), 128.1, 128.0, 127.5, 127.1,

126.8, 126.8, 126.6, 126.5, 126.5, 126.3, 126.2 (overlapped with 2C), 124.5, 123.6, 123.4, 123.1, 122.4 (overlapped with 2C), 51.2, 49.4, 37.1, 33.5, 32.3, 31.3, 21.9, 21.0.

ESIHRMS Found: m/z 278.1543; Calcd for $C_{19}H_{20}NO$ $(M+H)^+$ 278.1545.

IR (neat, cm^{-1}) 3062, 3019, 2936, 1636 [ν(C=O)], 1486, 1485, 1402, 1359, 1267, 1007.

4.4.28 *N*-(2-([1,1'-Biphenyl]-4-yl)ethyl)-*N*-methylacetamide



Prepared using 4-bromobiphenyl (**35**) (Sigma-Aldrich 281999) (116.0 mg, 0.498 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (8.2 mg, 20 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 60:40 to 40:60)
Yield: 44% yield (55.9 mg, 0.221 mmol, 16 h) as a colorless oil.

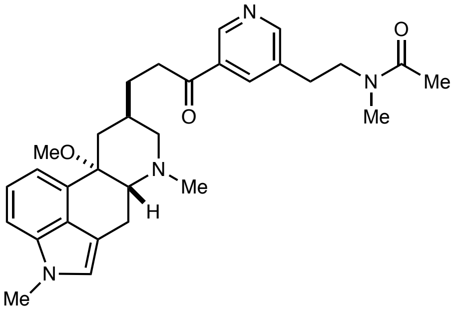
^{1}H NMR (400 MHz, CDCl$_3$) (mixture of rotamers) δ 7.64 – 7.50 (m, 4H), 7.47 – 7.38 (m, 2H), 7.37 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 3.61 (t, *J* = 7.6 Hz, 1H), 3.53 (t, *J* = 7.2 Hz, 1H), 2.97 (s, 1.5H), 2.90 (s, 1.5H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.07 (s, 1.5H), 1.90 (s, 1.5H).

^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.4, 140.8, 140.6, 139.7, 139.2, 138.3, 137.2, 129.2, 129.1, 128.8, 128.7, 127.4, 127.2, 127.1, 127.0, 126.9 (overlapped with 2C), 52.5, 49.6, 36.8, 34.4, 33.3 (overlapped with 2C), 21.9, 21.0.

ESIHRMS Found: m/z 254.1542; Calcd for $C_{17}H_{20}NO$ $(M+H)^+$ 254.1545.

IR (neat, cm^{-1}) 3053, 3028, 2932, 1632 [ν(C=O)], 1485, 1410, 1265, 1009.

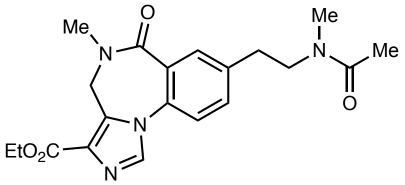
4.4.29 ((6aR,9R,10aS)-10a-Methoxy-4,7-dimethyl-4,6,6a,7,8,9,10,10a-octahydroindolo[4,3-*fg*]quinolin-9-yl)methyl 5-(2-(*N*-methylacetamido)ethyl)nicotinate



Prepared using nicergoline (**36**) (TCI N0904) (243.1 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 30:70)
Yield: 53% yield (127.3 mg, 0.252 mmol, 6 h) as a green oil.

^{1}H NMR (500 MHz, $CDCl_3$) (major rotamer) δ 9.10 (s, 1H), 8.65 (s, 1H), 8.17 (s, 1H), 7.27 – 7.17 (m, 2H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.80 (s, 1H), 4.48 – 4.36 (m, 1H), 4.36 – 4.26 (m, 1H), 3.78 (s, 3H), 3.62 (t, *J* = 14.9 Hz, 2H), 3.30 – 3.16 (m, 2H), 3.10 – 3.01 (m, 2H), 3.00 (s, 3H), 2.96 – 2.90 (m, 2H), 2.93 (s, 3H), 2.73 – 2.62 (m, 1H), 2.52 (s, 3H), 2.47 – 2.35 (m, 1H), 2.24 – 2.11 (m, 1H), 2.06 (s, 3H), 1.40 (dd, *J* = 13.3, 13.3 Hz, 1H).
(minor rotamer) δ 9.13 (s, 1H), 8.65 (s, 1H), 8.12 (s, 1H), 7.27 – 7.17 (m, 2H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.80 (s, 1H), 4.48 – 4.36 (m, 1H), 4.36 – 4.26 (m, 1H), 3.78 (s, 3H), 3.56 (t, *J* = 14.9 Hz, 2H), 3.30 – 3.16 (m, 2H), 3.10 – 3.01 (m, 2H), 3.00 (s, 3H), 2.97 (s, 3H), 2.96 – 2.90 (m, 2H), 2.73 – 2.62 (m, 1H), 2.52 (s, 3H), 2.47 – 2.35 (m, 1H), 2.24 – 2.11 (m, 1H), 1.97 (s, 3H), 1.40 (dd, *J* = 13.3, 13.3 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) (mixture of rotamers) δ 170.6, 170.1, 165.2, 164.9, 153.9, 153.7, 149.3, 148.9, 137.1 (overlapped with 2C), 137.0, 135.1, 134.5, 133.5, 129.4 (overlapped with 2C), 126.2, 126.0, 125.8, 125.4, 123.3 (overlapped with 2C), 121.4 (overlapped with 2C), 114.9, 114.9, 110.0 (overlapped with 2C), 109.0, 109.0, 73.5 (overlapped with 2C), 69.8 (overlapped with 2C), 68.1, 67.9, 60.4 (overlapped with 2C), 51.7, 49.5 (overlapped with 2C), 48.9, 43.0 (overlapped with 2C), 36.8 (overlapped with 2C), 33.3, 32.7, 31.7, 31.3, 30.6 (overlapped with 2C), 30.2, 30.1, 22.2, 21.8 (overlapped with 2C), 21.1.
ESIHRMS Found: m/z 505.2816; Calcd for $C_{29}H_{37}N_4O_4$ $(M+H)^+$ 505.2815.
IR (neat, cm^{-1}) 3053, 2941, 2787, 1717 [ν(C=O)], 1638 [ν(C=O)], 1465, 1421, 1304, 1206, 1115, 1070.

4.4.30 Ethyl 5-methyl-8-(2-(*N*-methylacetamido)ethyl)-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate



Prepared using ethyl 8-bromo-5-methyl-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate (**37**) (Sigma-Aldrich 901778) (72.9 mg, 0.200 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (103 μL, 1.00 mmol), Hantzsch ester (**3**) (61.3 mg, 0.242 mmol), K_2CO_3 (41.7 mg, 0.302 mmol), and H_2O (72 μL, 4.00 mmol) with K_2S_x (1.6 mg, 10 mol% per S) as the precatalyst in CH_3CN (1 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 20:80)
Yield: 81% yield (62.1 mg, 0.162 mmol, 11 h) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) (major rotamer) δ 7.93 – 7.89 (m, 2H), 7.58 – 7.52 (m, 1H), 7.44 – 7.37 (m, 1H), 5.34 – 4.98 (m, 1H), 4.49 – 4.17 (m, 3H), 3.64 (t, *J* = 7.3 Hz, 2H), 3.25 (s, 3H), 3.04 – 2.92 (m, 2H), 2.99 (s, 3H), 2.08 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H).

(minor rotamer) δ 7.89 – 7.87 (m, 2H), 7.49 – 7.44 (m, 1H), 7.44 – 7.37 (m, 1H), 5.34 – 4.98 (m, 1H), 4.49 – 4.17 (m, 3H), 3.60 (t, *J* = 7.3 Hz, 2H), 3.26 (s, 3H), 3.04 – 2.92 (m, 2H), 2.98 (s, 3H), 1.96 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H).

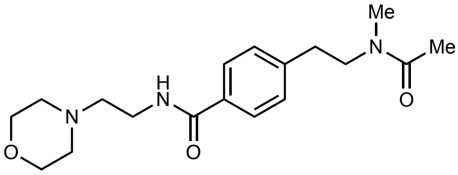
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.4, 170.1, 166.4, 166.1, 162.9, 162.8, 139.9, 138.8, 135.3, 135.2, 134.8, 134.8, 133.1, 132.9, 132.5, 132.5, 130.6, 130.2, 129.2, 128.8, 128.6, 128.5, 122.1, 121.9, 60.8, 60.8, 51.7, 48.7, 42.2 (overlapped with 2C), 36.5, 35.7, 35.7, 34.0, 33.2, 32.8, 21.8, 21.0, 14.2 (overlapped with 2C).

ESIHRMS Found: m/z 385.1877; Calcd for $C_{20}H_{25}N_4O_4$ $(M+H)^+$ 385.1876.

IR (neat, cm^{-1}) 3054, 2984,, 2928, 1726 [ν(C=O)], 1707 [ν(C=O)], 1643 [ν(C=O)], 1503, 1377, 1265, 1065.

MP: 156-158 °C.

4.4.31 4-(2-(*N*-Methylacetamido)ethyl)-*N*-(2-morpholinoethyl)benzamide



Prepared using moclobemide (**38**) (Sigma-Aldrich M3071) (53.9 mg, 0.201 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (103 μL, 1.00 mmol), Hantzsch ester (**3**) (60.9 mg, 0.240 mmol), K_2CO_3 (41.6 mg, 0.301 mmol), and H_2O (72 μL, 4.00 mmol) with K_2S_x (1.7 mg, 10 mol% per S) as the precatalyst in DMSO (1 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 20:80)
Yield: 36% yield (24.1 mg, 0.0723 mmol, 11 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.78 (br, 1H), 3.84 – 3.67 (m, 4H), 3.66 – 3.49 (m, 4H), 2.94 – 2.85 (m, 2H), 2.90 (s, 3H), 2.65 – 2.56 (m, 2H), 2.56 – 2.46 (m, 4H), 2.06 (s, 3H).
(minor rotamer) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.78 (br, 1H), 3.84 – 3.67 (m, 4H), 3.66 – 3.49 (m, 4H), 2.95 (s, 3H), 2.94 – 2.85 (m, 2H), 2.65 – 2.56 (m, 2H), 2.56 – 2.46 (m, 4H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ170.5 (overlapped with 2C), 167.2, 166.8, 142.9, 141.8, 133.1, 132.7, 129.0 (overlapped with 2C), 127.4, 127.1, 66.9 (overlapped with 2C), 56.9, 56.8, 53.3 (overlapped with 2C), 52.1, 49.2, 36.8, 36.0, 34.6, 33.6, 33.3, 30.3, 21.9, 21.0.

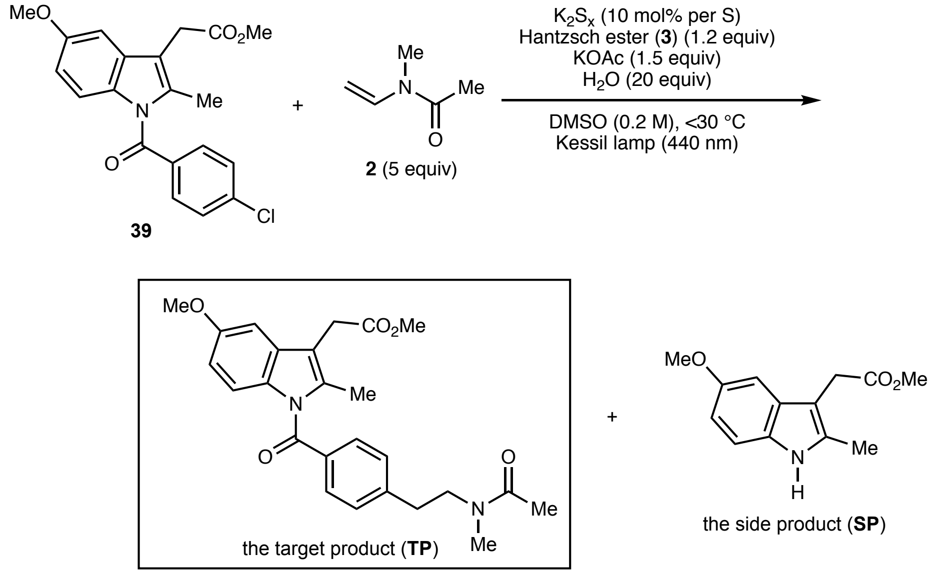
ESIHRMS Found: m/z 334.2132; Calcd for $C_{18}H_{28}N_3O_3$ $(M+H)^+$ 334.2131.

IR (neat, cm^{-1}) 3053, 2963, 2860, 2820, 1700 [ν(C=O)], 1636 [ν(C=O)], 1521, 1493, 1265, 1117.

4.4.32 Methyl 2-(5-methoxy-2-methyl-1-(4-(2-(*N*-methylacetamido)ethyl)benzoyl)-1*H*-indol-3-yl)acetate

We found that hydrolysis of the amide bond is the major side reaction, that is associated with the desired hydroarylation reaction even under milder basic reaction conditions. The reaction in the presence of KOAc provided the best yield (44% yield) of the hydroarylation product (Table S6, entry 1).

Table S6 Optimization of the reaction conditions for the hydroarylation with **39**



Entry	Variation from “the standard conditions”	Time (h)	Conversion of **39** (%)	Yield of **TP** (%)[a]	Yield of **SP** (%)[a]
1	none	6	>99	48 (44)	49
2	K_2CO_3 instead of KOAc	5	>99	26	64
3	K_2HPO_4 instead of KOAc	6	>99	28	52
4	KH_2PO_4 instead of KOAc	24	72	32	21

[a] ^{1}H NMR yields were given (isolated yield in parenthesis).

Prepared using indomethacin methyl ester (**39**) (185.7 mg, 0.499 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 5 equiv), and KOAc (74.5 mg, 0.759 mmol) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 10:90)
Yield: 44% yield (96.3 mg, 0.221 mmol, 6 h) as a colorless oil.

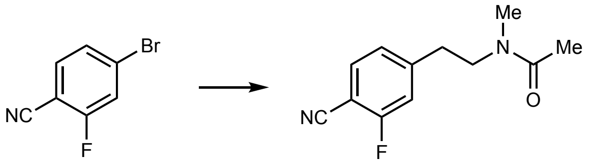
^{1}H NMR (400 MHz, $CDCl_3$): (major rotamer) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.64 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 3.64 (t, *J* = 7.1 Hz, 2H), 3.00 – 2.93 (m, 2H), 2.92 (s, 3H), 2.37 (s, 3H), 2.07 (s, 3H).
(minor rotamer) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.64 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 3.58 (t, *J* = 7.1 Hz, 2H), 2.99 – 2.93 (m, 2H), 2.96 (s, 3H), 2.37 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): (mixture of rotamers) δ 171.4, 171.3, 170.5, 170.3, 169.2, 169.0, 155.9, 155.8, 144.8, 143.5, 136.0, 135.9, 134.2, 133.6, 130.9, 130.9, 130.5, 130.4, 130.2, 130.0, 129.1, 129.1, 114.9, 114.9, 112.2, 112.0, 111.5, 111.4, 101.1, 101.0, 55.6, 52.1, 52.0, 49.2, 36.9, 34.8, 33.8, 33.4, 30.1, 30.0, 29.6, 29.5, 21.9, 21.1, 13.3, 13.2.

ESIHRMS Found: m/z 437.2074; Calcd for $C_{25}H_{29}N_2O_5$ $(M+H)^+$ 437.2076.

IR (neat, cm^{-1}) 3053, 2930, 1738 [ν(C=O)], 1681 [ν(C=O)], 1636 [ν(C=O)], 1479, 1358, 1315, 1265, 1225, 1069, 1036.

4.4.33 *N*-(4-Cyano-3-fluorophenethyl)-*N*-methylacetamide



40

Prepared using 4-bromo-2-fluorobenzonitrile (**40**) (Fluorochem 009059) (100.3 mg, 0.501 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.3 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 53% yield (58.8 mg, 0.267 mmol, 8 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 7.57 – 7.52 (m, 1H), 7.17 – 7.05 (m, 2H), 3.65 – 3.58 (m, 2H), 2.98 – 2.88 (m, 2H), 2.95 (s, 3H), 2.07 (s, 3H).
(minor rotamer) δ 7.61 – 7.57 (m, 1H), 7.17 – 7.05 (m, 2H), 3.58 – 3.53 (m, 2H), 2.98 – 2.88 (m, 2H), 2.94 (s, 3H), 1.93 (s, 3H).

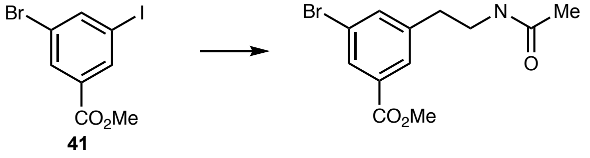
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.6, 170.1, 163.1 (d, $^{1}J_{C\text{-}F}$ = 260.2 Hz), 163.2 (d, $^{1}J_{C\text{-}F}$ = 260.0 Hz), 148.0 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 146.9 (d, $^{3}J_{C\text{-}F}$ = 6.1 Hz), 133.7, 133.3, 125.3 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 125.2 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 116.8 (d, $^{2}J_{C\text{-}F}$ = 19.3 Hz), 116.6 (d, $^{2}J_{C\text{-}F}$ = 19.3 Hz), 114.0, 113.6, 99.7 (d, $^{2}J_{C\text{-}F}$ = 15.7 Hz), 99.3 (d, $^{2}J_{C\text{-}F}$ = 15.4 Hz), 51.4, 48.6, 36.7, 34.8, 33.7, 33.3, 21.8, 21.0.

^{19}F NMR (376 MHz, CDCl$_3$) (major rotamer) δ -106.72.
(minor rotamer) δ -105.88,

ESIHRMS Found: m/z 243.0910; Calcd for $C_{12}H_{13}N_2OFNa$ $(M+Na)^+$ 243.0910.

IR (neat, cm^{-1}) 3052, 2936, 2237 [ν(C≡N)], 1634 [ν(C=O)], 1570, 1431, 1410, 1364, 1265, 1113, 1011.

4.4.34 Methyl 3-bromo-5-(2-(*N*-methylacetamido)ethyl)benzoate

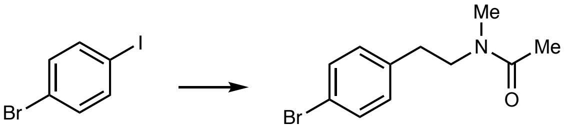


41

Prepared using methyl 3-bromo-5-iodobenzoate (**41**) (Fluorochem 222436) (170.7 mg, 0.501 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.4 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 66% yield (103.2 mg, 0.328 mmol, 8 h) as a colorless oil.

<u>^{1}H NMR (400 MHz, $CDCl_3$):</u> (major rotamer) δ 8.02 (s, 1H), 7.83 (s, 1H), 7.57 (s, 1H), 3.92 (s, 3H), 3.61 – 3.55 (m, 2H), 2.93 (s, 3H), 2.92 – 2.78 (m, 2H), 2.08 (s, 3H).
(minor rotamer) δ 8.06 (s, 1H), 7.79 (s, 1H), 7.52 (s, 1H), 3.93 (s, 3H), 3.61 – 3.55 (m, 2H), 2.95 (s, 3H), 2.92 – 2.78 (m, 2H), 1.98 (s, 3H).
<u>^{13}C NMR (100 MHz, $CDCl_3$):</u> (mixture of rotamers) δ 170.5, 170.2, 165.6, 165.4, 141.6, 140.5, 136.1, 135.9, 132.2, 131.9, 130.9, 130.5, 128.5, 128.3, 122.6, 122.3, 52.4, 52.3, 51.9, 49.2, 36.8, 34.2, 33.3, 33.0, 21.8, 21.0.
<u>ESIHRMS</u> Found: m/z 336.0213; Calcd for $C_{13}H_{16}NO_3BrNa$ $(M+Na)^+$ 336.0211.
<u>IR (neat, cm^{-1})</u> 3057, 2951, 1714 [ν(C=O)], 1630 [ν(C=O)], 1487, 1438, 1406, 1360, 1281, 1206, 1113, 1011, 683 [ν(C−Br)].

4.4.35 *N*-(4-Bromophenethyl)-*N*-methylacetamide

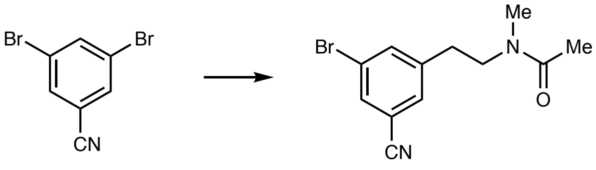


42

Prepared using 1-bromo-4-iodobenzene (**42**) (Fluorochem 005440) (142.2 mg, 0.503 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.0 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 40:60 to 60:40)
Yield: 58% yield (75.0 mg, 0.293 mmol, 3 h) as a colorless oil.

<u>^{1}H NMR (500 MHz, $CDCl_3$)</u> (major rotamer) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 3.55 (t, *J* = 7.5 Hz, 2H), 2.88 (s, 3H), 2.80 (m, 2H), 2.06 (s, 3H).
(minor rotamer) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 3.49 (t, *J* = 7.2 Hz, 2H), 2.93 (s, 3H), 2.80 (m, 2H), 1.87 (s, 3H).
<u>^{13}C NMR (125 MHz, $CDCl_3$)</u> (mixture of rotamers) δ 170.4, 170.3, 138.1, 137.1, 131.8, 131.5, 130.5, 130.4, 120.6, 120.1, 52.2, 49.3, 36.8, 34.1, 33.3, 33.1, 21.9, 20.9.
<u>ESIHRMS</u> Found: m/z 278.0158; Calcd for $C_{11}H_{14}NOBrNa$ $(M+Na)^+$ 278.0156.
<u>IR (neat, cm^{-1})</u> 3052, 2932, 1632 [ν(C=O)], 1489, 1406, 1265, 1072, 1013, 650 [ν(C−Br)].

4.4.36 *N*-(3-Bromo-5-cyanophenethyl)-*N*-methylacetamide

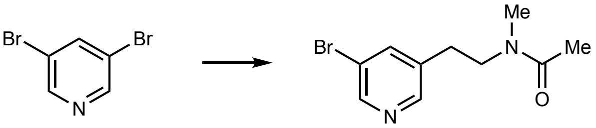


43

Prepared using methyl 3,5-dibromobenzonitrile (**43**) (Fluorochem 024164) (131.1 mg, 0.502 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with K_2S_x (4.1 mg, 10 mol% per S) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 50:50 to 20:80)
Yield: 67% yield (94.7 mg, 0.337 mmol, 6 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) (major rotamer) δ 7.64 (s, 1H), 7.63 (s, 1H), 7.46 (s, 1H), 3.57 (t, *J* = 7.5 Hz, 2H), 2.97 (s, 3H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.08 (s, 3H).
(minor rotamer) δ 7.70 (s, 1H), 7.59 (s, 1H), 7.44 (s, 1H), 3.54 (t, *J* = 7.5 Hz, 2H), 2.95 (s, 3H), 2.90 (d, *J* = 7.5 Hz, 2H), 1.99 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) (mixture of rotamers) δ 170.5, 170.0, 142.6, 141.6, 136.5, 136.3, 133.0, 132.6, 130.9, 130.8, 123.1, 122.8, 117.2, 116.9, 114.4, 114.0, 51.6, 48.8, 36.7, 34.1, 33.3, 32.9, 21.7, 21.0.
ESIHRMS Found: m/z 303.0113; Calcd for $C_{12}H_{13}N_2OBrNa$ $(M+Na)^+$ 303.0109.
IR (neat, cm^{-1}) 3061, 2934, 2231 [ν(C≡N)], 1630 [ν(C=O)], 1568, 1485, 1404, 1360, 1240, 1038, 1011, 685 [ν(C−Br)].

4.4.37 *N*-(2-(5-Bromopyridin-3-yl)ethyl)-*N*-methylacetamide



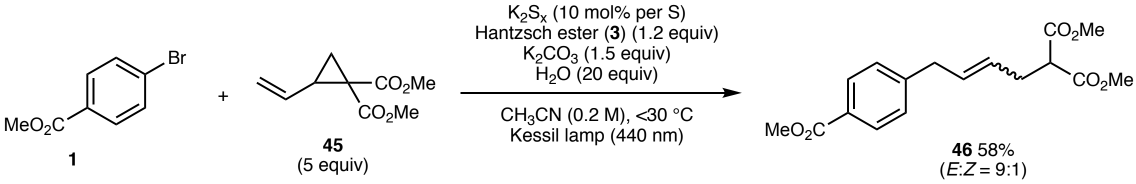
44

Prepared using methyl 3,5-dibromopyridine (**44**) (Sigma-Aldrich 120162) (118.3 mg, 0.499 mmol) and *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 5 equiv) with *i*-Pr_3SiSH (11 μL, 0.0512 mmol, 10 mol%) as the precatalyst in CH_3CN (2.5 mL).
Purification: flash column chromatography (silica gel, MeOH:EtOAc = 0:100 to 10:90)
Yield: 61% yield (78.3 mg, 0.305 mmol, 5 h) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 8.54 (s, 1H), 8.39 (s, 1H), 7.74 (s, 1H), 3.58 (t, *J* = 7.3 Hz, 2H), 2.95 (s, 3H), 2.90 – 2.79 (m, 2H), 2.08 (s, 3H).
(minor rotamer) δ 8.59 (s, 1H), 8.39 (s, 1H), 7.67 (s, 1H), 3.54 (t, *J* = 7.6 Hz, 2H), 2.96 (s, 3H), 2.90 – 2.79 (m, 2H), 1.98 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) (mixture of rotamers) δ 170.6, 170.1, 149.4, 148.9, 148.1, 148.0, 138.8, 138.7, 136.3, 135.2, 120.8, 120.6, 51.7, 49.0, 36.8, 33.4, 31.6, 30.4, 21.8, 21.1.
ESIHRMS Found: m/z 279.0105; Calcd for $C_{10}H_{13}N_2OBrNa$ $(M+Na)^+$ 279.0109.

IR (neat, cm^{-1}) 3040, 2934, 1626 [ν(C=O)], 1491, 1423, 1364, 1308, 1196, 1098, 1022, 706 [ν(C−Br)].

4.4.38 Dimethyl 2-(4-(4-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (46)



Prepared using methyl 4-bromobenzoate (**1**) (107.5 mg, 0.500 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**45**) (460.6 mg, 2.50 mmol) with K_2S_x (4.2 mg, 10 mol% per S) as the precatalyst in DMSO (2.5 mL).
Purification: flash column chromatography (silica gel, Hexane:EtOAc = 90:10)
Yield: 58% yield (E:Z=9:1, 92.4 mg, 0.288 mmol, 6 h) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$): (for the *E*-isomer) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.67 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.50 (dt, *J* = 15.3, 7.3 Hz, 1H), 3.90 (s, 3H), 3.70 (s, 6H), 3.45 (t, *J* = 7.6 Hz, 1H), 3.37 (d, *J* = 6.8 Hz, 2H), 2.64 (dd, *J* = 7.6, 7.3 Hz, 2H).
(*Z*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.85 – 5.66 (m, 1H), 5.57 – 5.50 (m, 1H), 3.90 (s, 3H), 3.73 (s, 6H), 3.49 (d, *J* = 7.3 Hz, 2H), 3.46 (t, *J* = 7.6 Hz, 1H), 2.77 (dd, *J* = 7.6, 7.3 Hz, 2H).
^{13}C NMR (125 MHz, CDCl$_3$): (for the *E*-isomer) δ 169.2, 167.0, 145.7, 131.4, 129.7, 128.4, 128.0, 127.6, 52.4, 51.9, 51.6, 38.8, 31.7.
ESIHRMS Found: m/z 321.1337; Calcd for $C_{17}H_{21}O_6$ (M+H)$^+$ 321.1338.
IR (neat, cm^{-1}) 3001, 2953, 2845, 1741 [ν(C=O)], 1712 [ν(C=O)], 1611, 1558, 1435, 1278, 1193, 1178, 1153, 1111, 1020.

5 Deuterium labelling experiments

5.1 Deuterium labelling experiments using D_2O

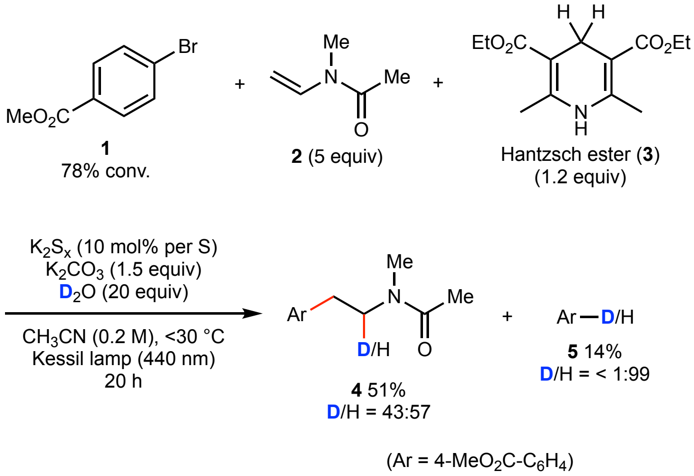


Figure S5 Deuterium labelling experiments with D_2O

The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3**) followed the general procedure of the hydroarylation reaction (Figure S5). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.3 mg, 0.499 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.2 mg, 10 mol% per S), Hantzsch ester (**3**) (152.7 mg, 0.603 mmol, 1.2 equiv), K_2CO_3 (103. 4 mg, 0.748 mmol), D_2O (200 µL, 10 mmol, 20 equiv) and CH_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 20 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The resulting residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (59.5 mg, 0.253 mmol) in 51% yield as a colorless oil. The deuterium incorporation rate (D/H = 43:57) was determined by integration of the ^1H NMR spectrum.

5.2 Deuterium labelling experiment using deuterated Hantzsch ester (3-d_2)

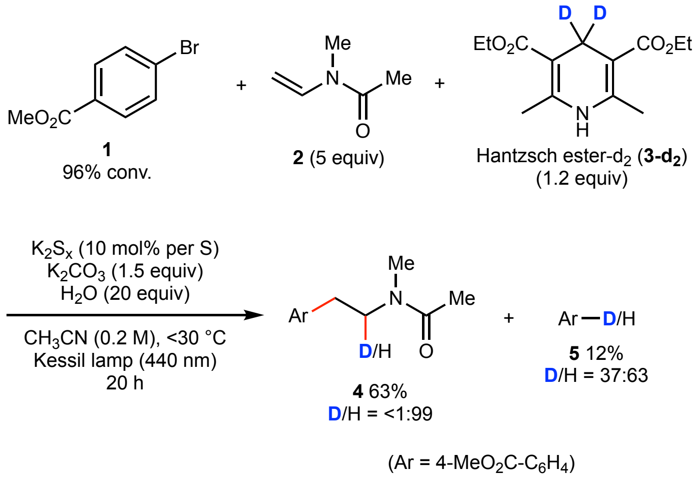


Figure S6 Deuterium labelling experiments with deuterated Hantzsch ester (**3-*d*₂**)

The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3-d_2**) followed the general procedure of the hydroarylation reaction (Figure S6). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.7 mg, 0.501 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.3 mg, 10 mol% per S), Hantzsch ester (**3-d_2**) (153.5 mg, 0.601 mmol, 1.2 equiv), K_2CO_3 (103.8 mg, 0.751 mmol), H_2O (180 µL, 10 mmol, 20 equiv) and CH_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 20 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude residue. The resulting residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (74.8 mg, 0.318 mmol) in 63% yield as a colorless oil. The deuterium incorporation rate (D/H < 1:99) was determined by integration of the ^{1}H NMR spectrum.

5.3 Deuterium labelling experiment using deuterated Hantzsch ester (3-*d*$_2$) and D$_2$O

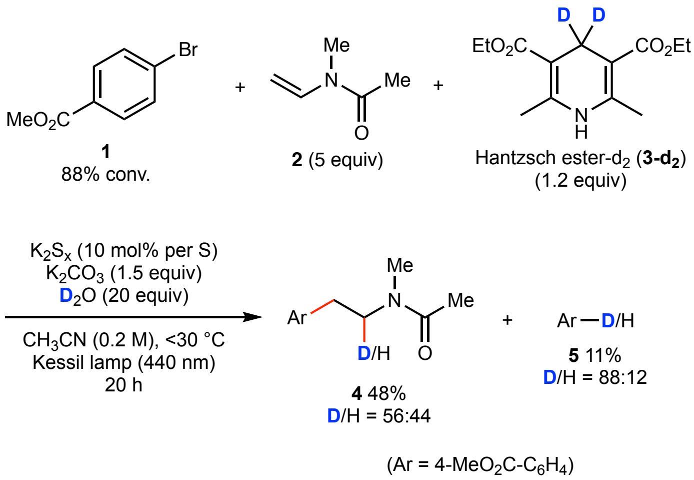


Figure S7 Deuterium labelling experiments with deuterated Hantzsch ester (**3-*d*$_2$**) and D$_2$O

The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3-*d*$_2$**) and D$_2$O followed the general procedure of the hydroarylation reaction (Figure S7). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.5 mg, 0.500 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 μL, 2.50 mmol, 5 equiv), K$_2$S$_x$ (4.3 mg, 10 mol% per S), Hantzsch ester (**3-*d*$_2$**) (153.0 mg, 0.599 mmol, 1.2 equiv), K$_2$CO$_3$ (103.3 mg, 0.747 mmol), D$_2$O (200 μL, 10 mmol, 20 equiv) and CH$_3$CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 20 h. The reaction mixture was diluted with H$_2$O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over MgSO$_4$, filtered and concentrated in vacuo to afford the crude residue. The resulting residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (56.1 mg, 0.238 mmol) in 48% yield as a colorless oil. The deuterium incorporation rate (D/H = 56:44) was determined by integration of the ^{1}H NMR spectrum.

5.4 Deuterium labelling experiment using deuterated Hantzsch ester (3-*d*$_3$) and D_2O

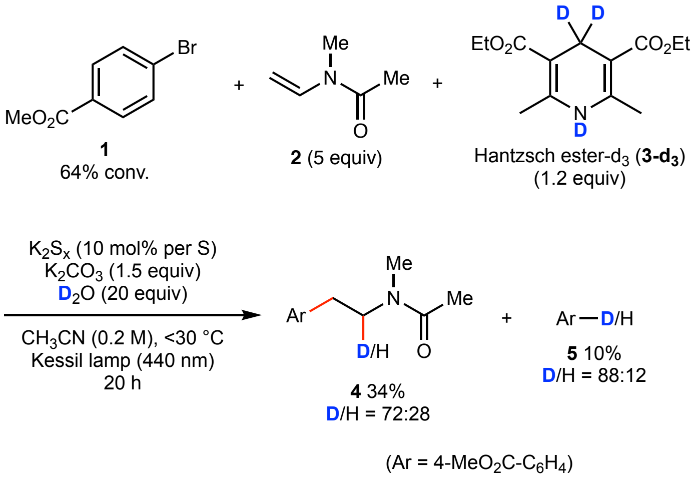


Figure S8 Deuterium labelling experiments with deuterated Hantzsch ester (**3-*d*$_3$**) and D_2O

The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3-*d*$_3$**) and D_2O followed the general procedure of the hydroarylation reaction (Figure S8). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.6 mg, 0.500 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.2 mg, 10 mol% per S), Hantzsch ester (**3-*d*$_3$**) (154.4 mg, 0.602 mmol, 1.2 equiv), K_2CO_3 (103.4 mg, 0.748 mmol), D_2O (200 µL, 10 mmol, 20 equiv) and CH_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 20 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude residue. The resulting residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (40.1 mg, 0.170 mmol) in 34% yield as a colorless oil. The deuterium incorporation rate (D/H = 72:28) was determined by integration of the ^{1}H NMR spectrum.

5.5 Deuterium labelling experiment using deuterated Hantzsch ester (3-*d*$_3$), D_2O and CD_3CN

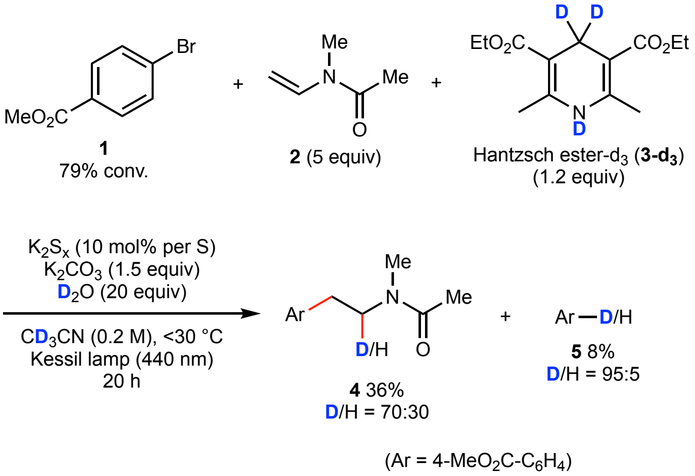


Figure S9 Deuterium labelling experiments with deuterated Hantzsch ester (**3-*d*$_3$**), D2O and CD_3CN

The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3-*d*$_3$**), D_2O and CD_3CN followed the general procedure of the hydroarylation reaction (Figure S9). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.2 mg, 0.499 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.1 mg, 10 mol% per S), Hantzsch ester (**3-*d*$_3$**) (154.1 mg, 0.601 mmol, 1.2 equiv), K_2CO_3 (103.7 mg, 0.750 mmol), D_2O (200 µL, 10 mmol, 20 equiv) and CD_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 20 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude residue. The resulting residue was purified by flash column chromatography (silica gel, hexane:ethyl acetate = 50:50 to 20:80) to give the product **4** (42.1 mg, 0.179 mmol) in 36% yield as a colorless oil. The deuterium incorporation rate (D/H = 70:30) was determined by integration of the ^{1}H NMR spectrum. This result and those in sections 5.3 and 5.4 suggest that allylic methyl groups of the Hantzsch ester (**3**) could also function as a hydrogen donor in these cases.

5.6 Deuterium labelling experiment in CD_3CN

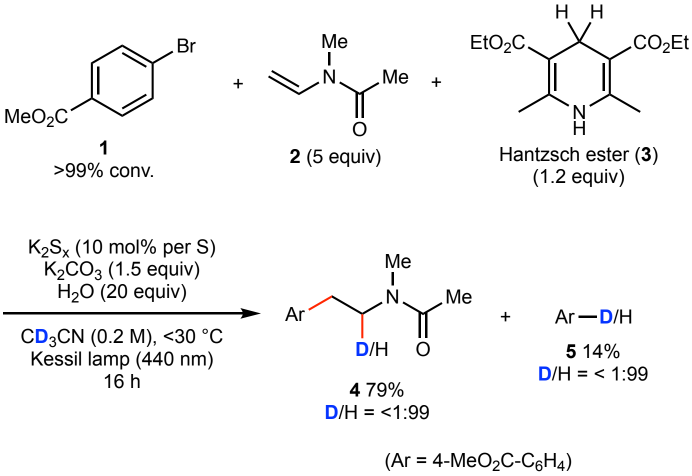


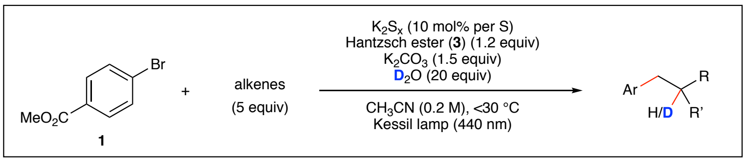
Figure S10 Deuterium labelling experiments with CD_3CN

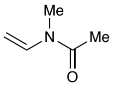
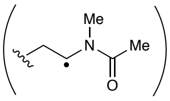
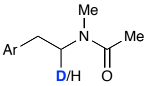
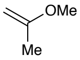
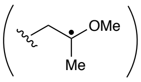
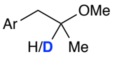
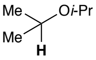
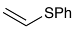
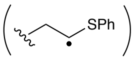
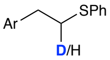
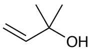
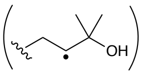
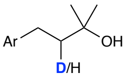
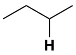
The deuterium labelling experiments of the coupling reaction between methyl 4-bromobenzoate (**1**) and *N*-methyl-*N*-vinylacetamide (**2**) with Hantzsch ester (**3**) followed the general procedure of the hydroarylation reaction (Figure S10). To a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (107.0 mg, 0.498 mmol), *N*-methyl-*N*-vinylacetamide (**2**) (258 µL, 2.50 mmol, 5 equiv), K_2S_x (4.2 mg, 10 mol% per S), Hantzsch ester (**3**) (152.5 mg, 0.601 mmol, 1.2 equiv), K_2CO_3 (103. 6 mg, 0.750 mmol), H_2O (180 µL, 10 mmol, 20 equiv) and CD_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred with irradiation of blue light (Kessil lamp, λ_{max} = 440 nm) for 16 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude residue, which was analyzed by the ^1H NMR measurement with 1,1,2,2-tetrachloroethane (21 µL, 0.20 mmol) as an internal standard. The yield of **4** was 79% and the deuterium incorporation rate was D/H < 1:99.

5.7 Deuterium labelling experiments using D_2O with different alkenes

The deuterium labelling experiments for the hydroarylation between methyl 4-bromobenzoate (**1**) and selected alkenes (**2**, **10**, **12**, and **16**) in the presence of D_2O were conducted (Table S7). The experiments protocol followed the general procedure: to a 25 mL sealed tube with a magnetic stir bar was added methyl 4-bromobenzoate (**1**) (0.50 mmol), alkene (5 equiv), K_2S_x (4.1-4.3 mg, 10 mol% per S), Hantzsch ester (**3**) (1.2 equiv), K_2CO_3 (1.5 equiv), D_2O (200 µL, 20 equiv) and CH_3CN (2.5 mL). The solution was degassed 3 times through freeze-pump-thaw (frozen at –78 °C and degassed via vacuum evacuation and backfilled with argon). The reaction mixture was stirred under irradiation with visible light (Kessil lamp, λ_{max} = 440 nm, 20 W) for 20-24 h. The reaction mixture was diluted with H_2O (20 mL) and ethyl acetate (50 mL). The aqueous layer was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude residue. The resulting residue was purified by flash column chromatography to give the product. The percent of deuterium incorporation (D/H) was determined by the integration of ^1H NMR spectrum.

Table S7 Deuterium labelling experiments with D_2O using different alkenes



Alkenes		Radical intermediates	Conversion of 1 (%)	Products		D/H ratio	reference BDE[10] (kcal/mol)
	**2**		78%		51%	43:57	105 $(\mathbf{CH}_3)_2NCHO$ 93 $(CH_3)_2\mathbf{CH}NHAc$
	**11**		77%		58%	61:39	93-94 
	**13**		92%		67%	54:46	93 $\mathbf{CH}_3SPh$ 92 $CH_3\mathbf{CH}_2SEt$
	**17**		>99%		56%	43:57	98-99 

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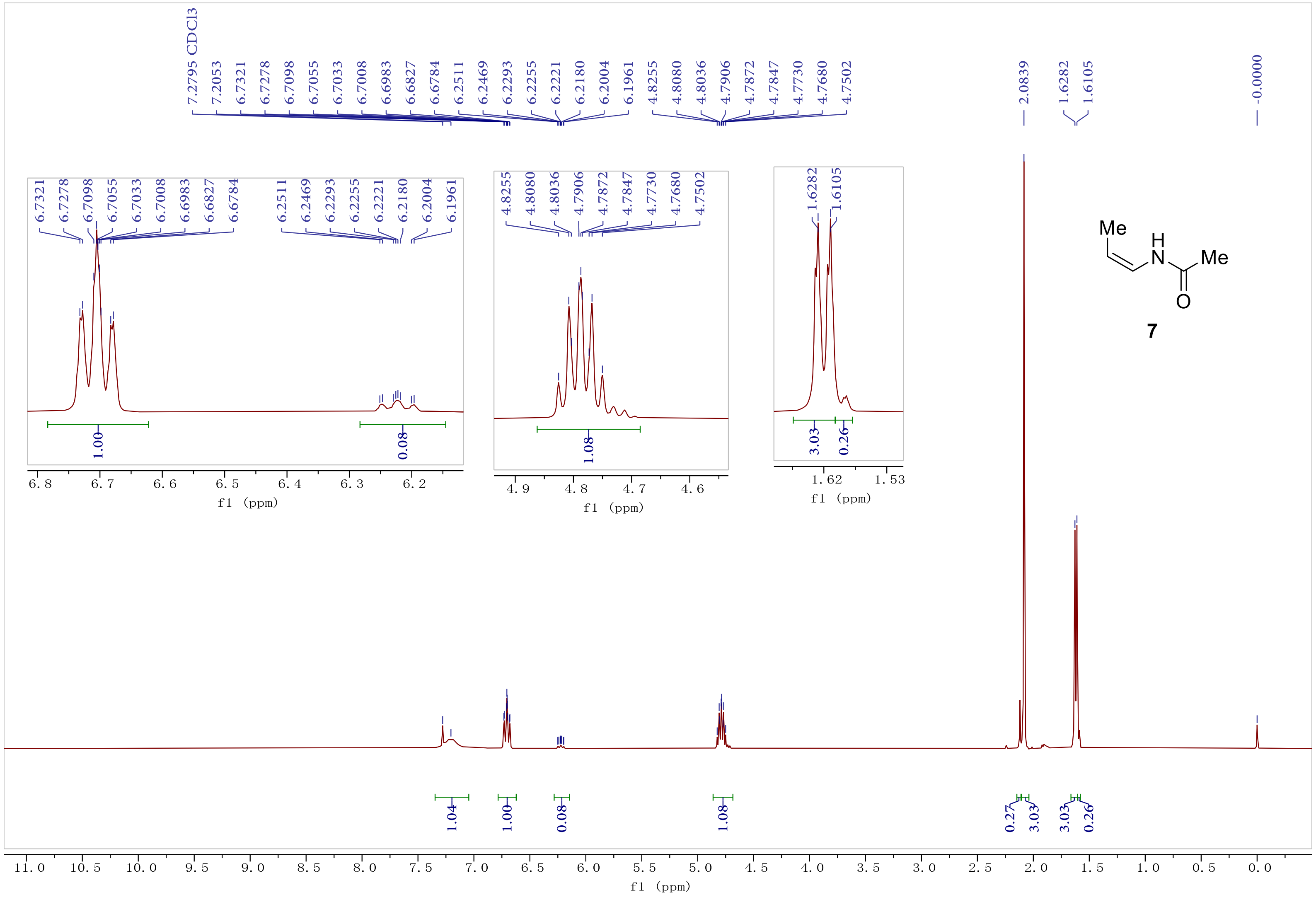
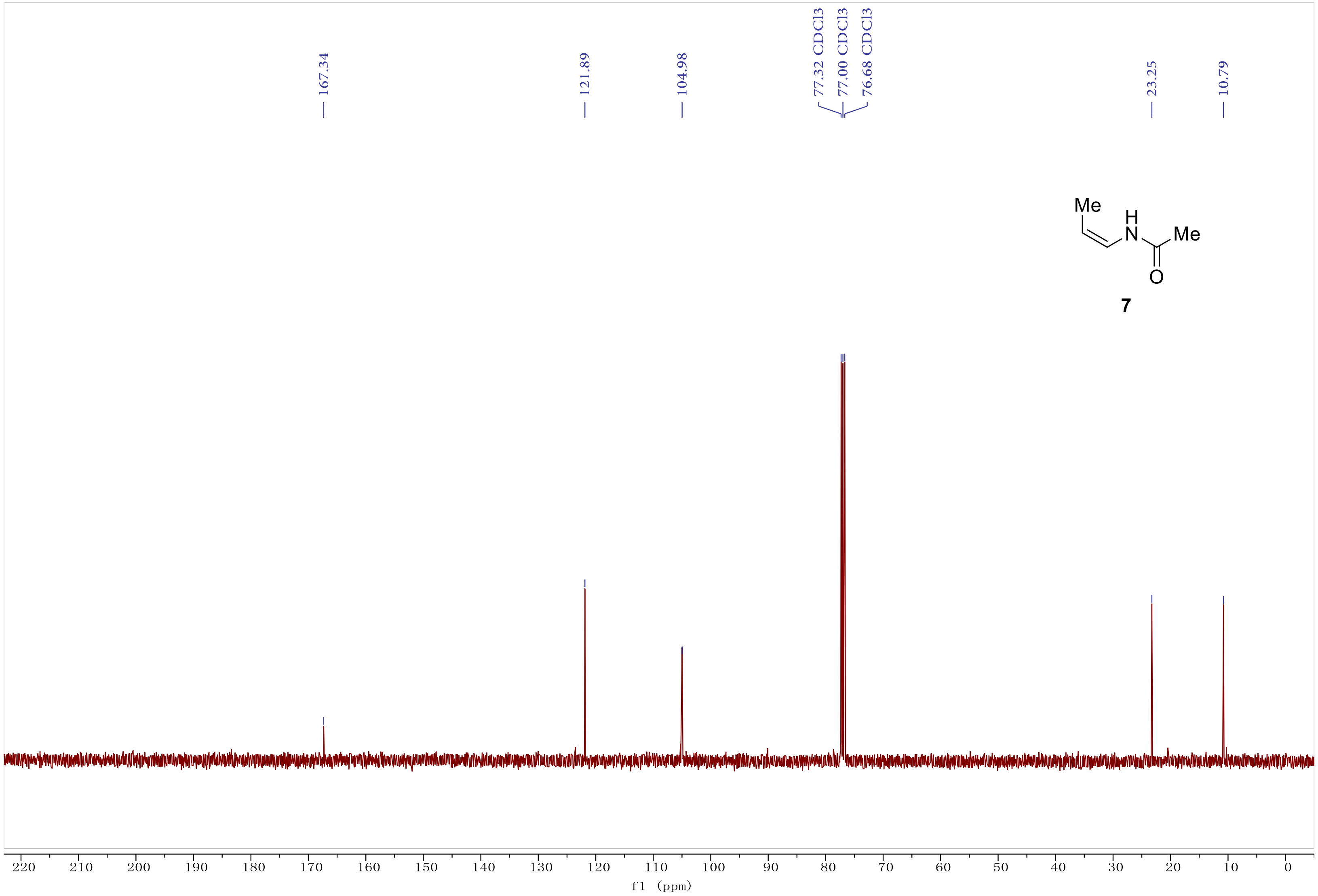
7 NMR spectra

7.1. (*Z*)-*N*-(Prop-1-en-1-yl)acetamide (7)

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

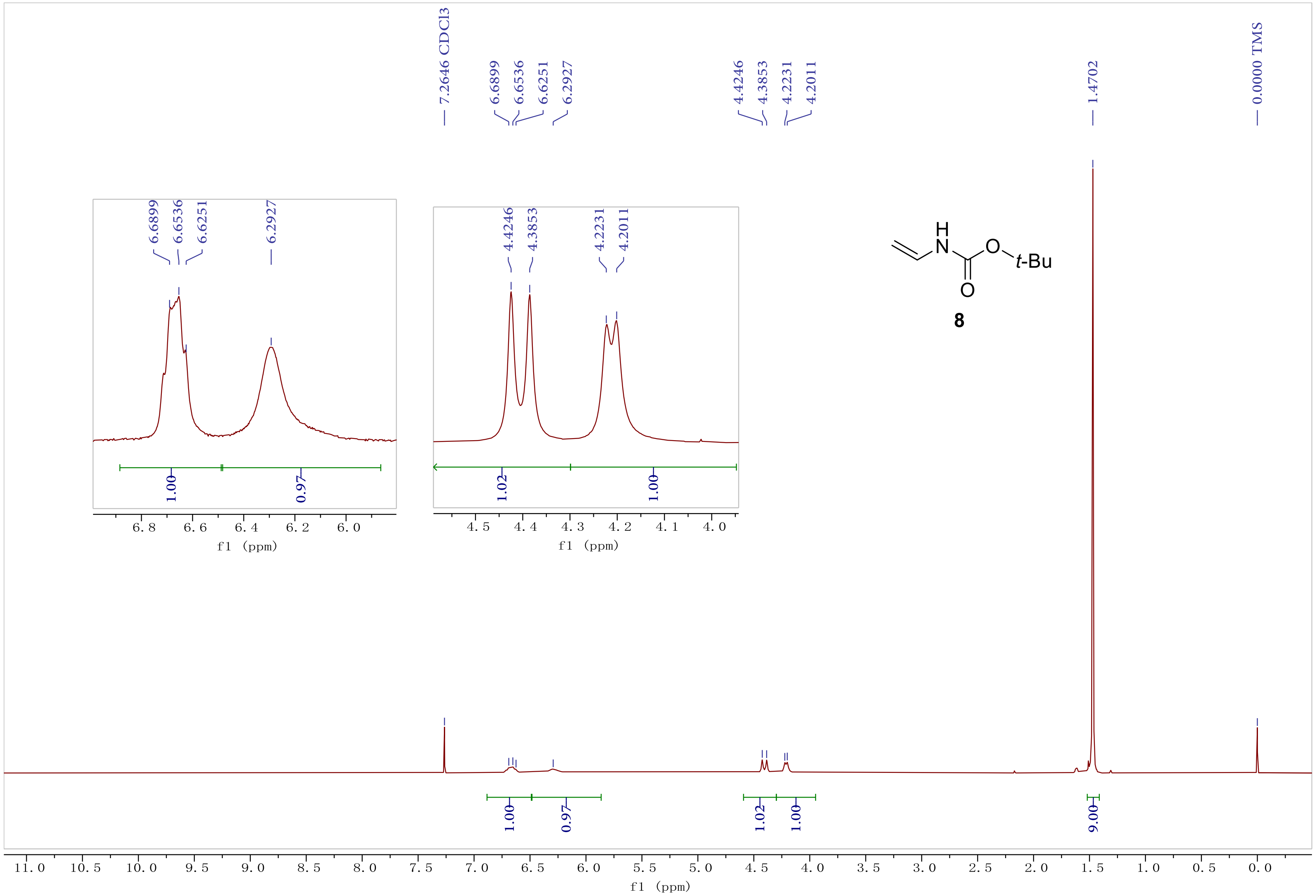


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

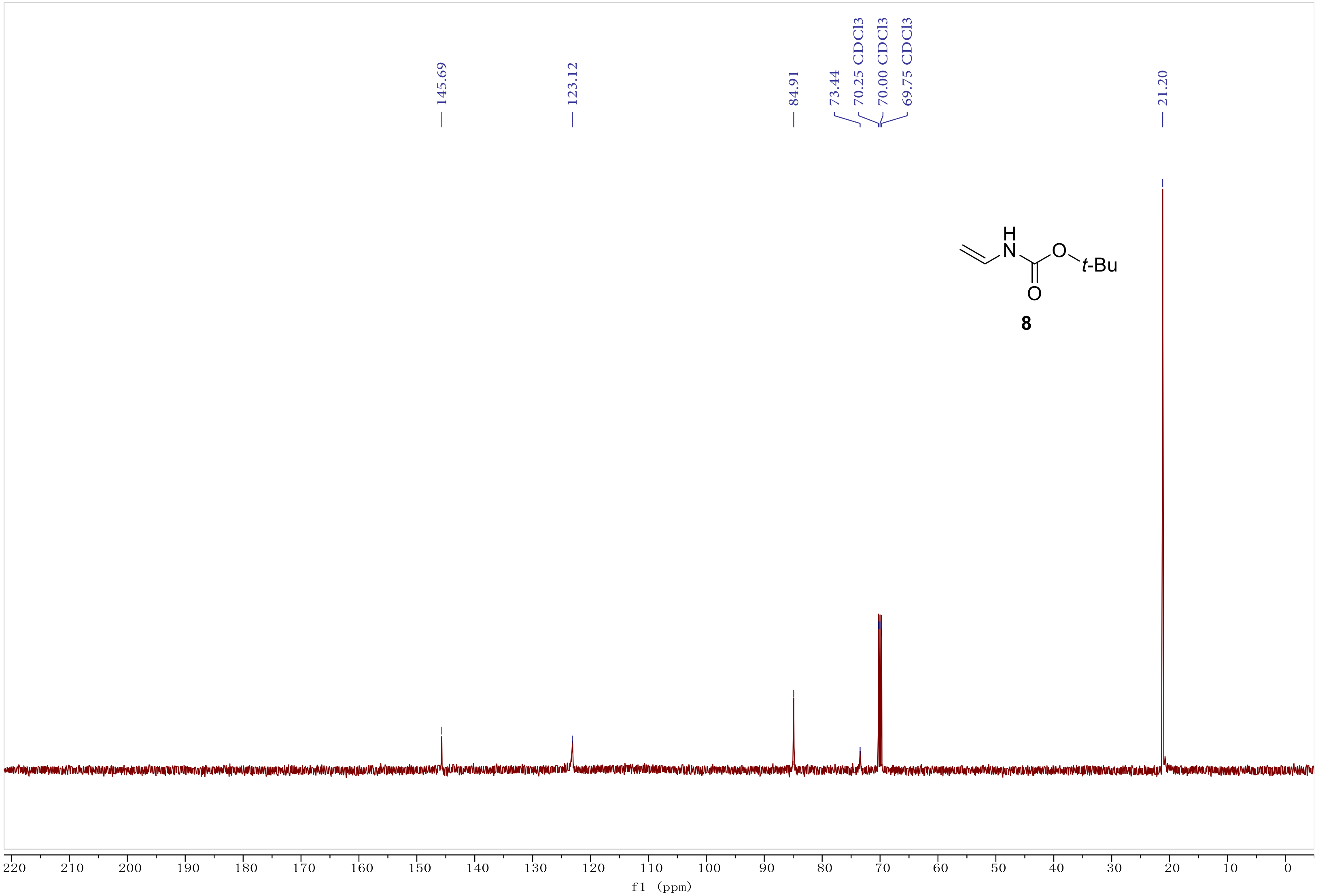


7.2. *tert*-Butyl vinylcarbamate (8)

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

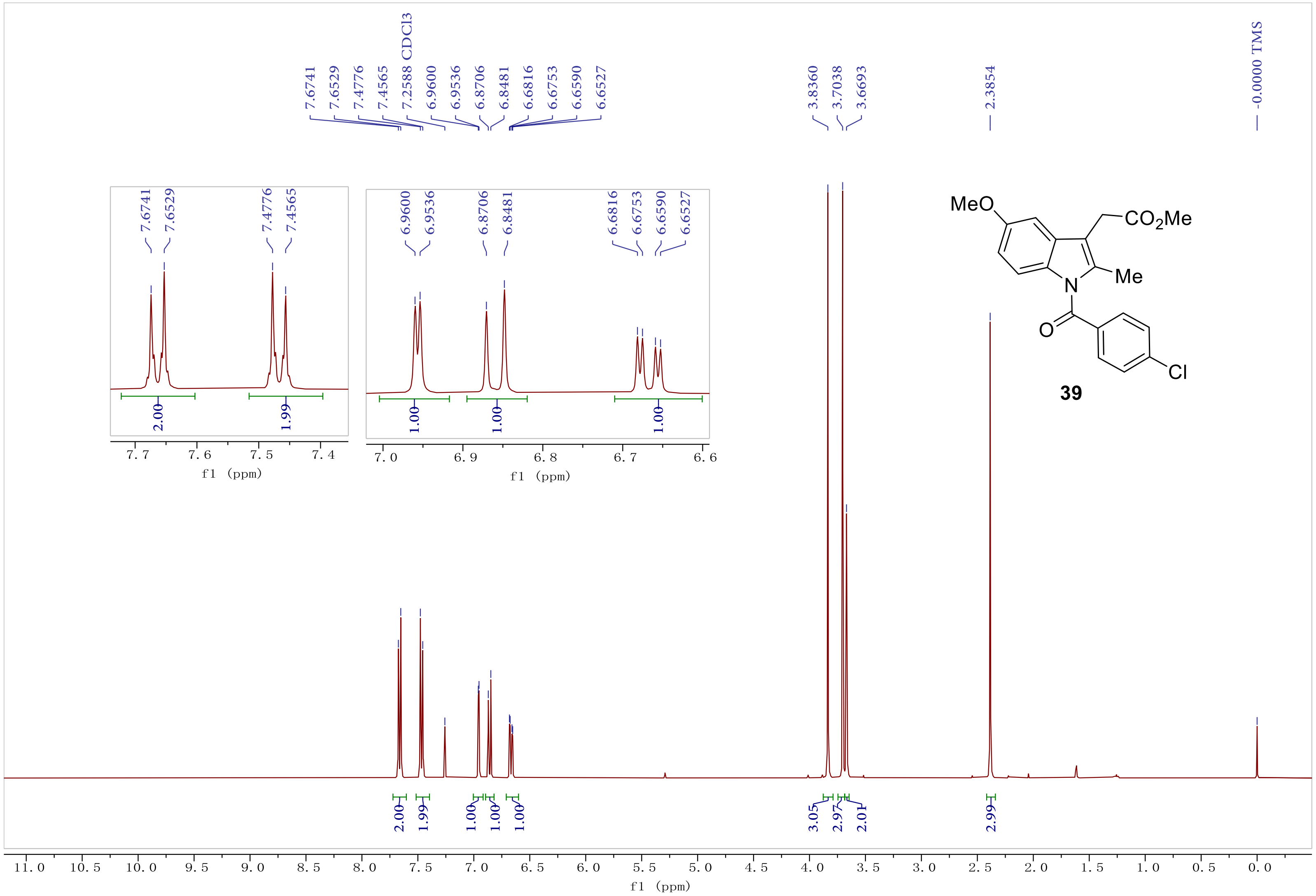


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

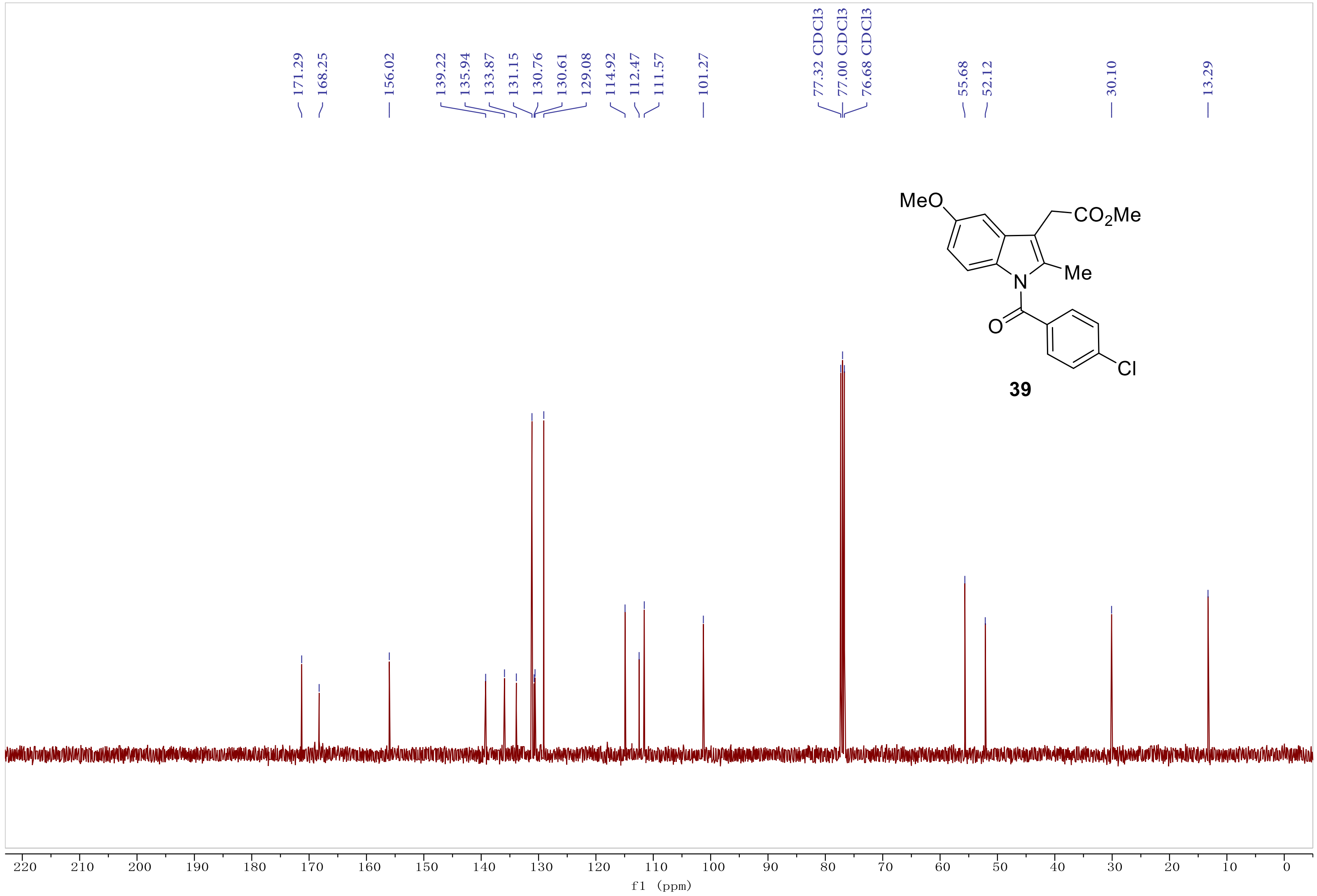


7.3. Indomethacin methyl ester (39)

^{1}H NMR spectrum (400 MHz) in $CDCl_3$



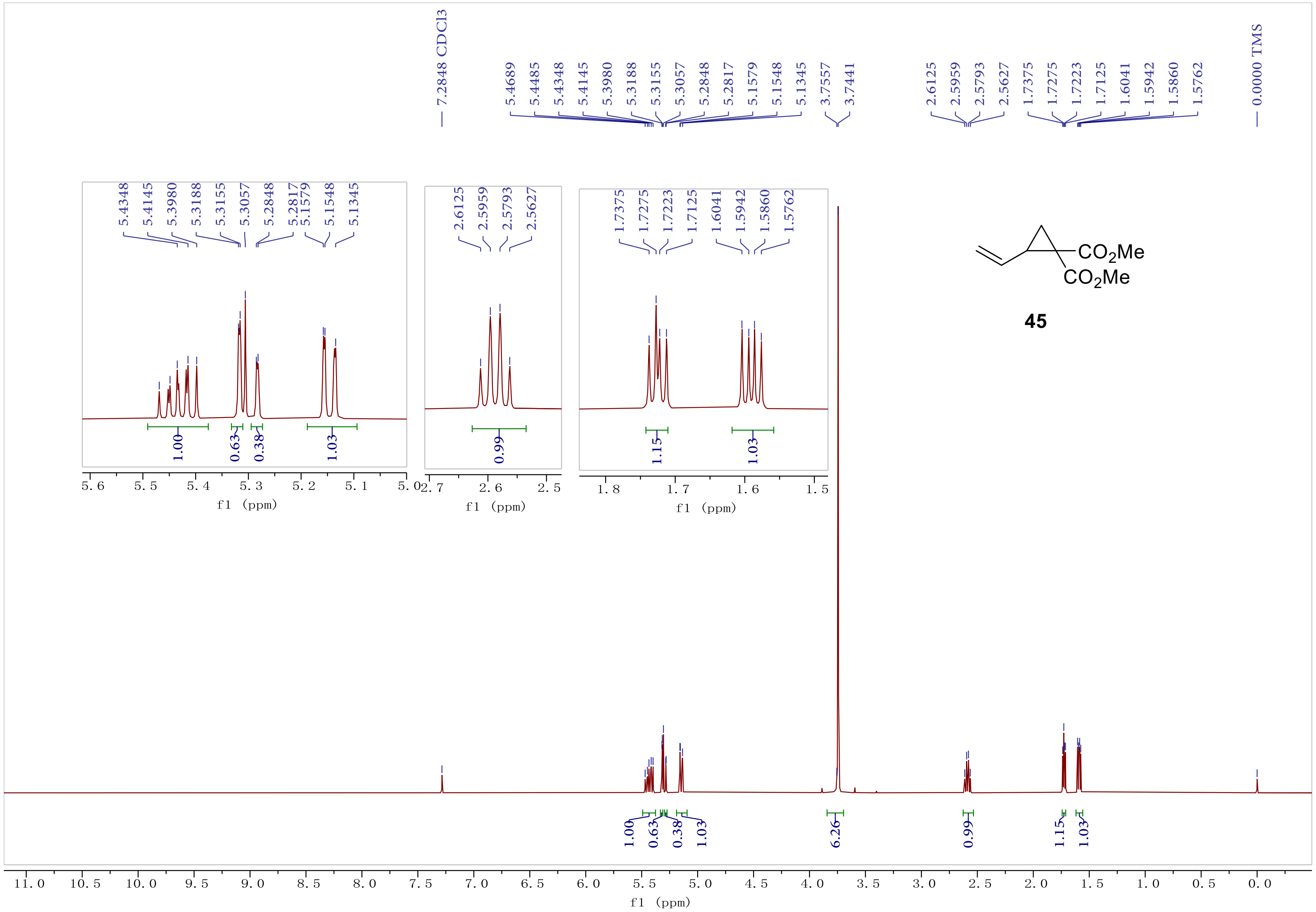
^{13}C NMR spectrum (100 MHz) in $CDCl_3$



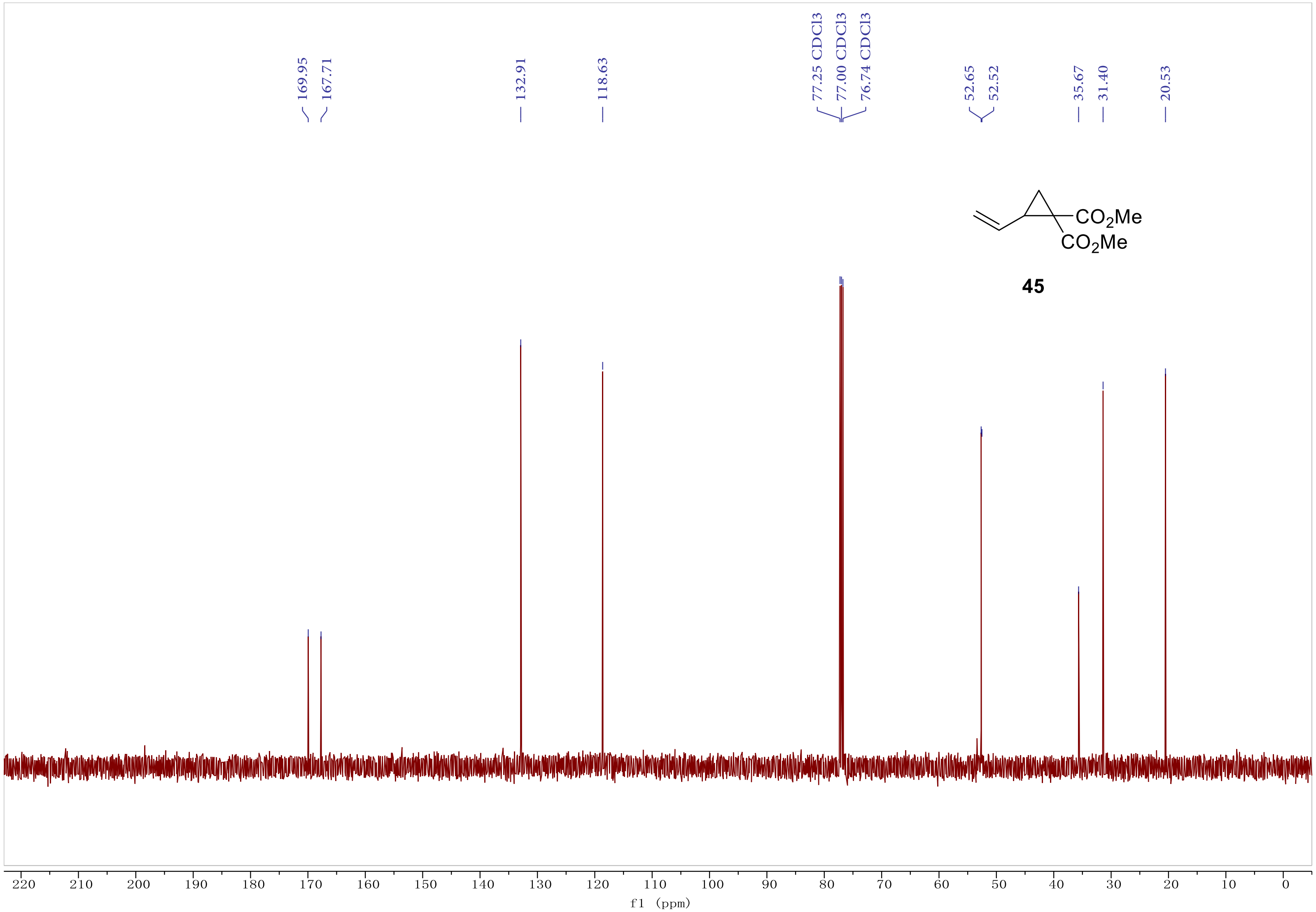
39

7.4. Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (45)

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

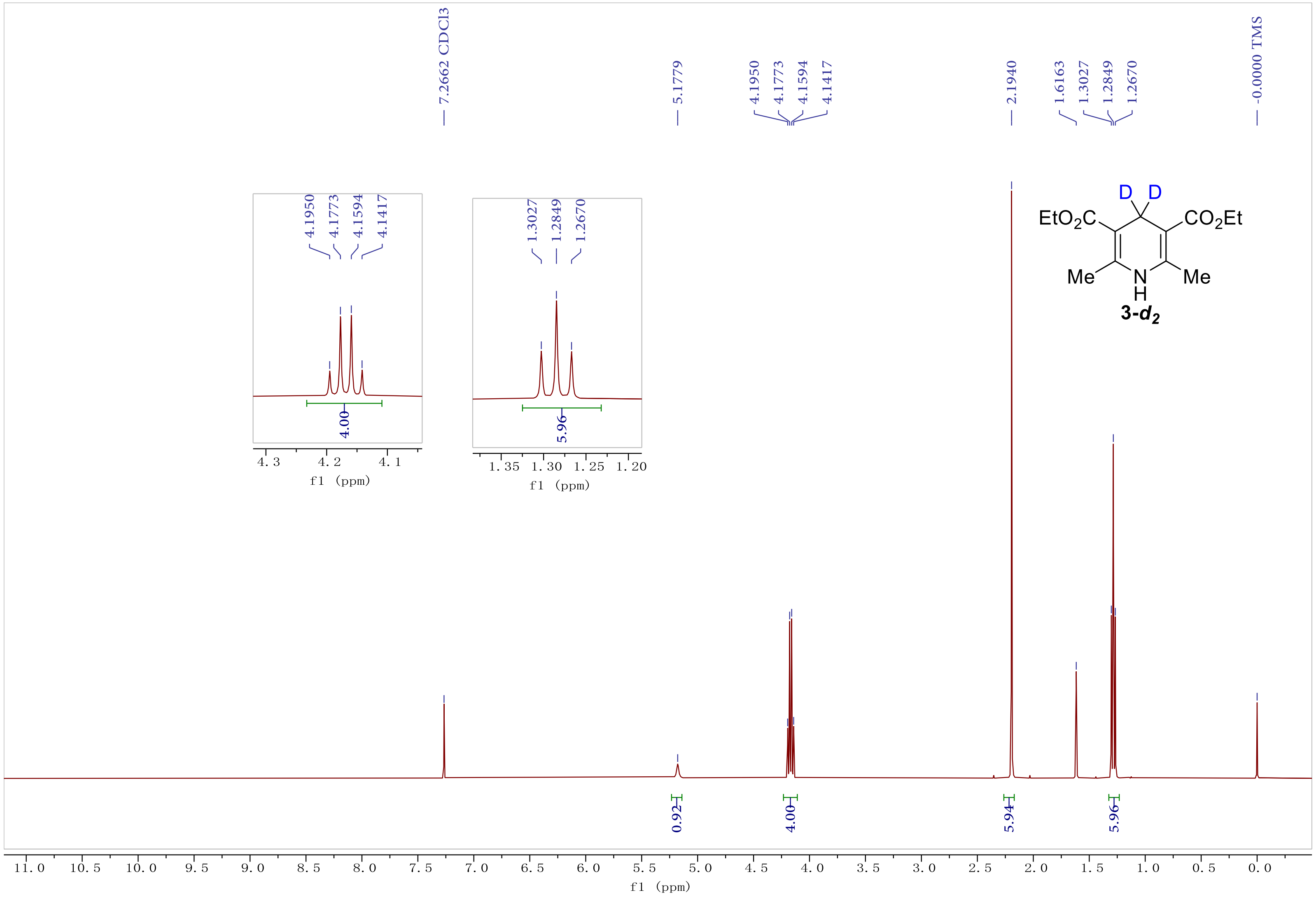


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

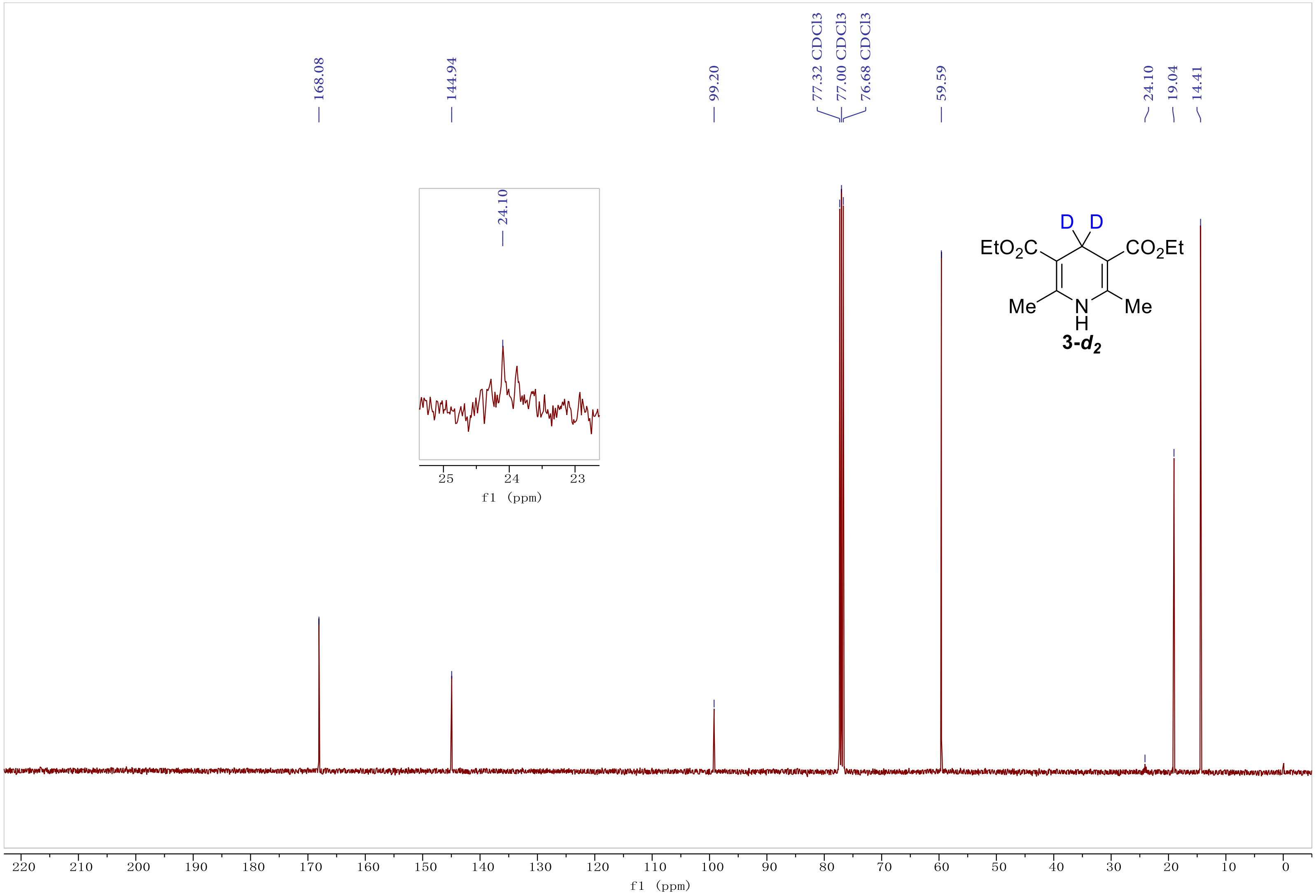


7.5. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-*d*₂ (3-*d*₂)

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

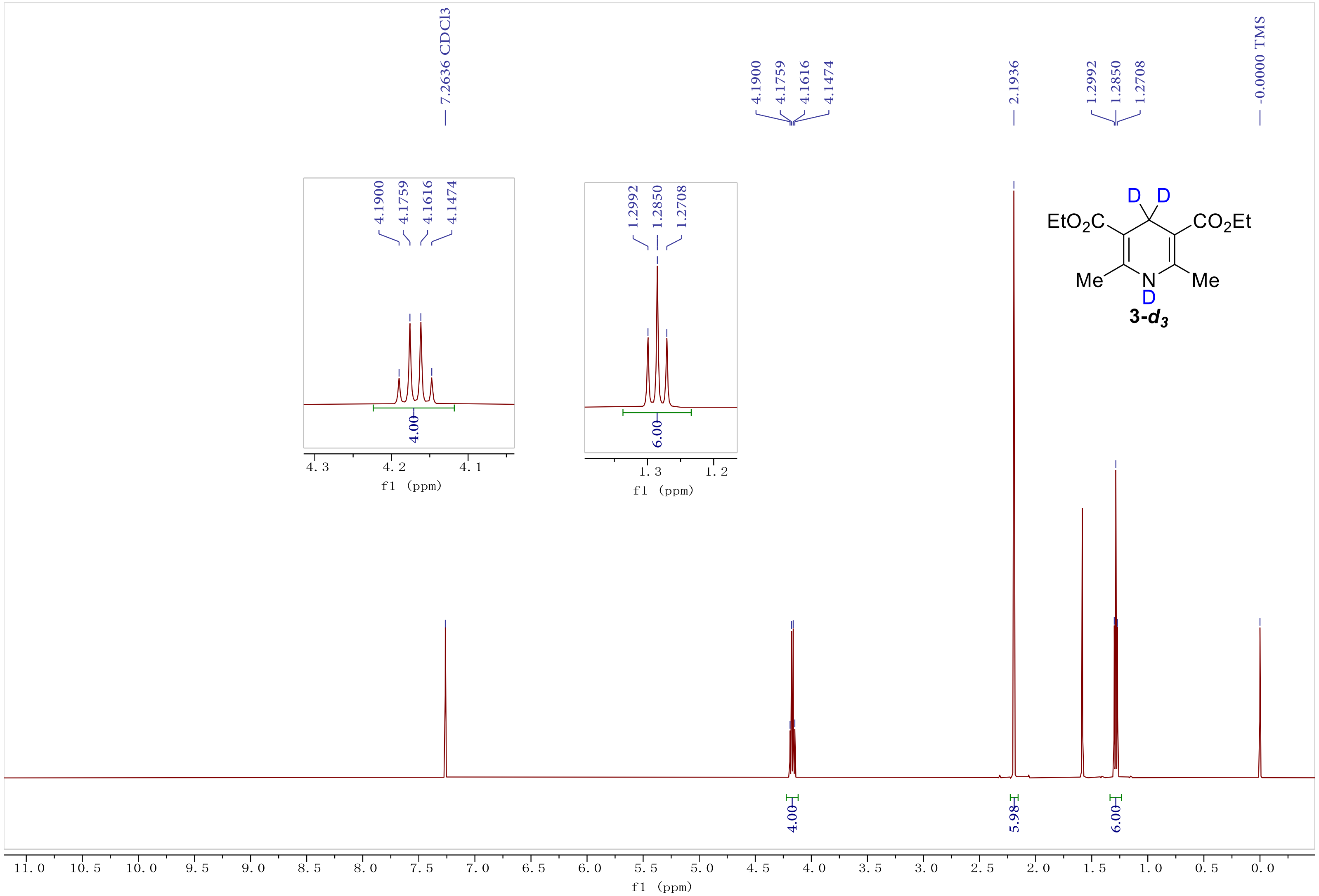


^{13}C NMR spectrum (100 MHz) in CDCl$_3$

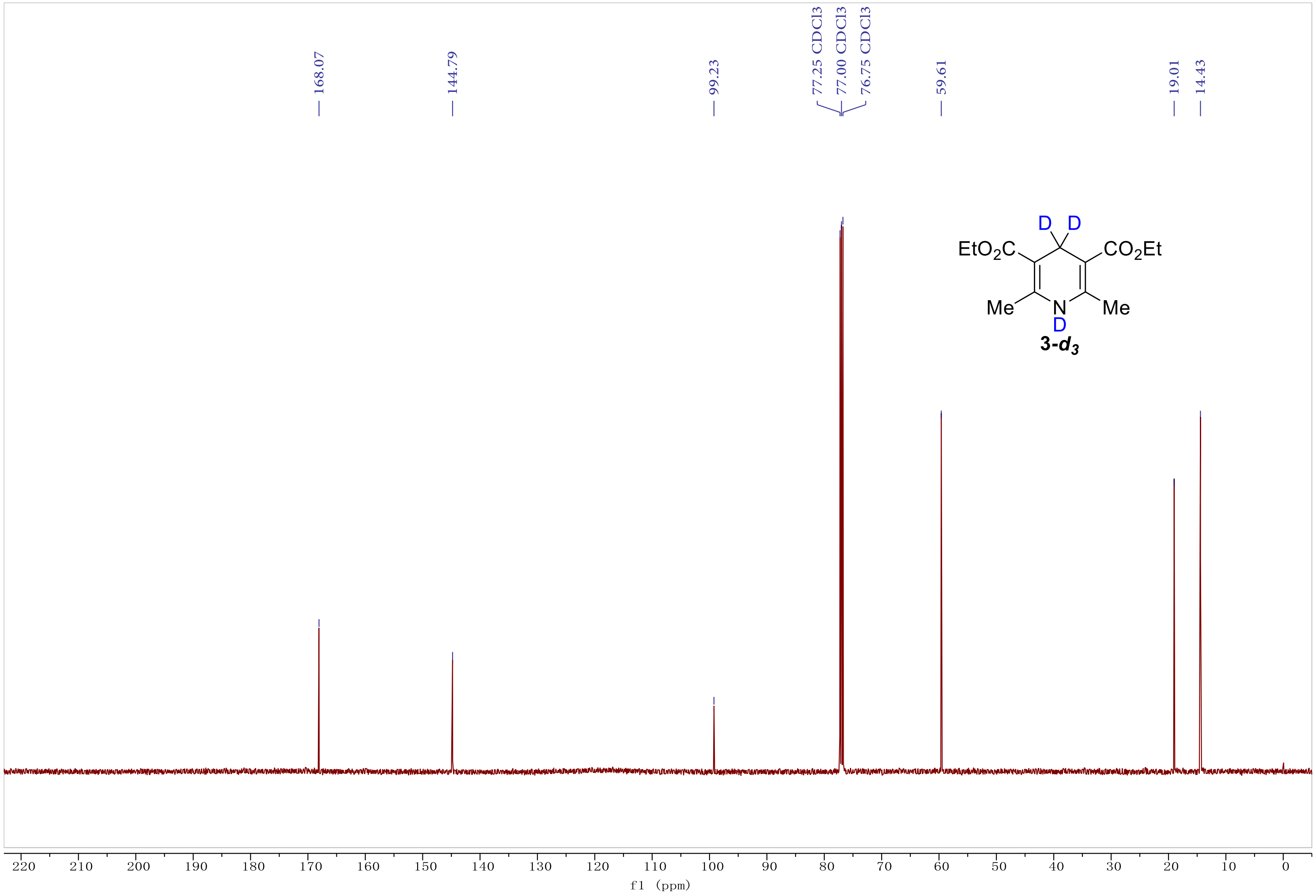


7.6. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-1,4,4-*d*3 (3-*d*3)

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

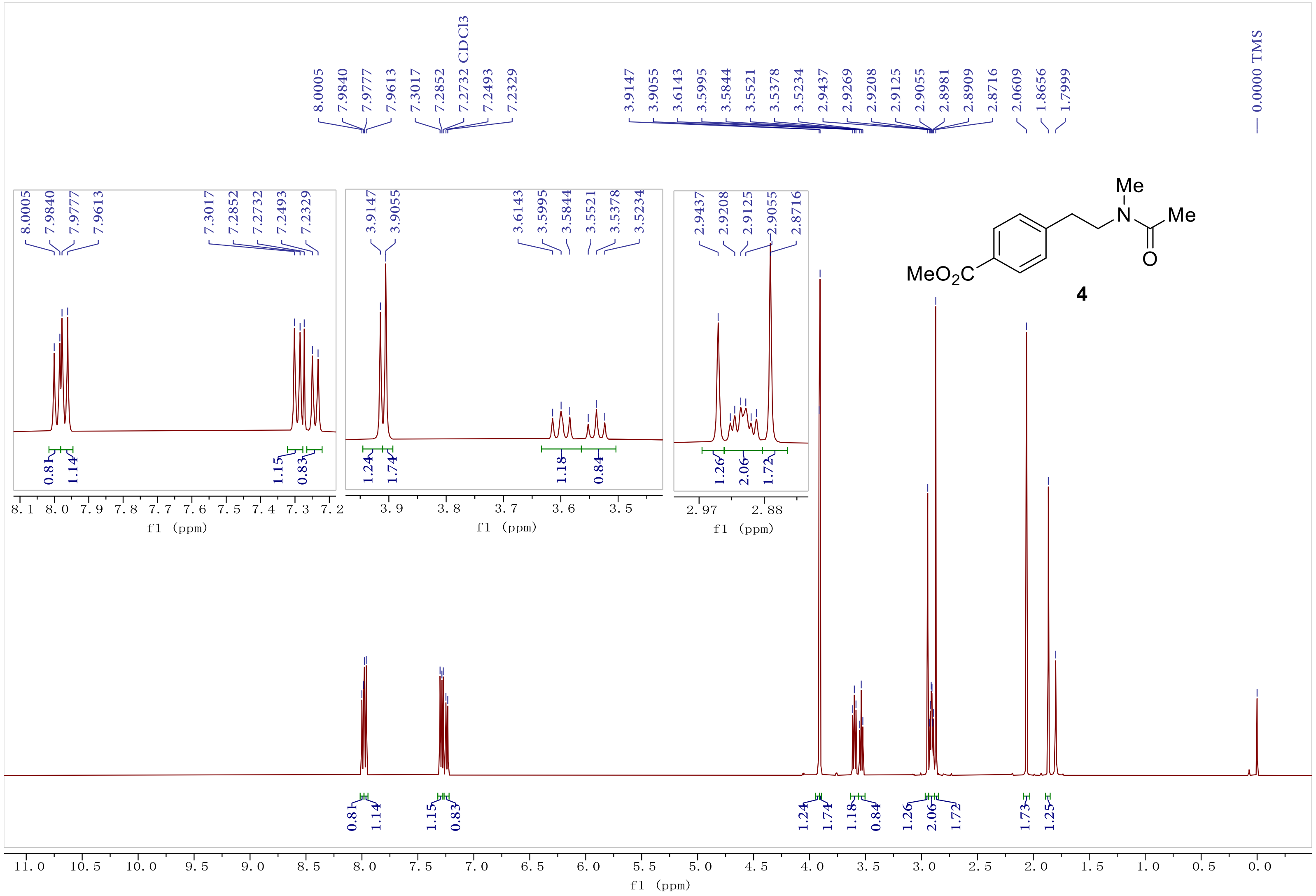


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

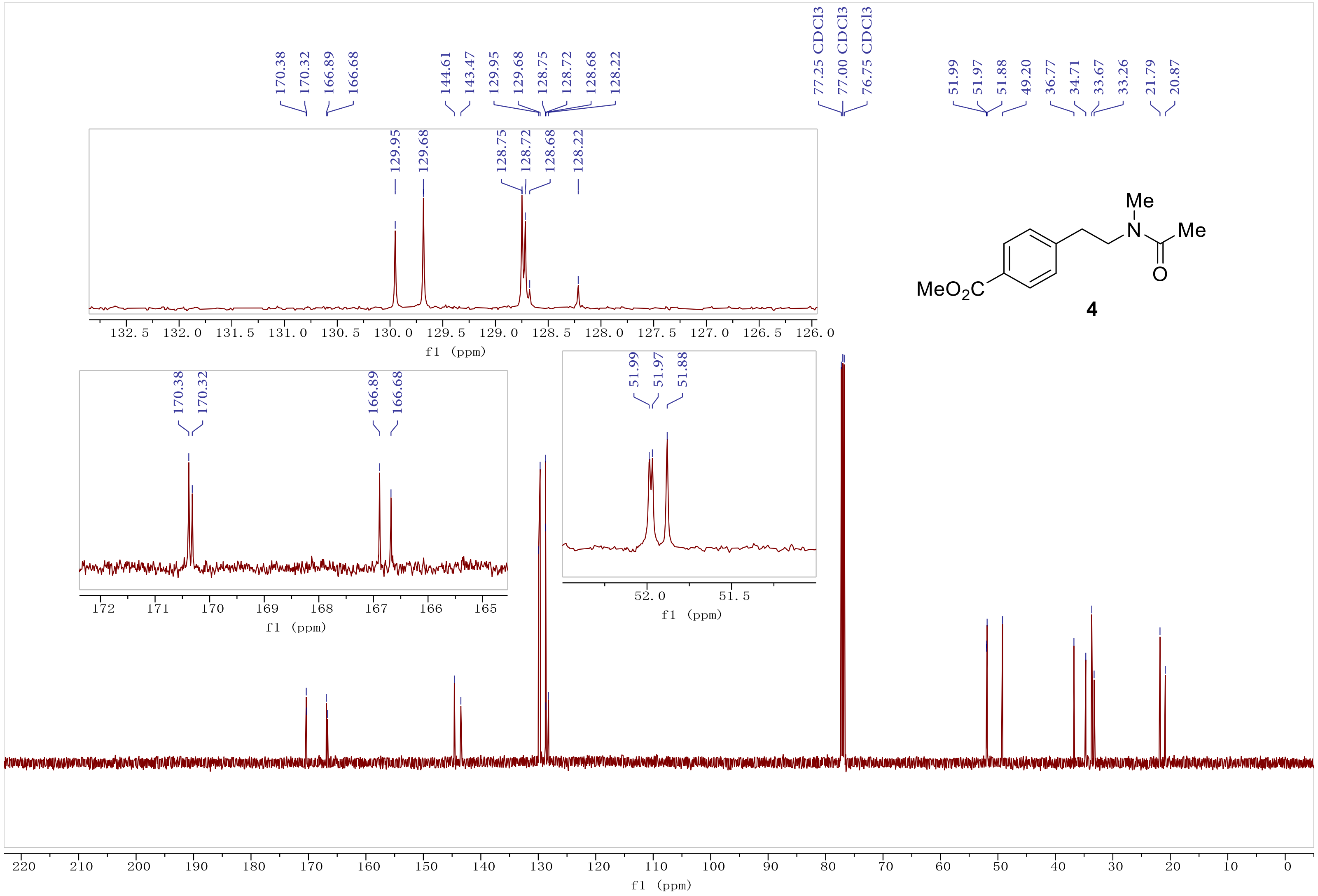


7.7. Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

^{1}H NMR spectrum (500 MHz) in $CDCl_3$



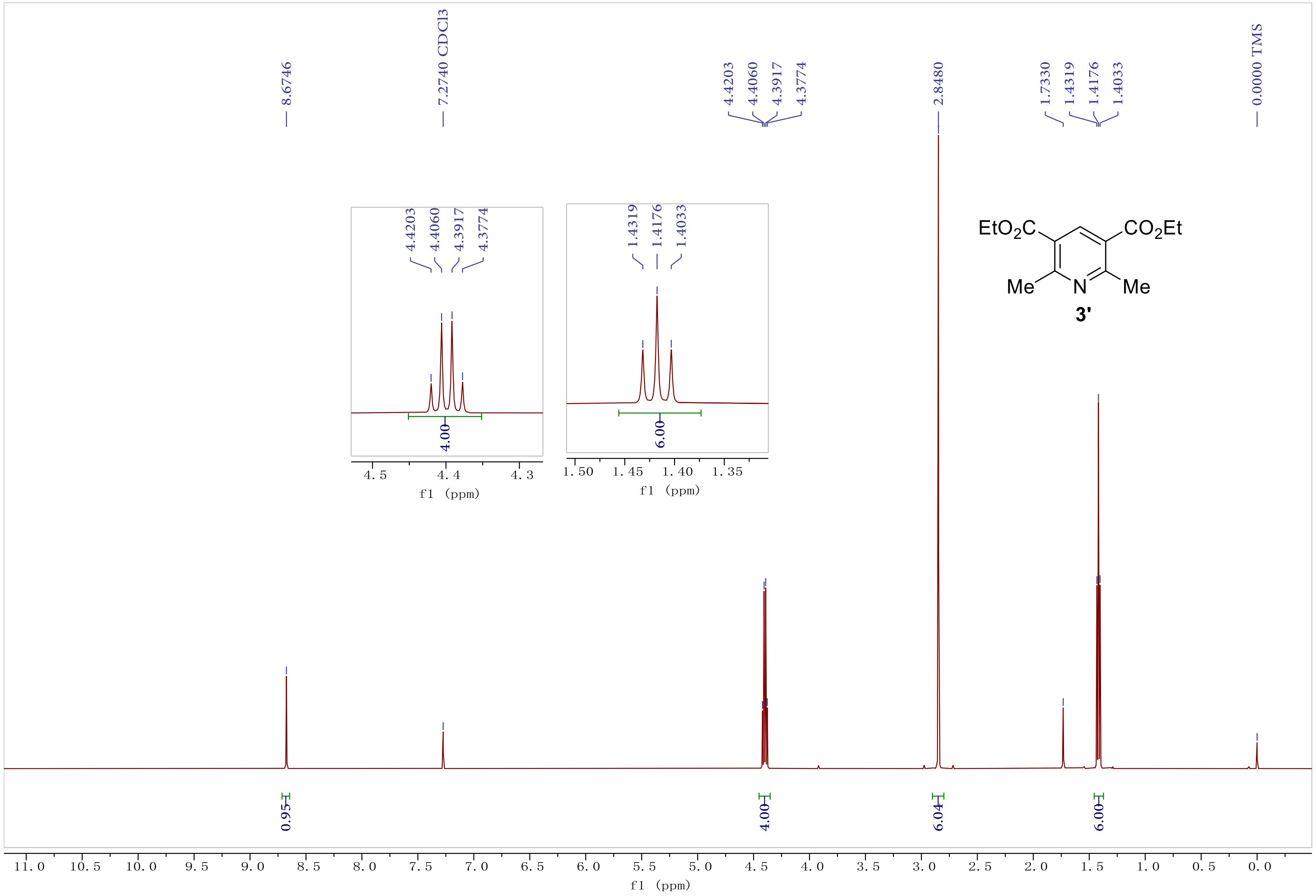
^{13}C NMR spectrum (125 MHz) in $CDCl_3$



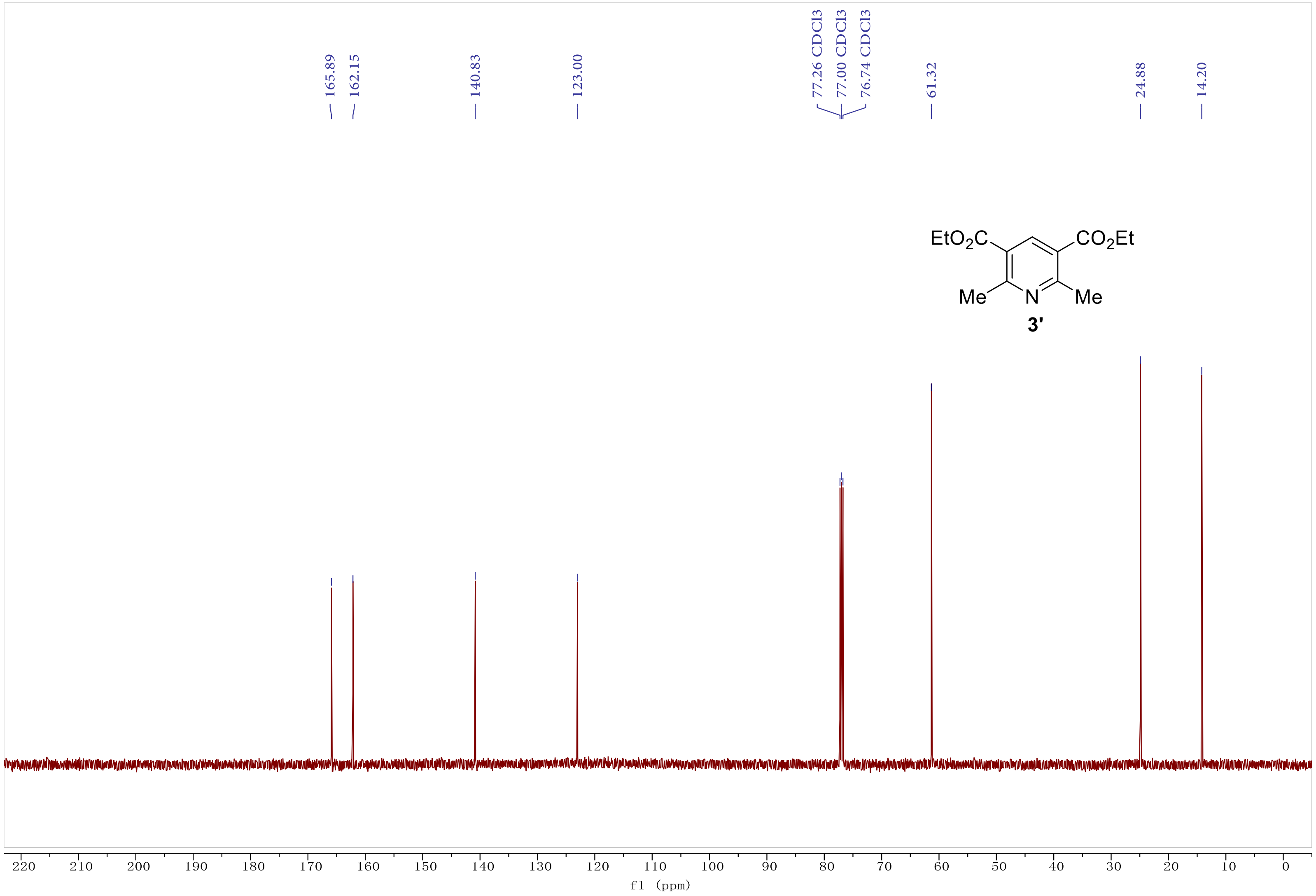
4

7.8. Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (3’)

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

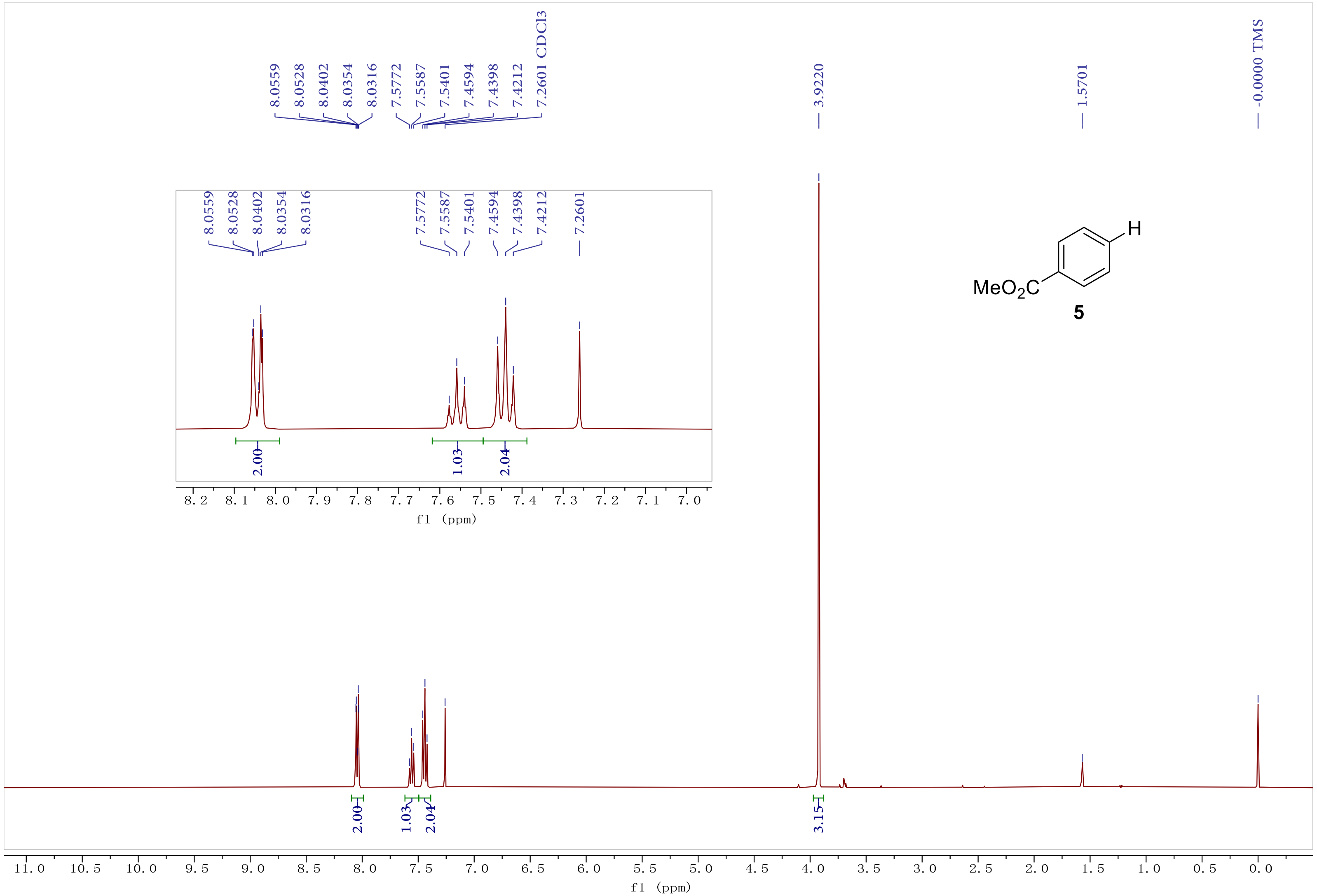


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

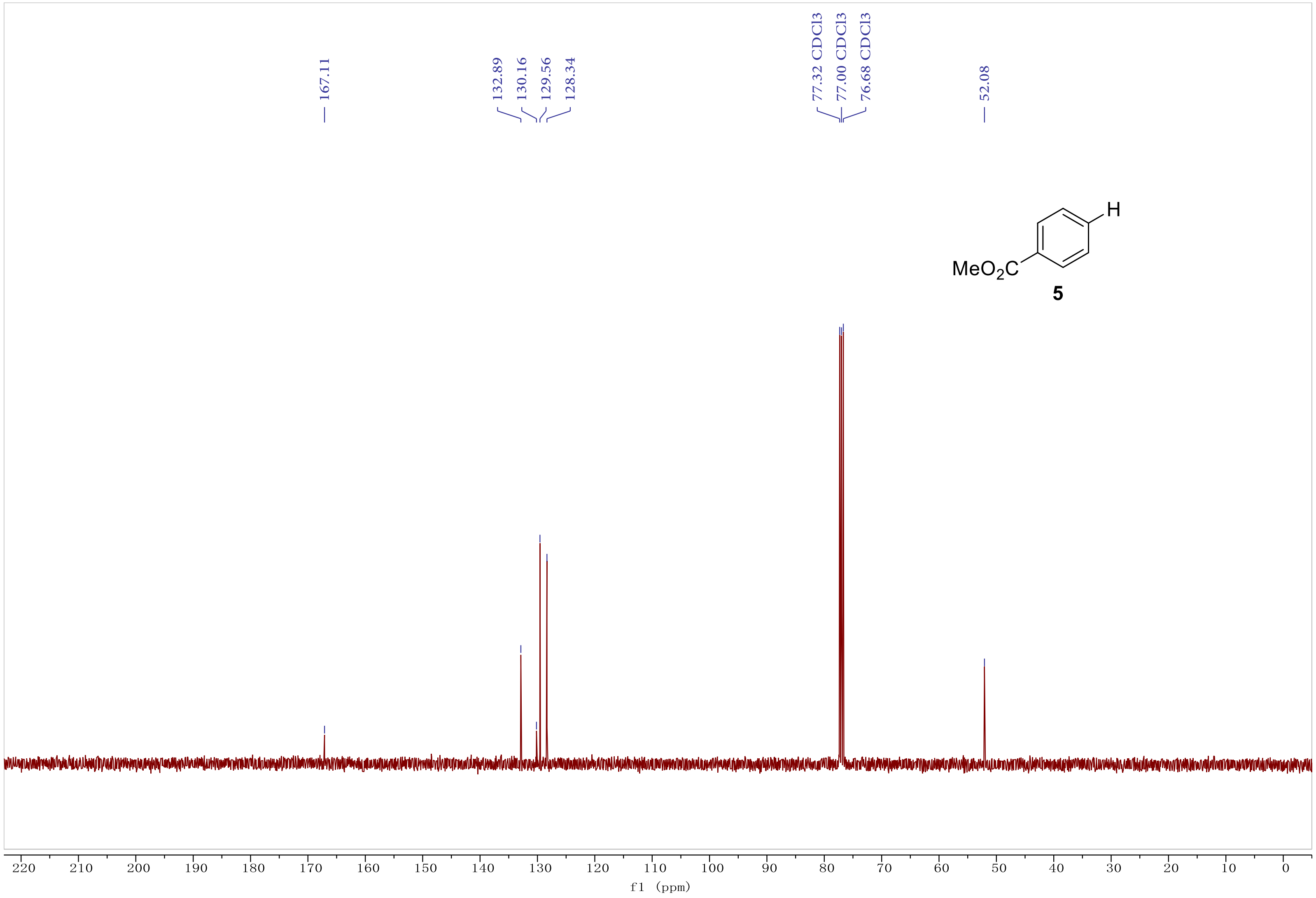


7.9. Methyl benzoate (5)

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

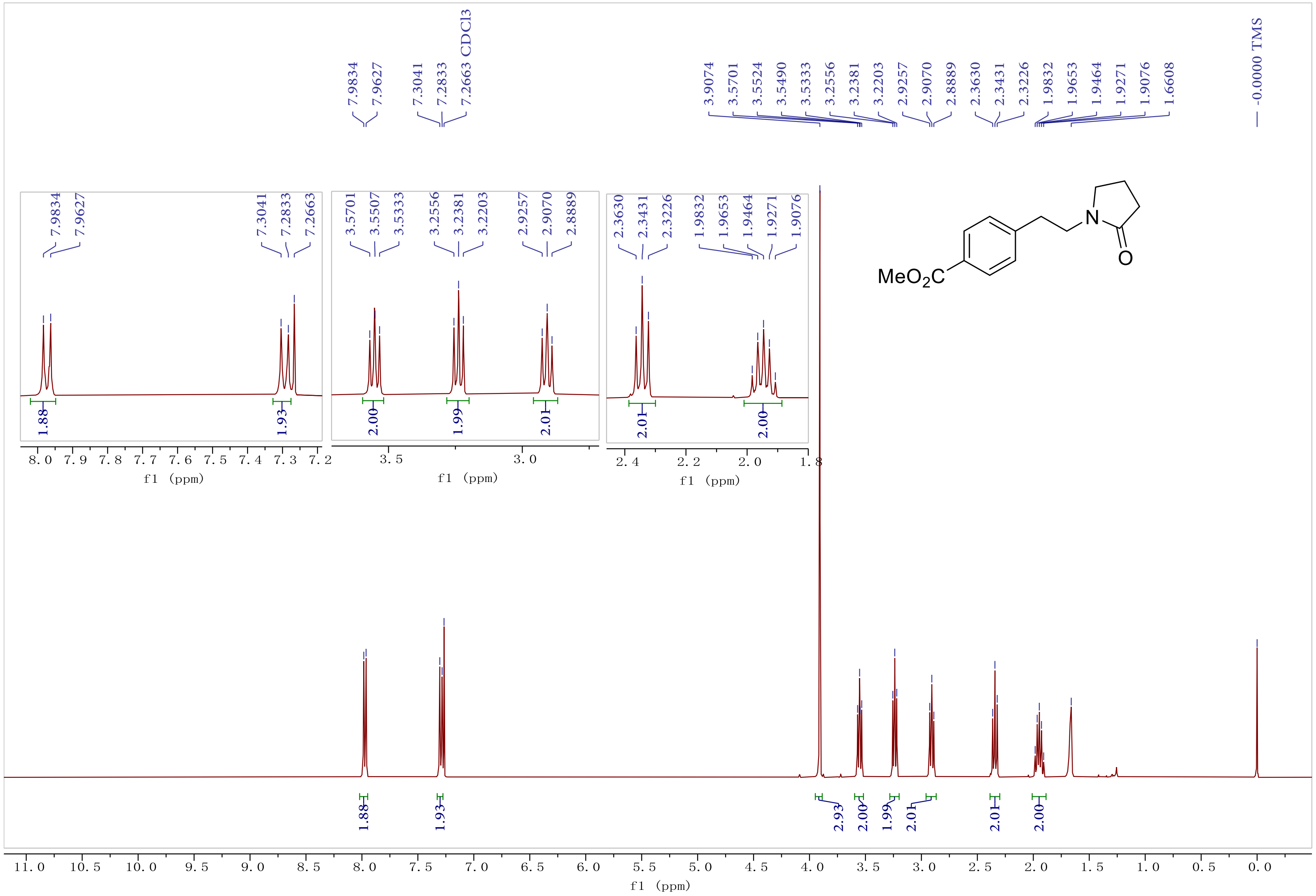


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

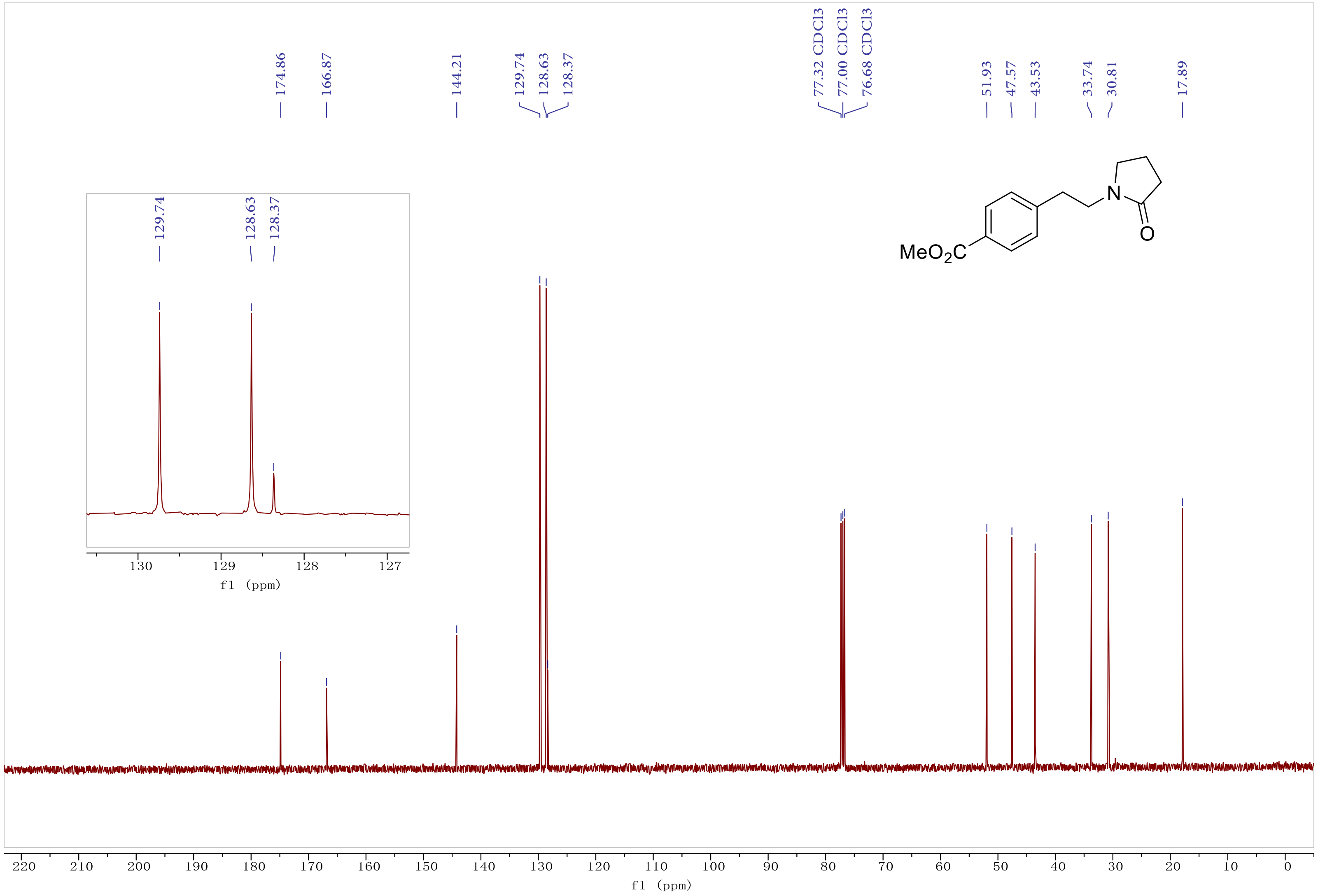


7.10. Methyl 4-(2-(2-oxopyrrolidin-1-yl)ethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

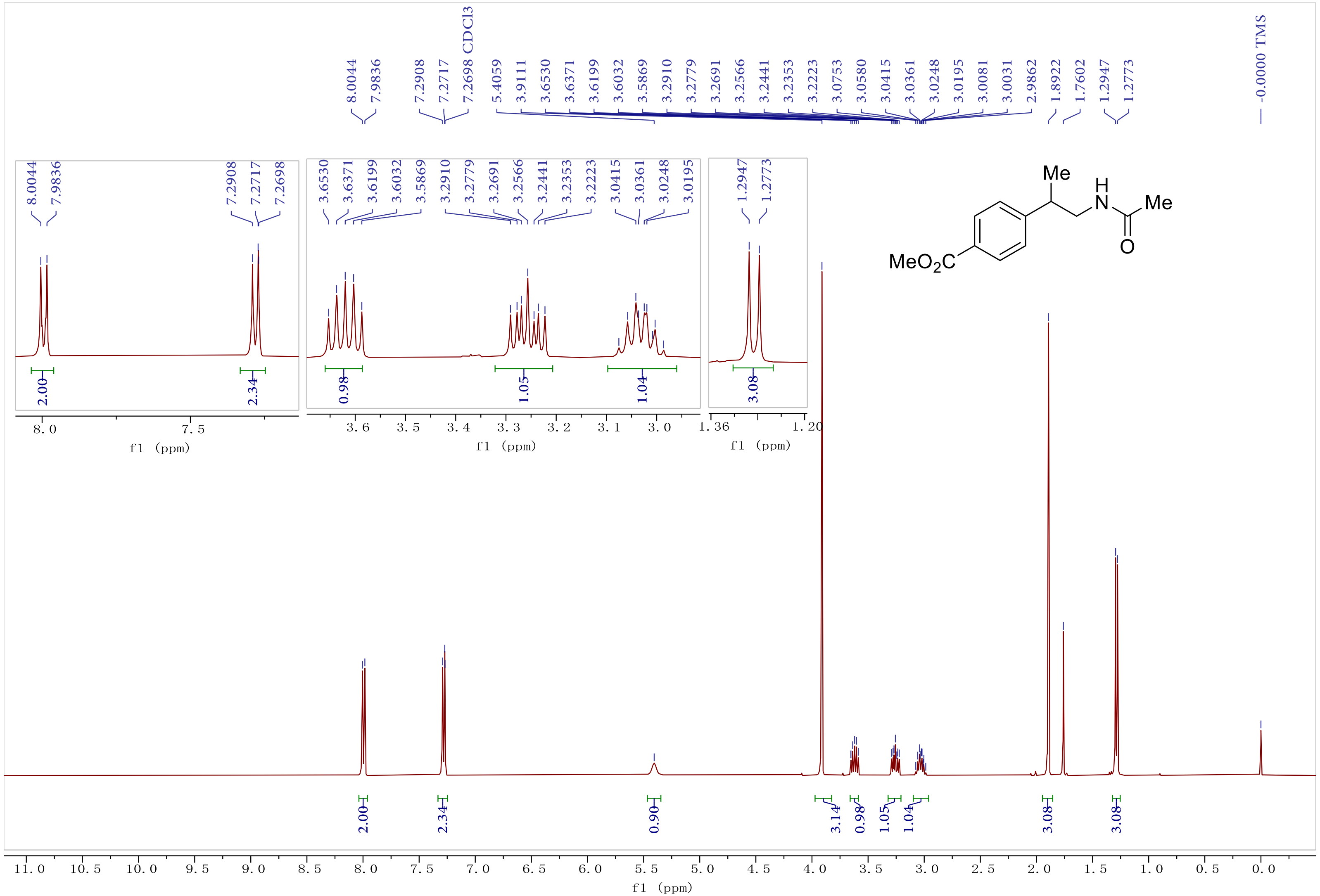


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

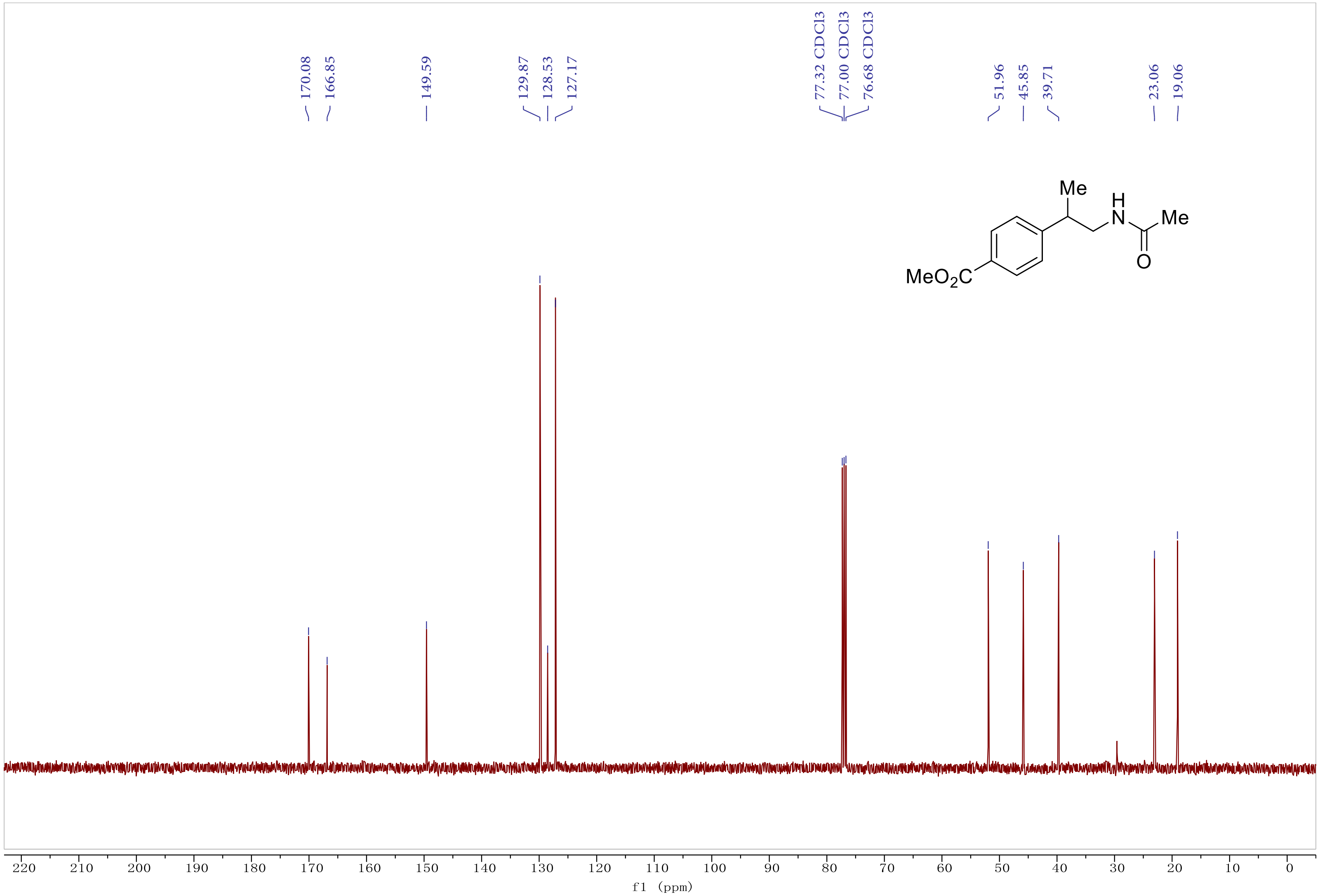


7.11. Methyl 4-(1-acetamidopropan-2-yl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

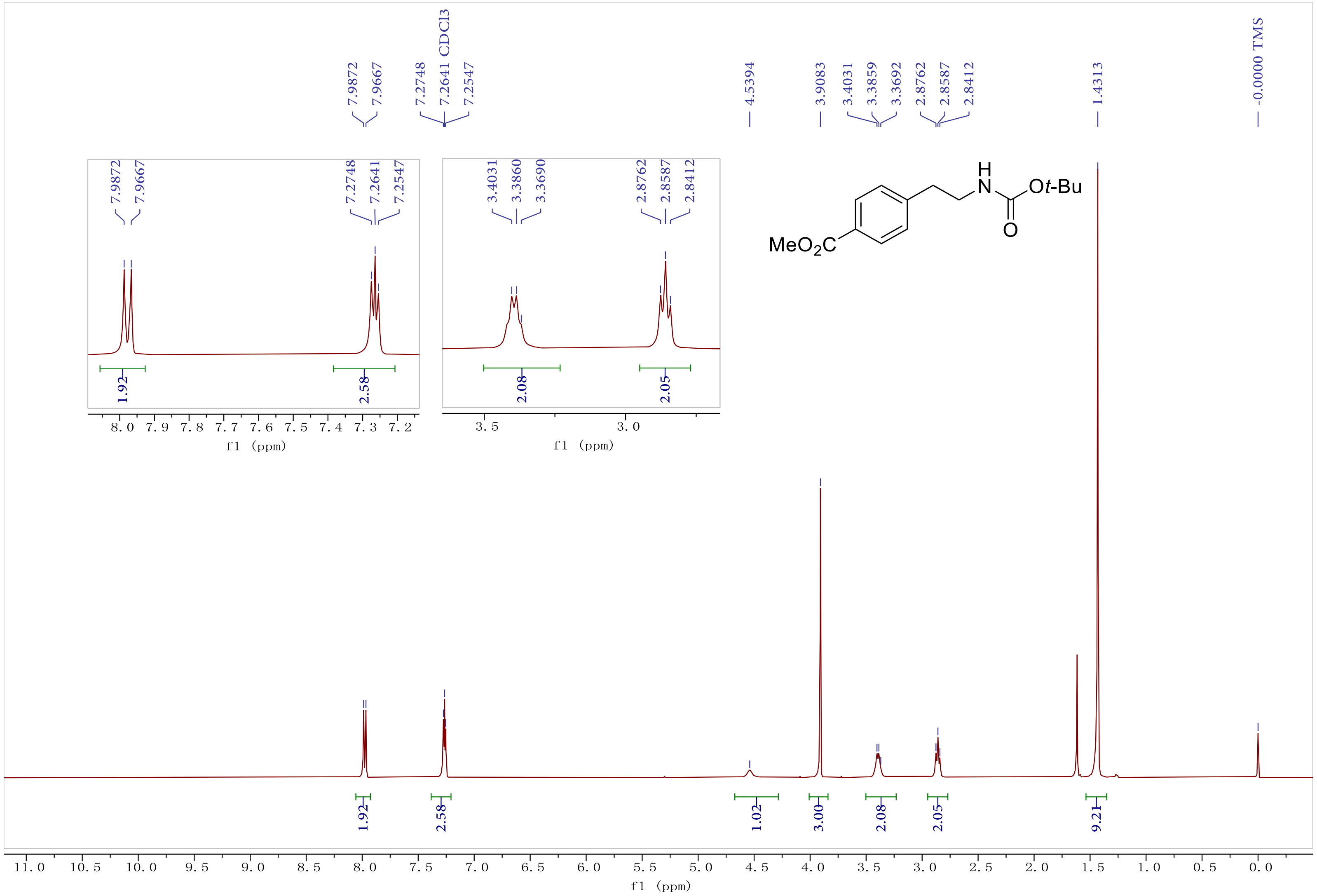


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

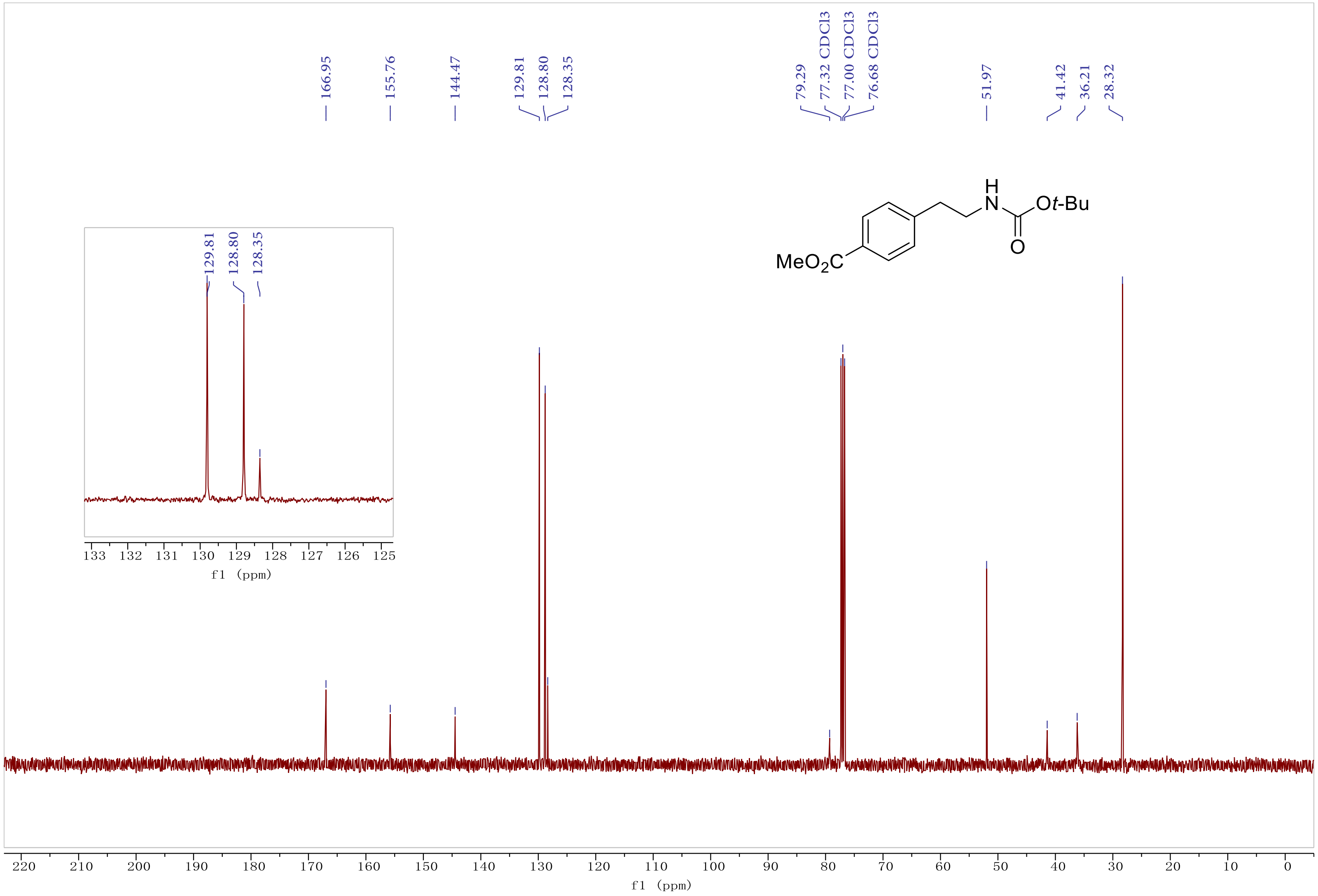


7.12. Methyl 4-(2-((*tert*-butoxycarbonyl)amino)ethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

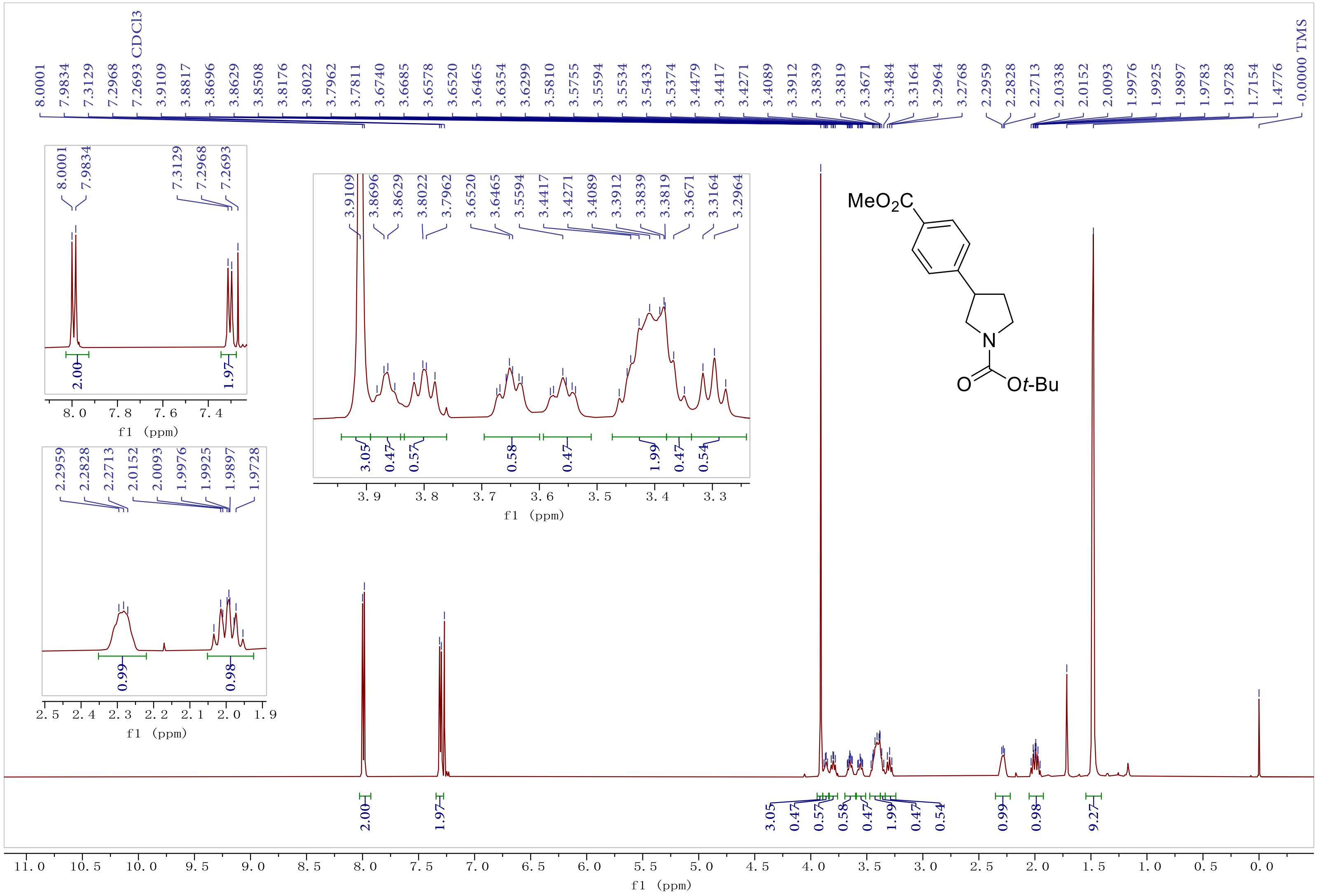


^{13}C NMR spectrum (100 MHz) in CDCl$_3$

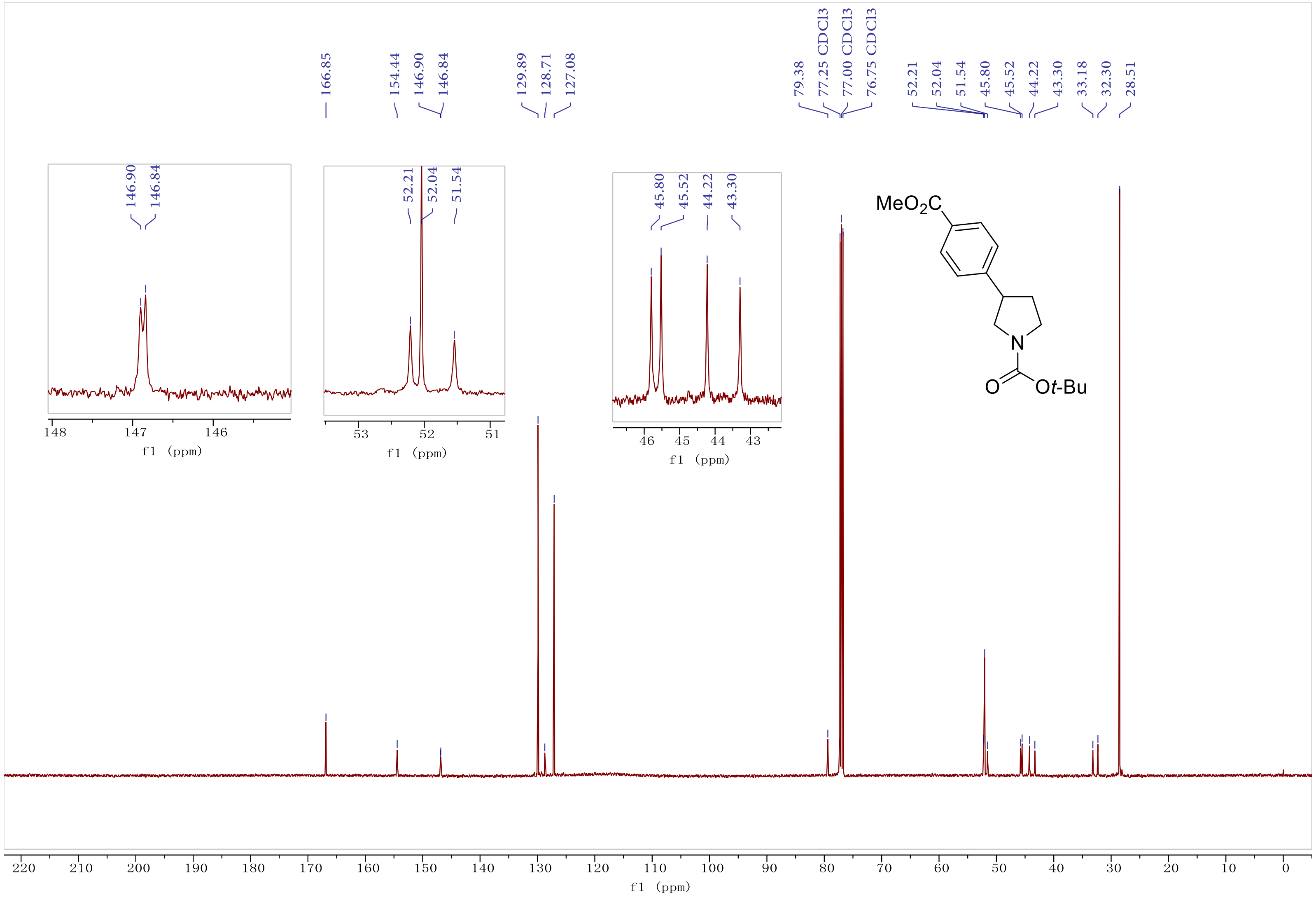


7.13. *tert*-Butyl 3-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

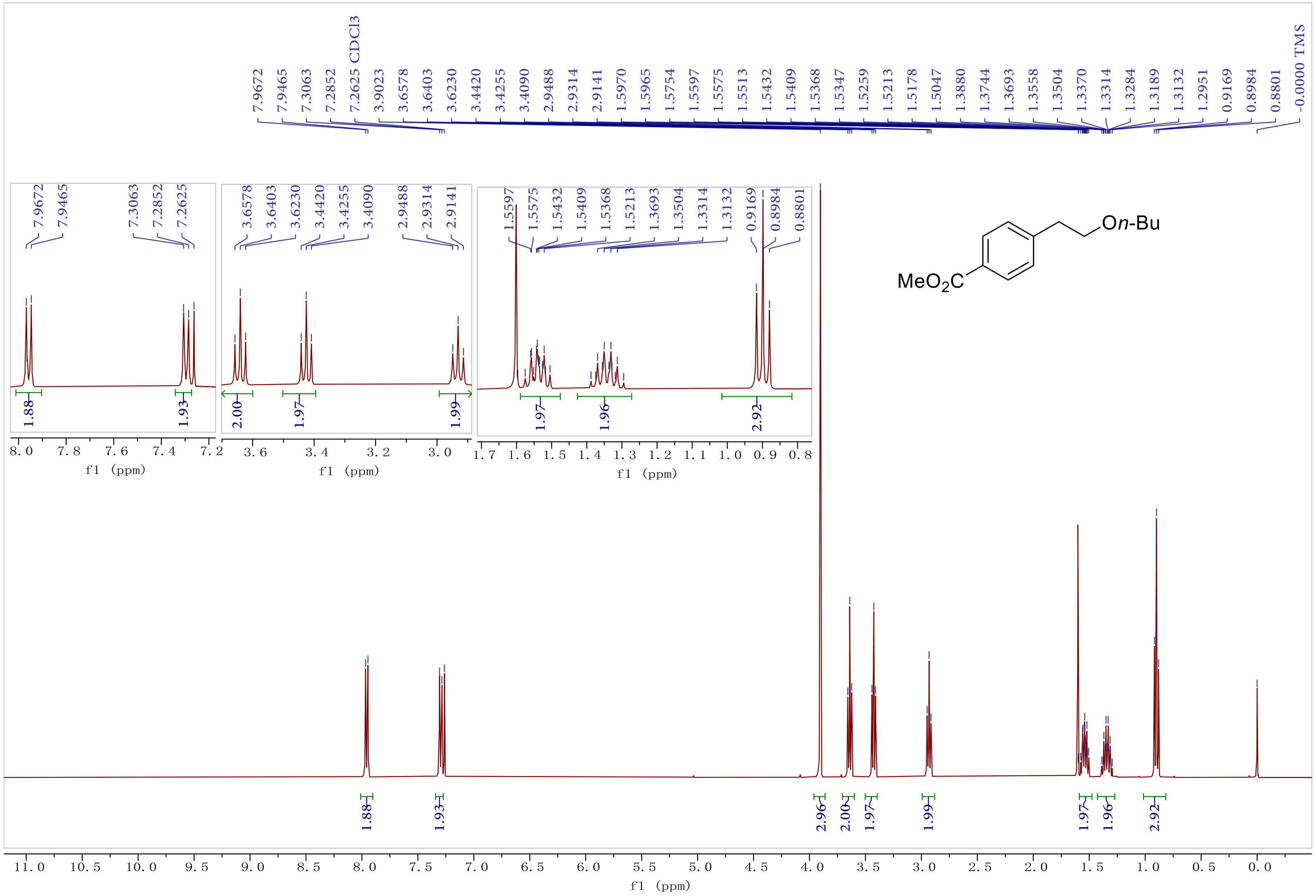


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

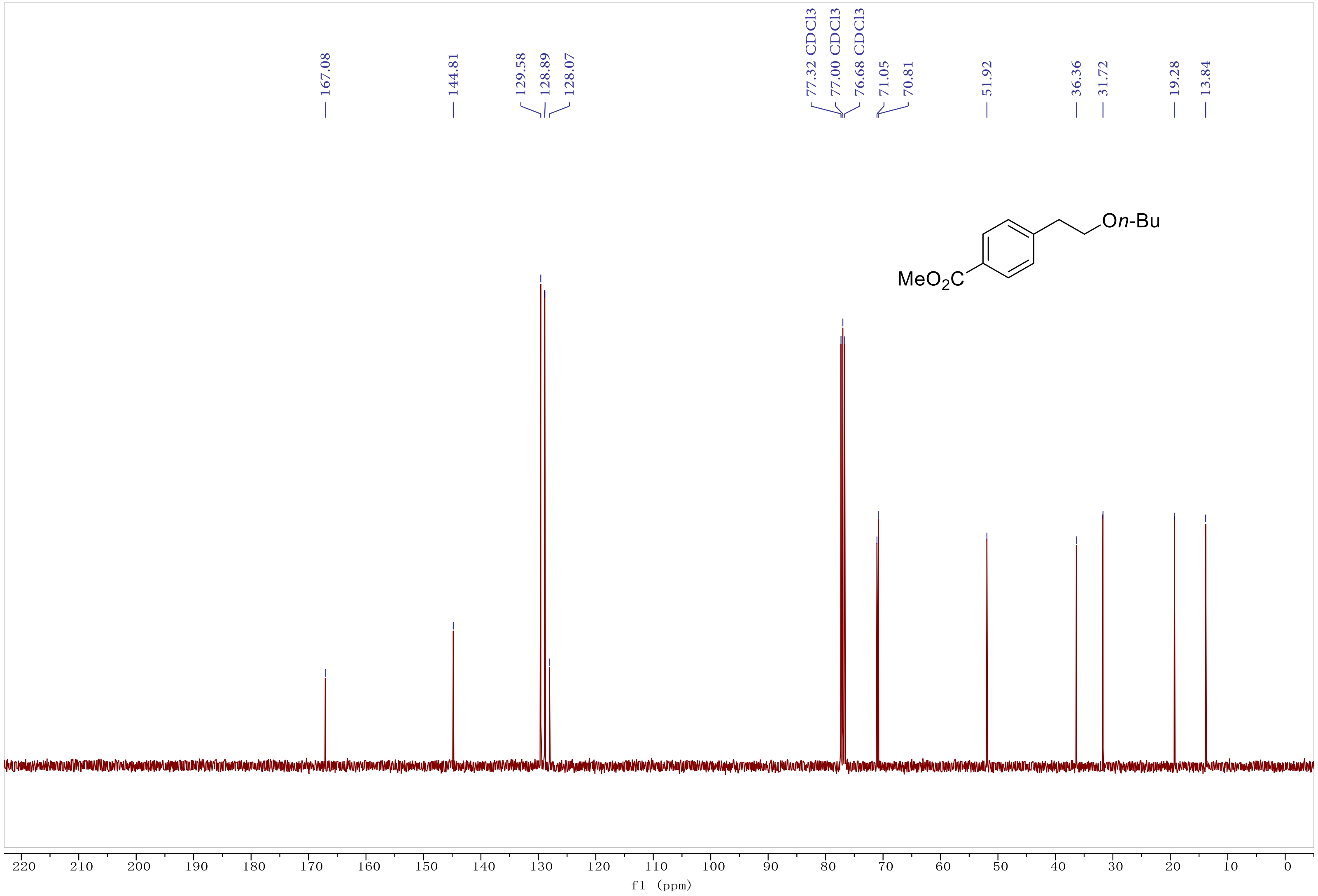


7.14. Methyl 4-(2-butoxyethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

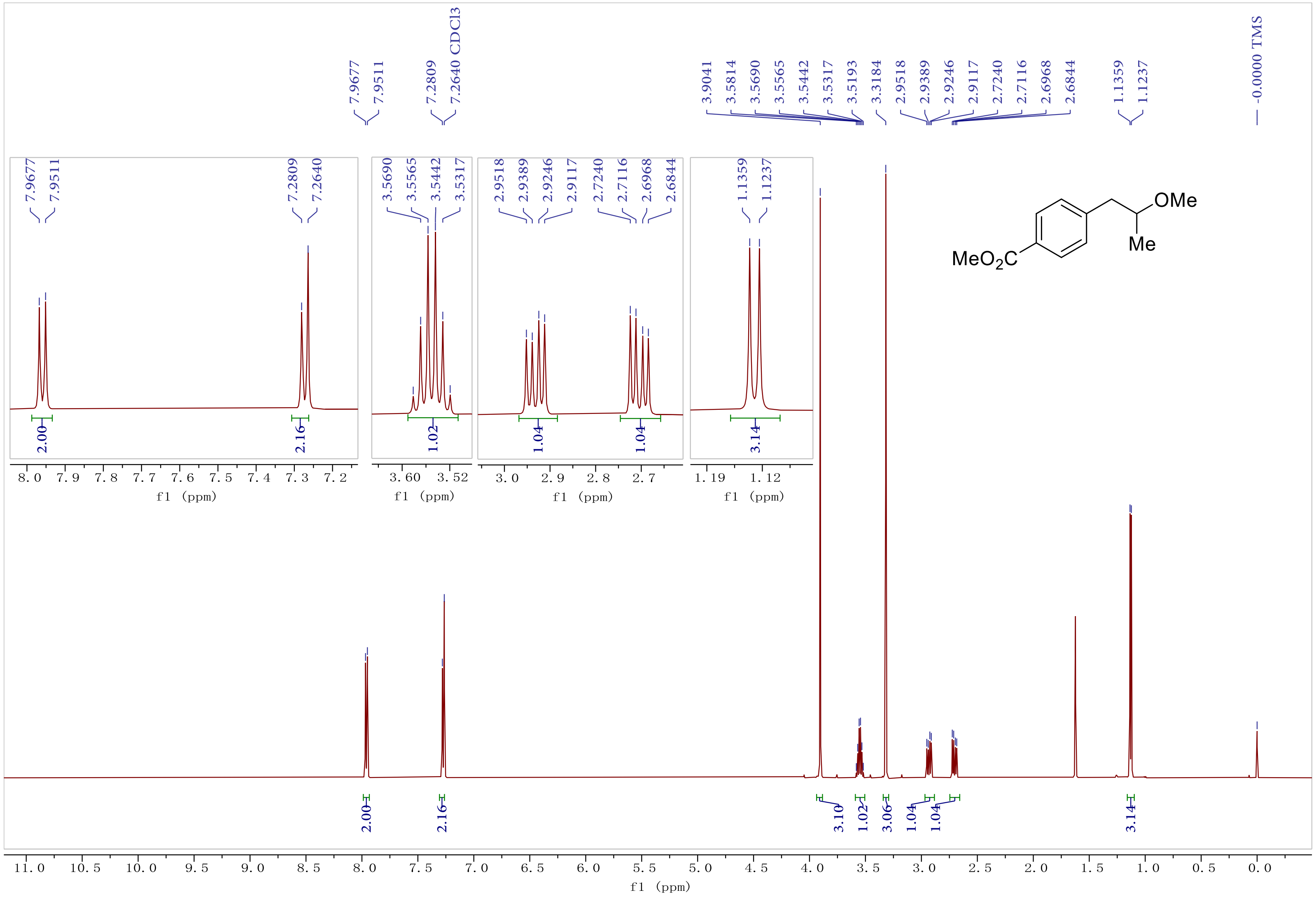


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

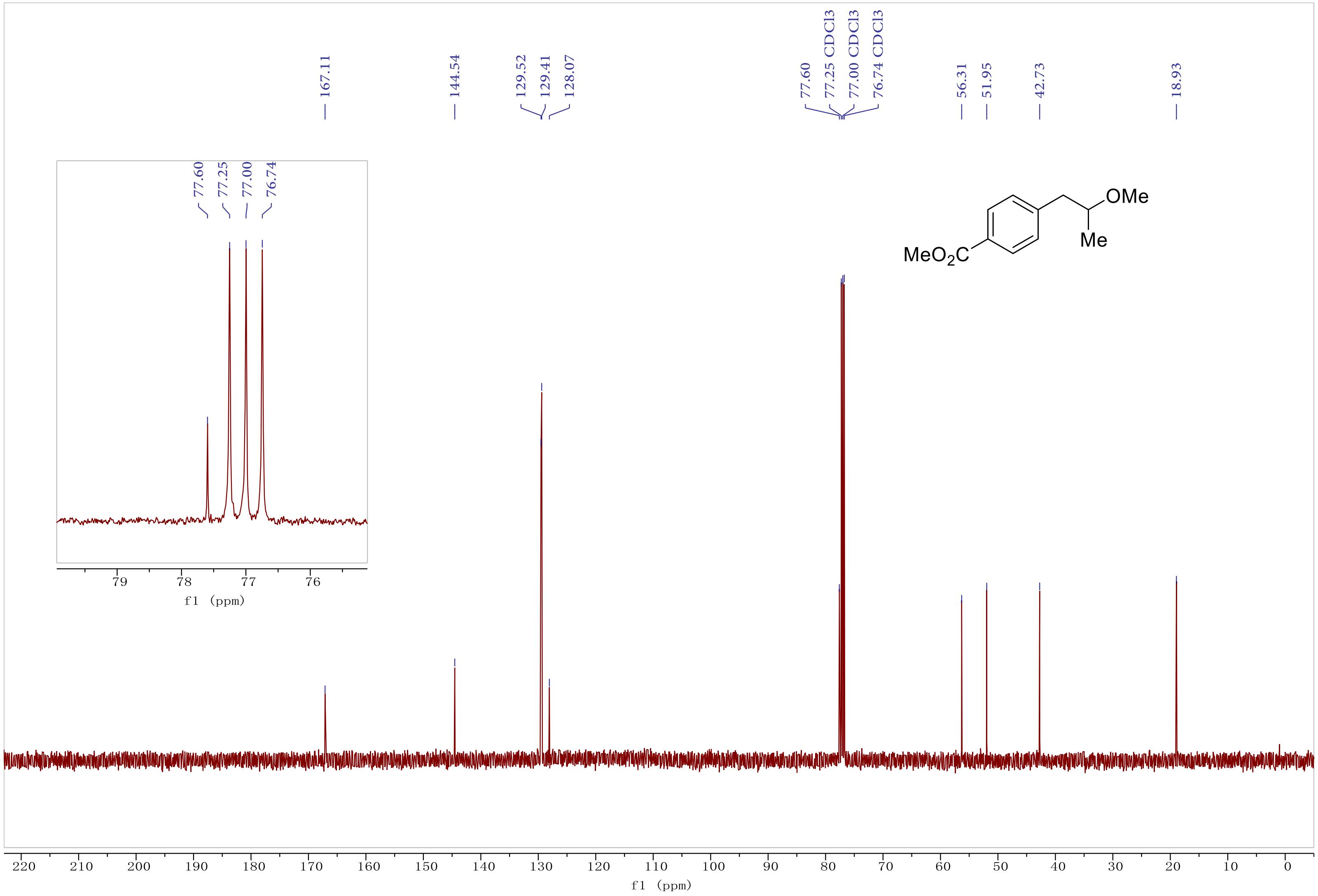


7.15. Methyl 4-(2-methoxypropyl)benzoate

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

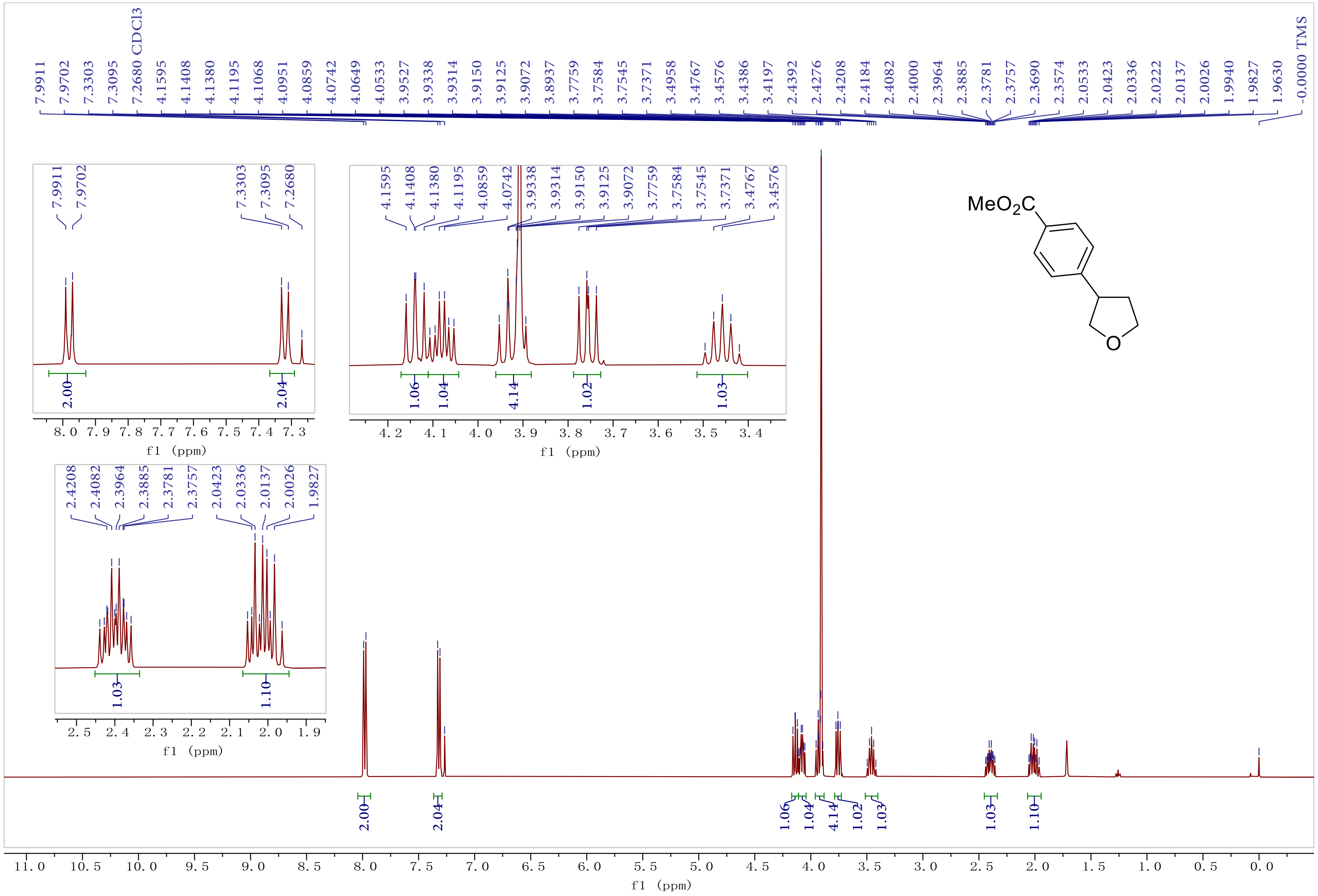


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

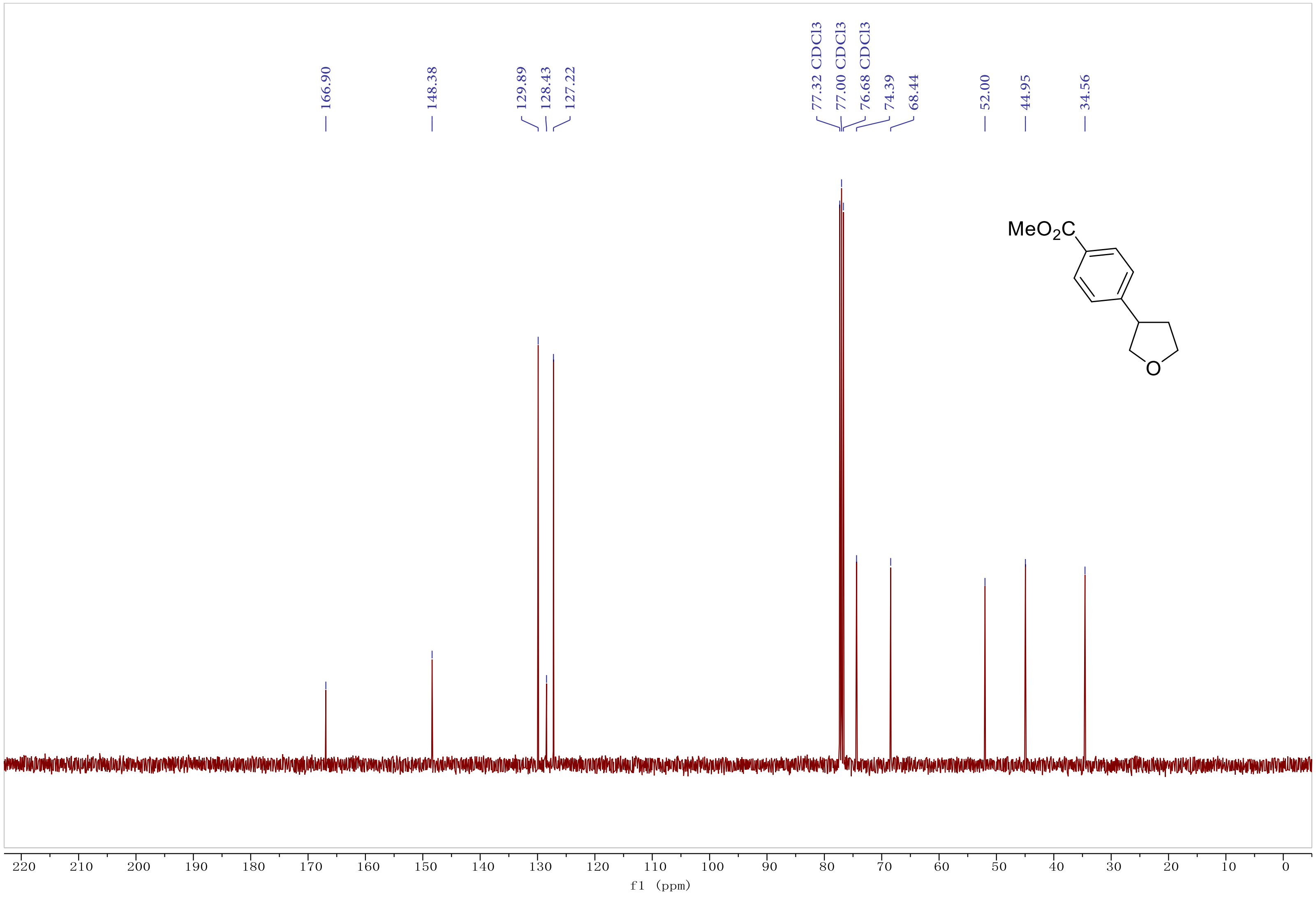


7.16. Methyl 4-(tetrahydrofuran-3-yl)benzoate

^{1}H NMR spectrum (400 MHz) in CDCl$_3$

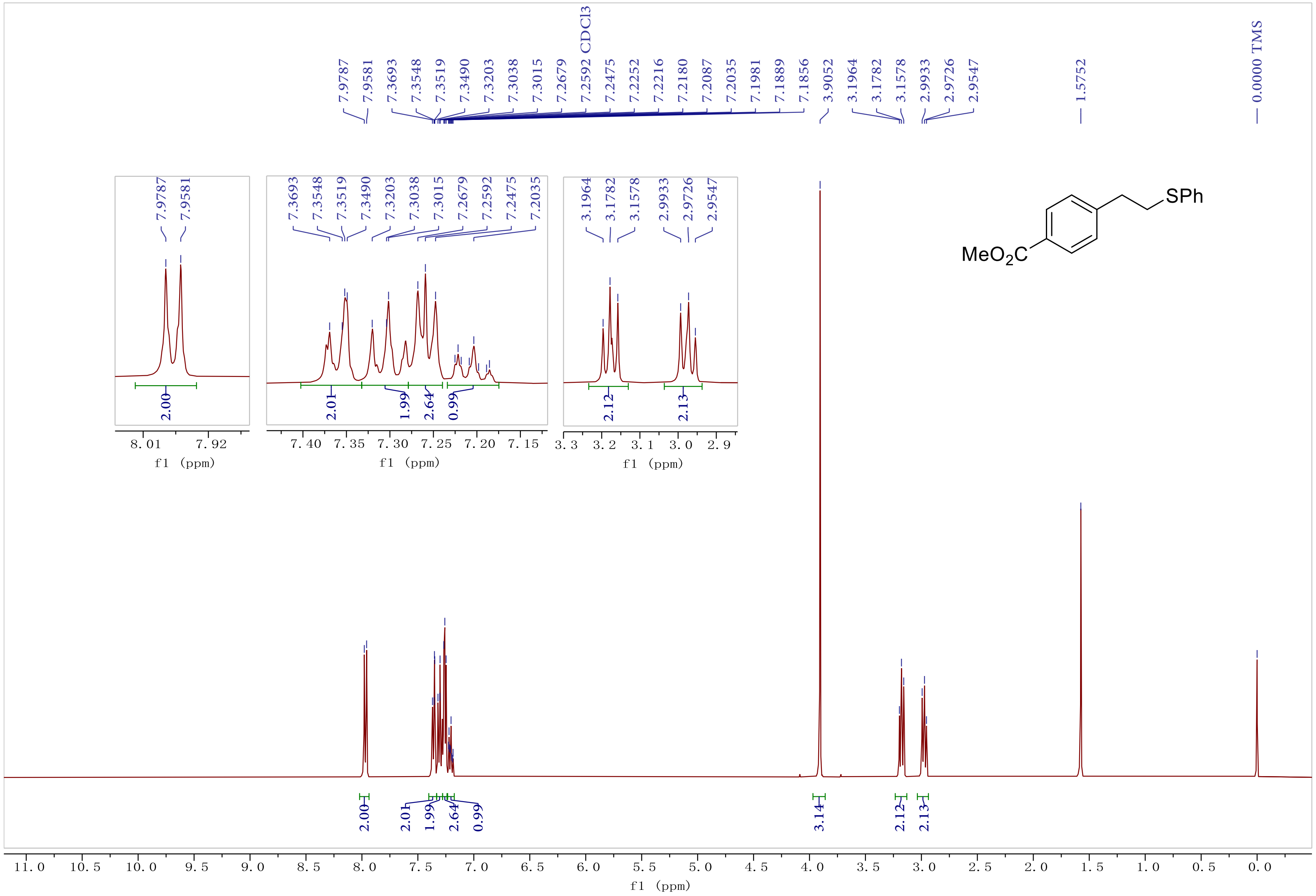


^{13}C NMR spectrum (100 MHz) in CDCl$_3$

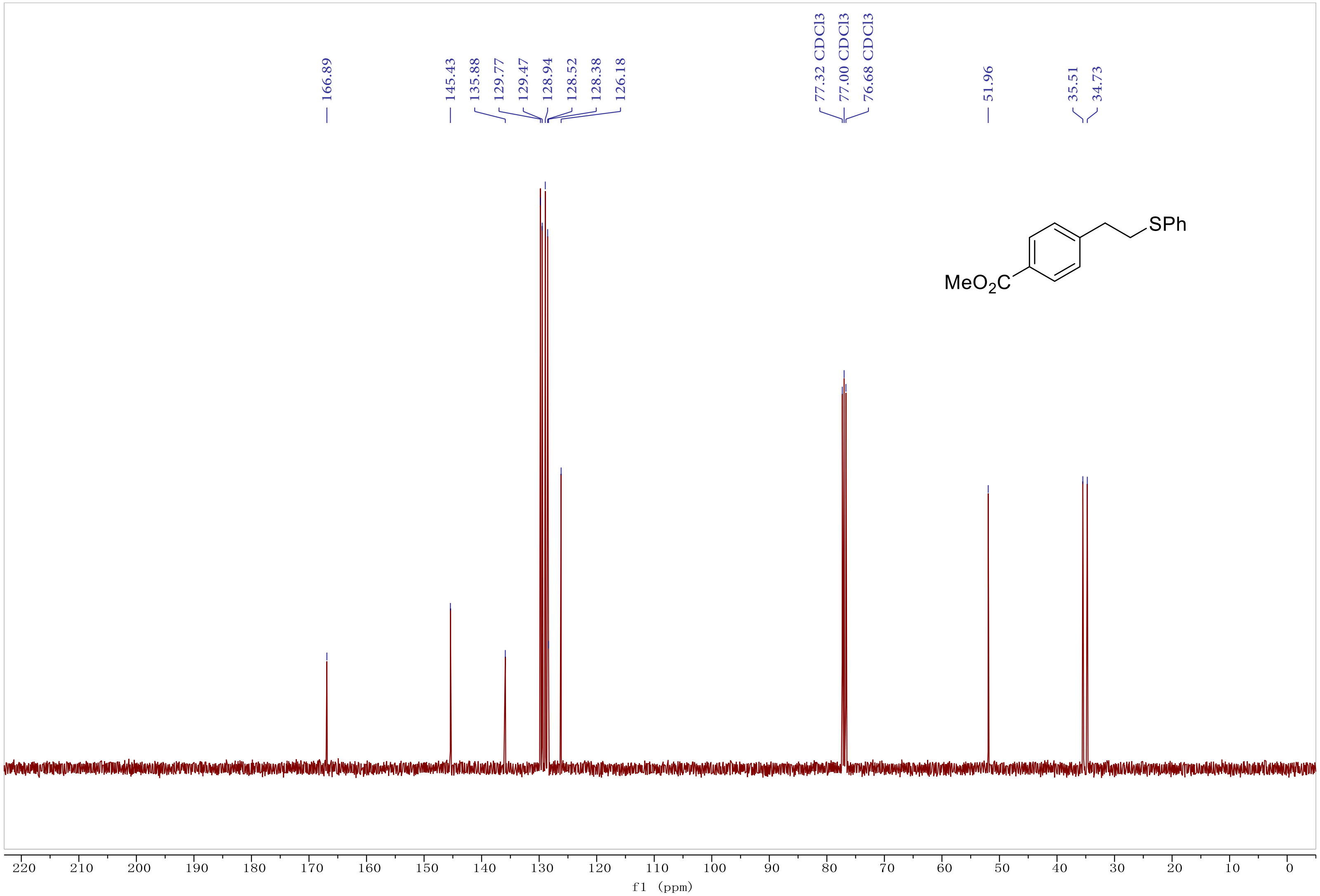


7.17. Methyl 4-(2-(phenylthio)ethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

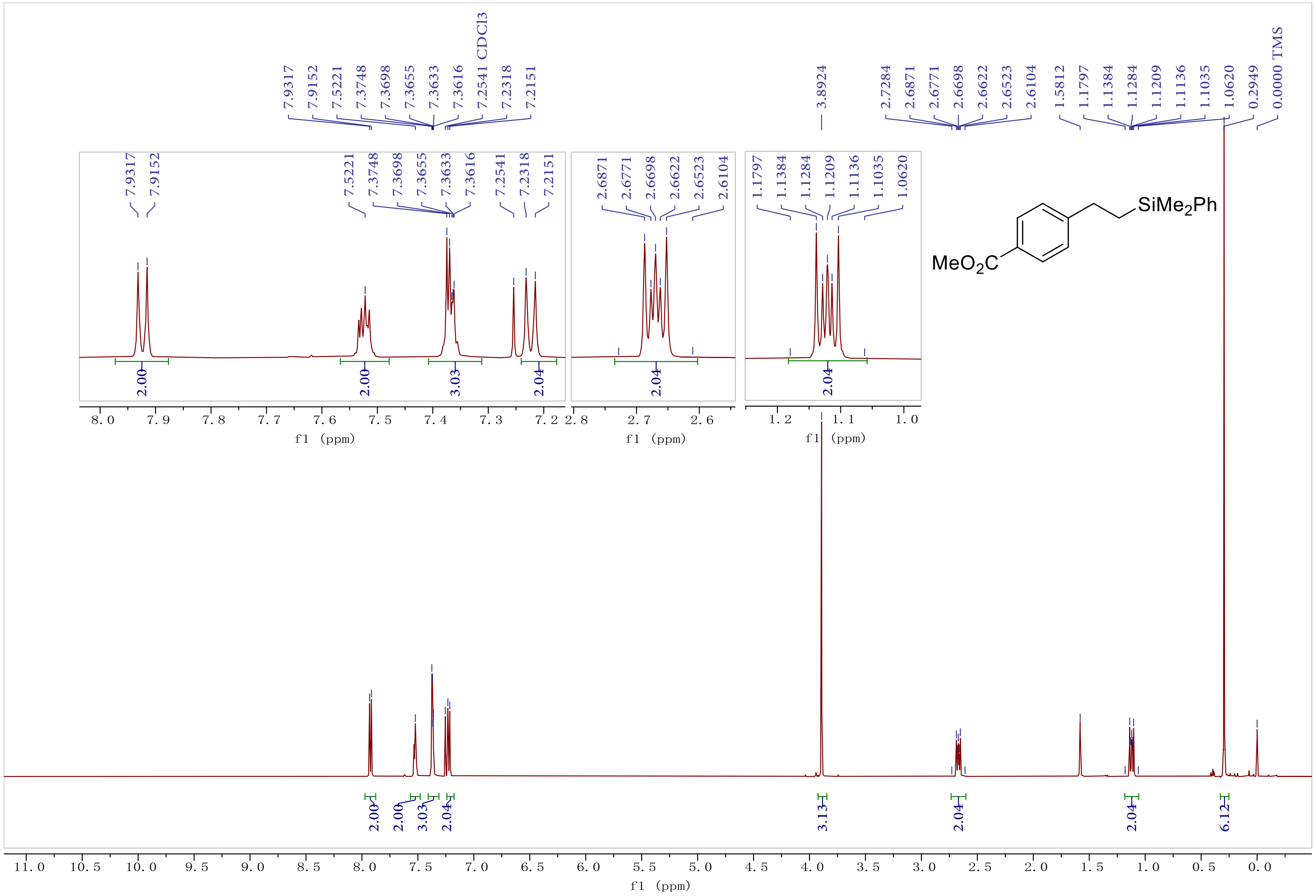


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

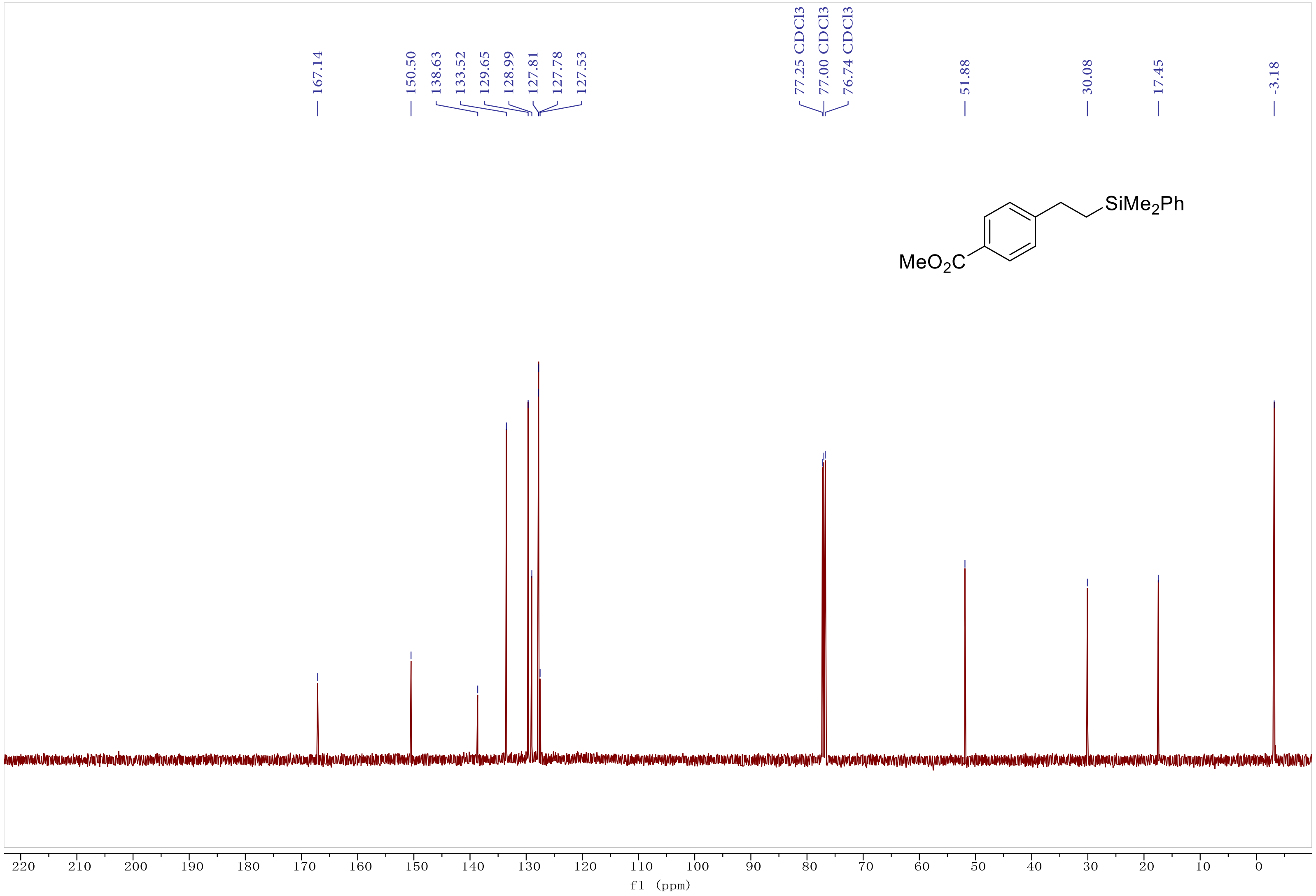


7.18. Methyl 4-(2-(dimethyl(phenyl)silyl)ethyl)benzoate

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

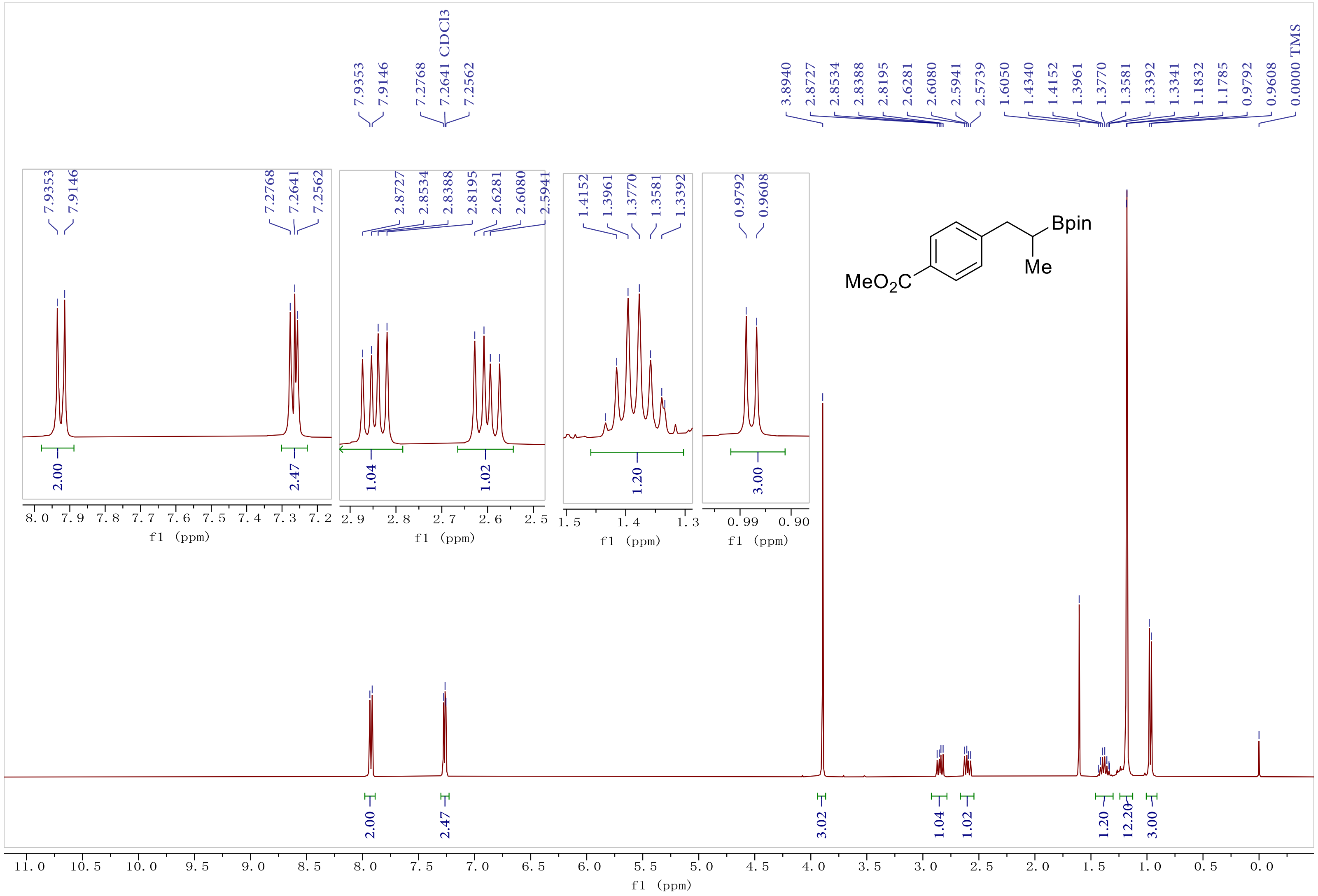


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

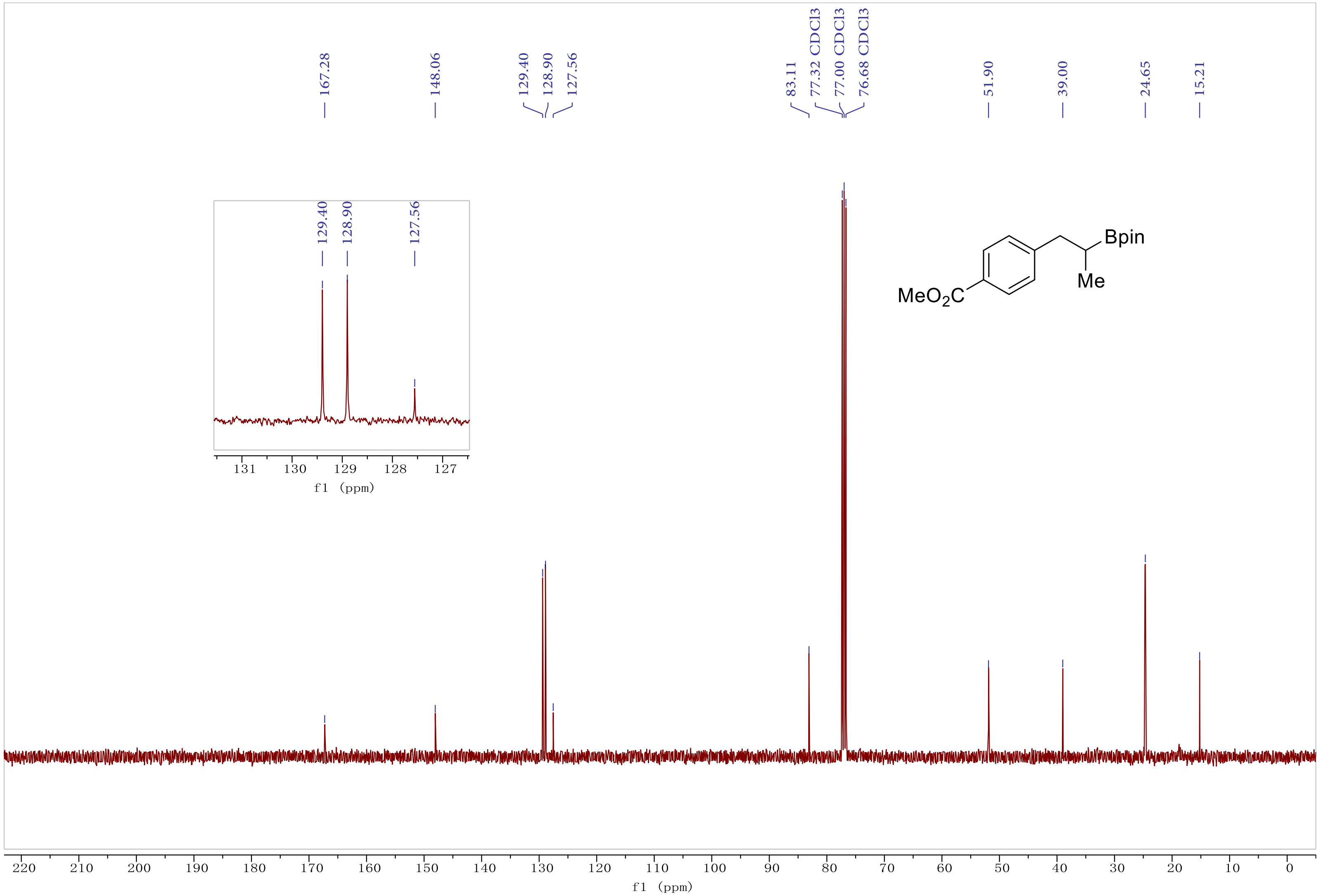


7.19. Methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate

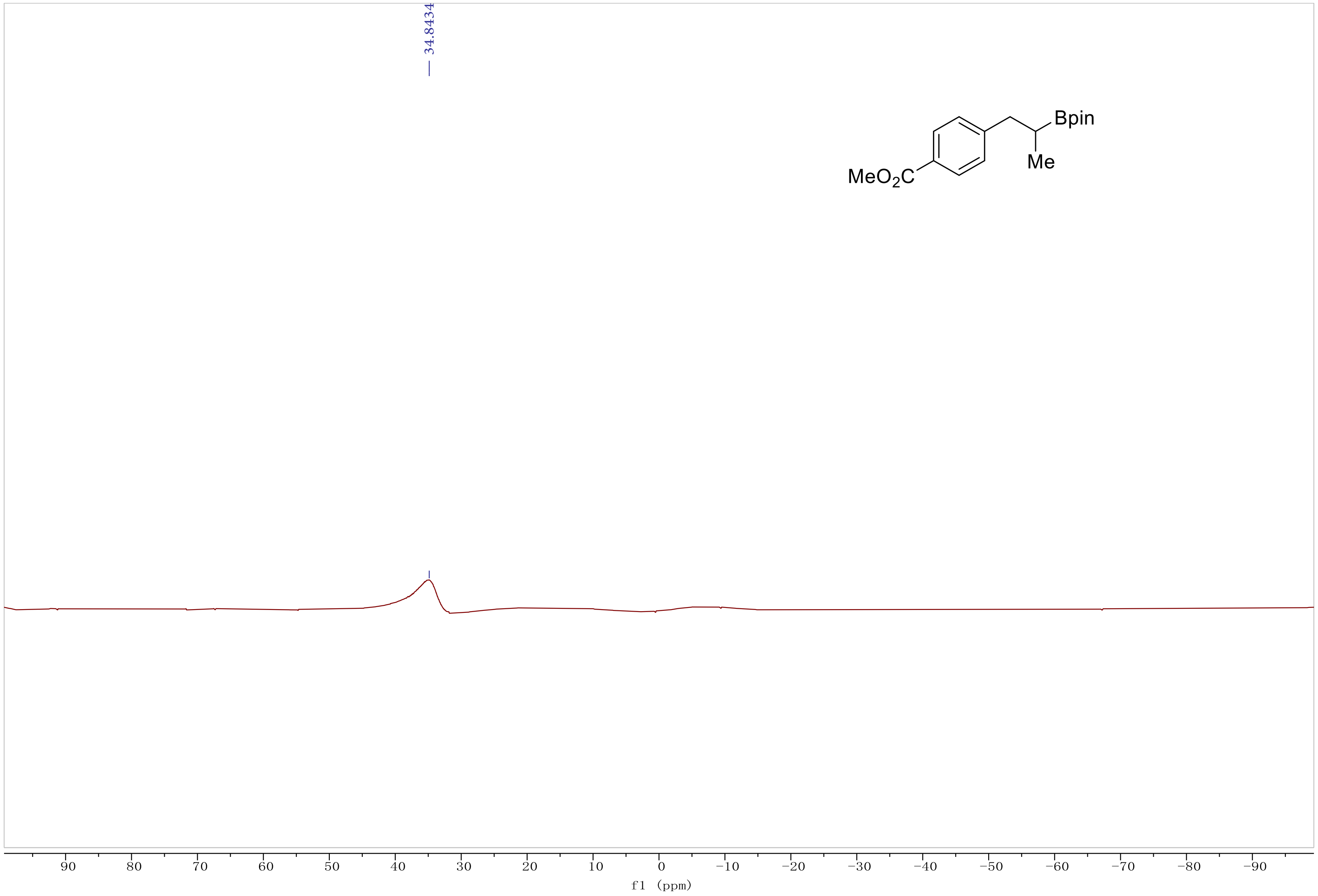
^{1}H NMR spectrum (400 MHz) in $CDCl_3$



^{13}C NMR spectrum (100 MHz) in $CDCl_3$

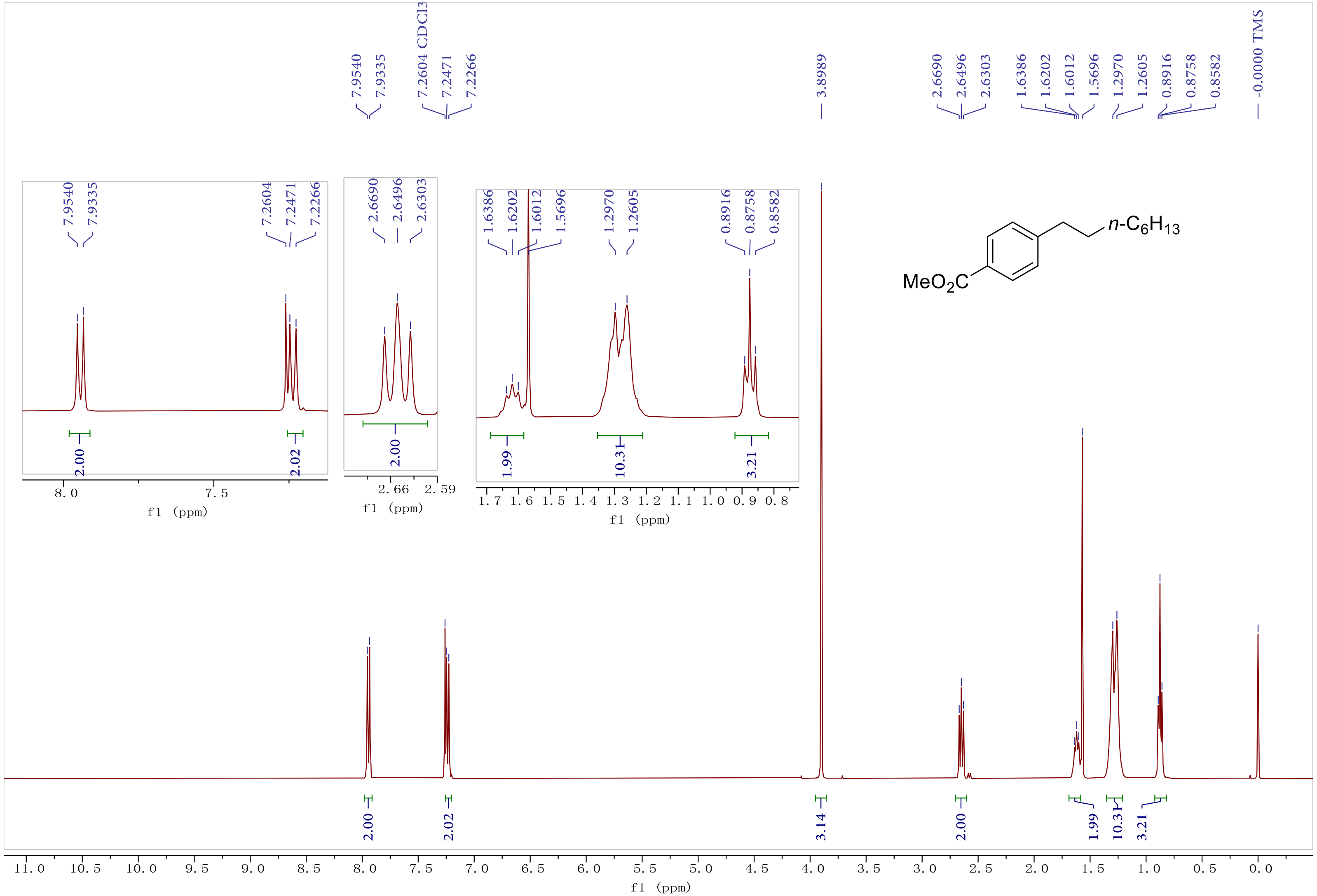


^{11}B NMR spectrum (128 MHz) in CDCl$_3$



7.20. Methyl 4-octylbenzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$



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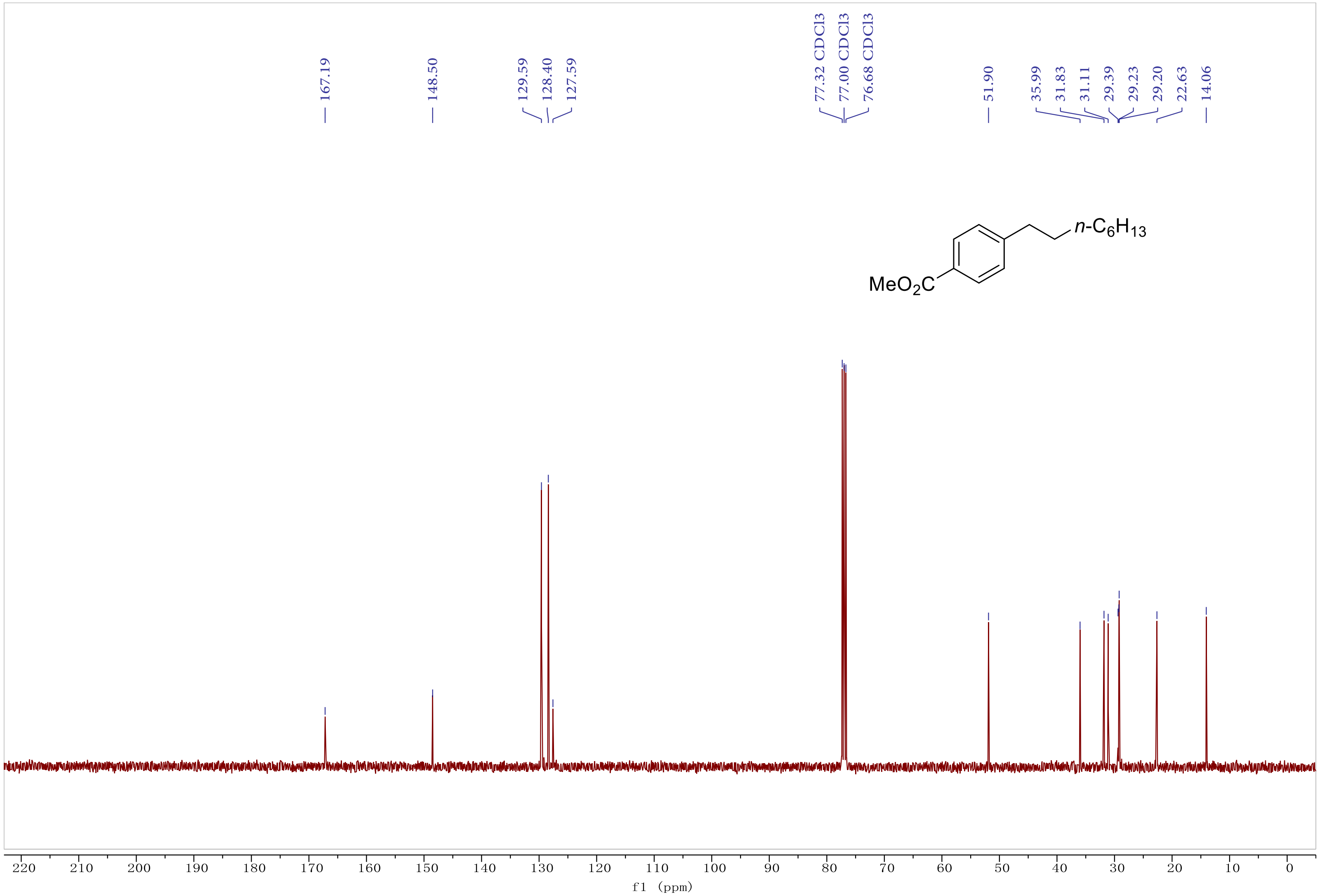
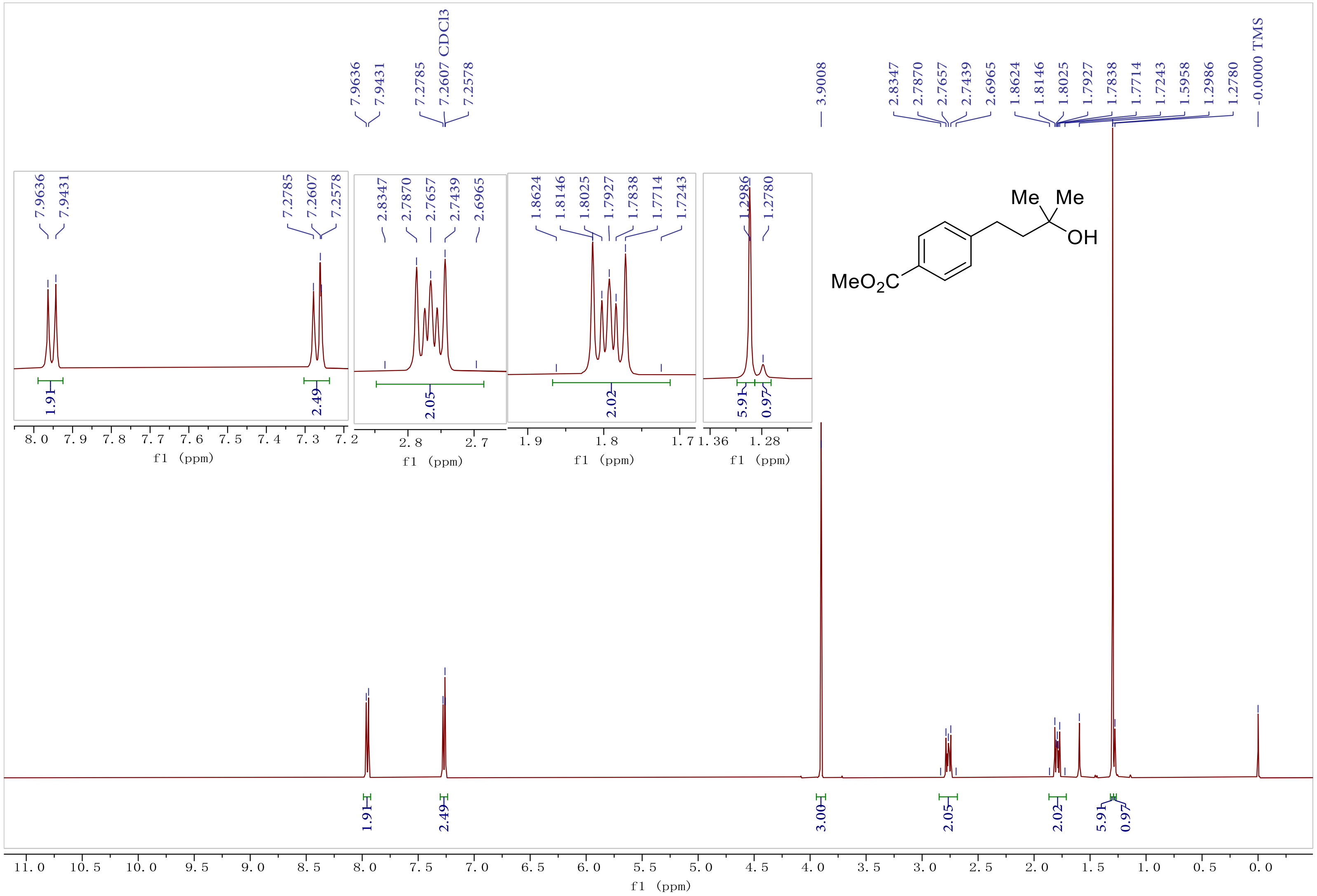


7.21. Methyl 4-(3-hydroxy-3-methylbutyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$



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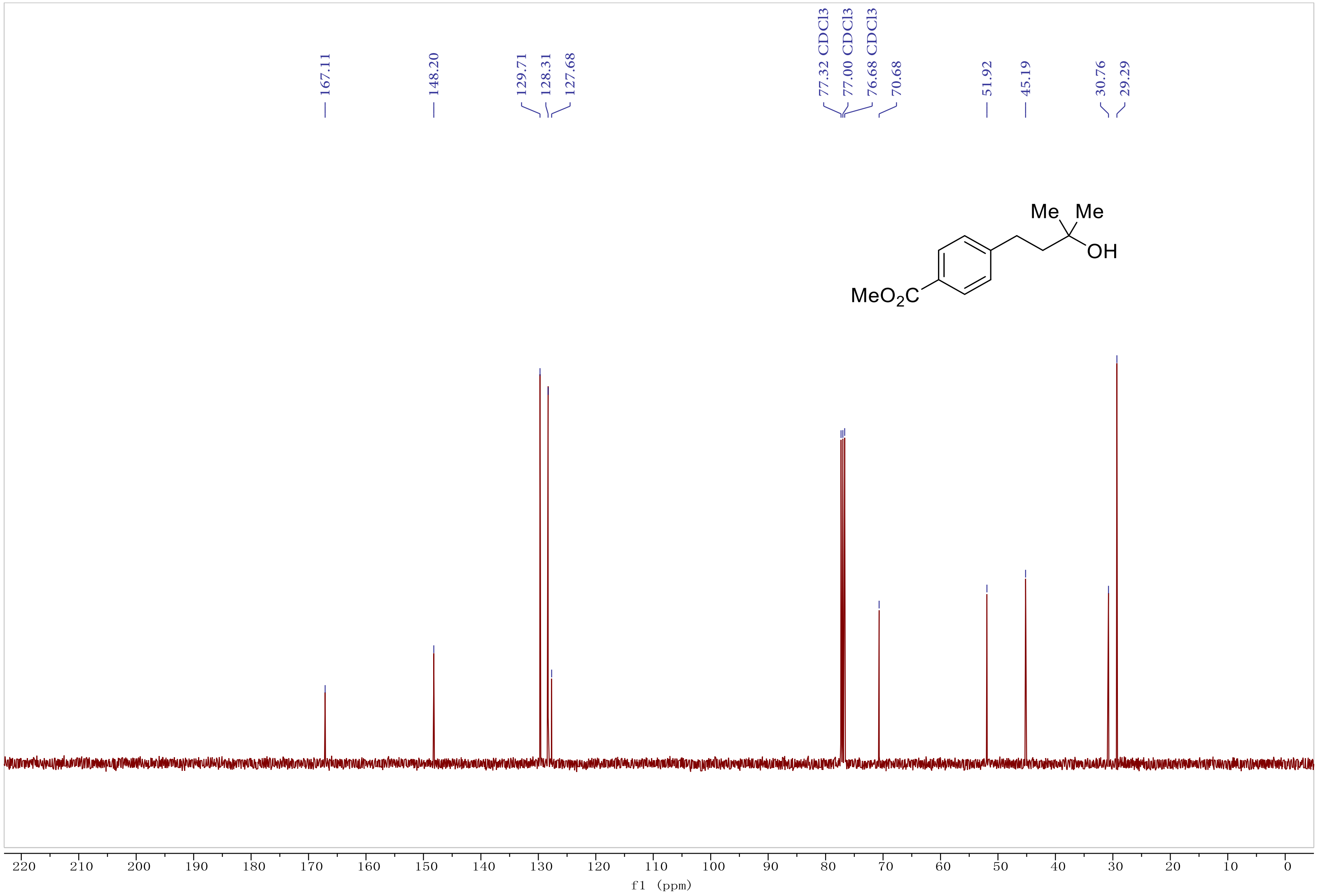
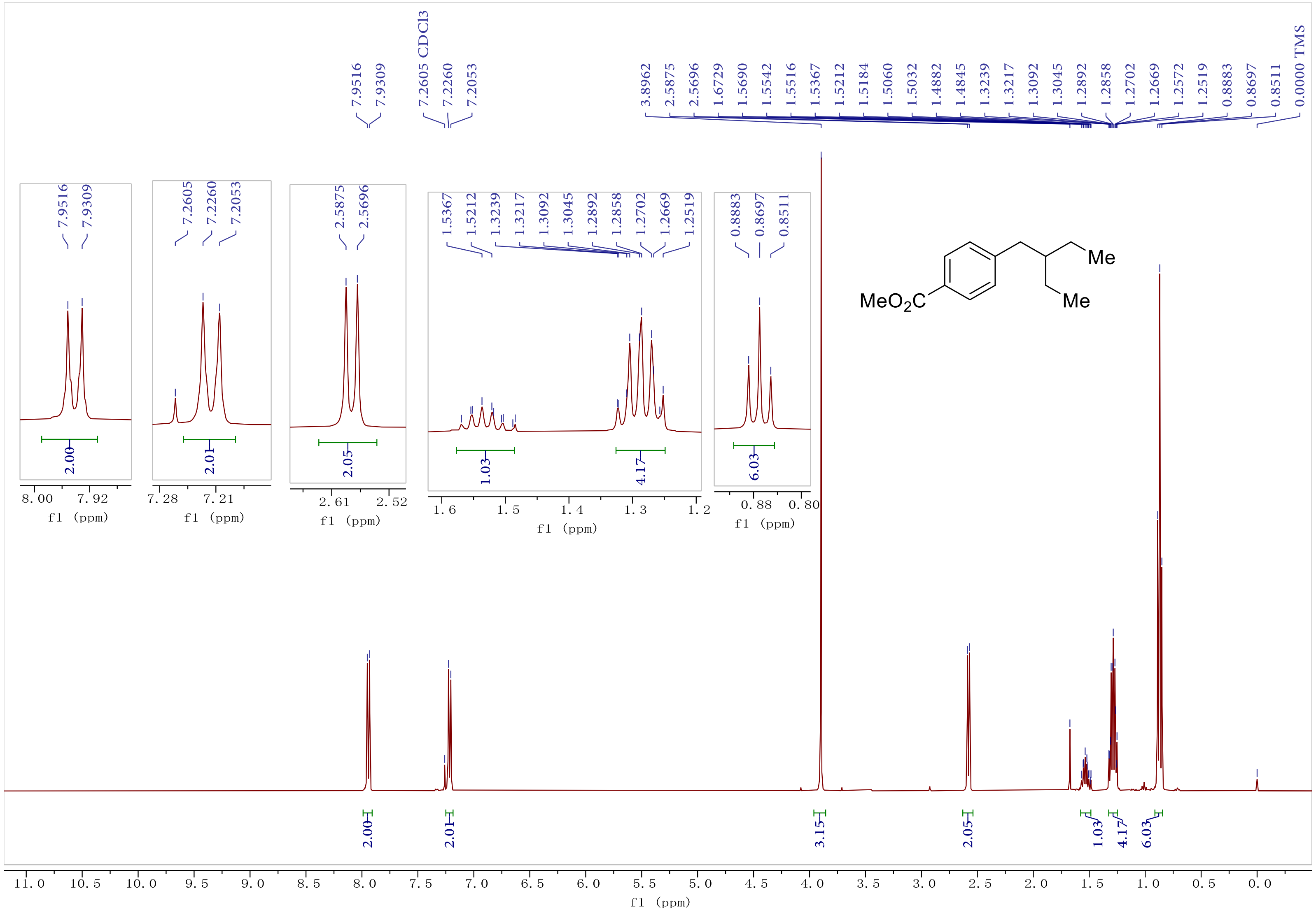
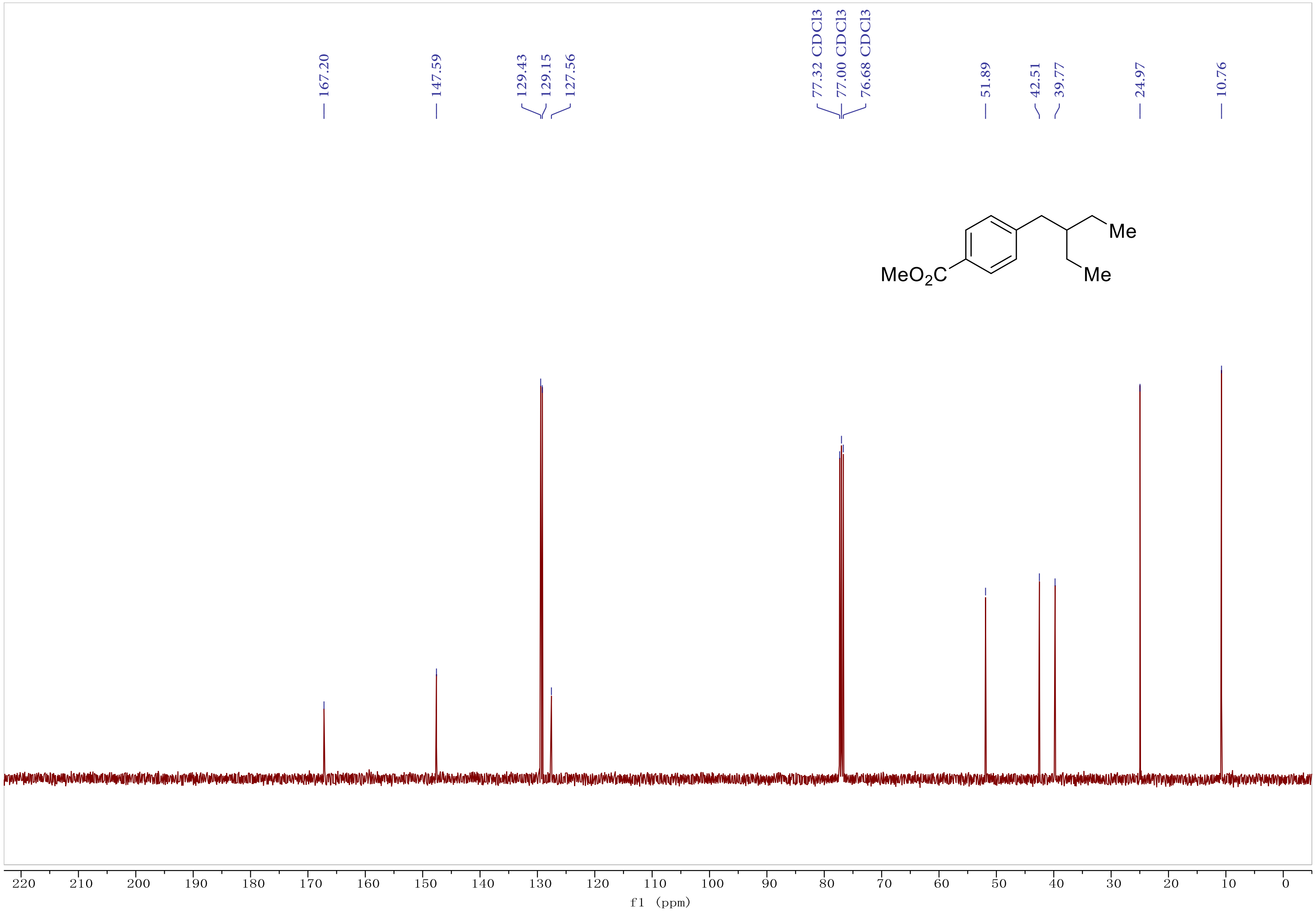


7.22. Methyl 4-(2-ethylbutyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

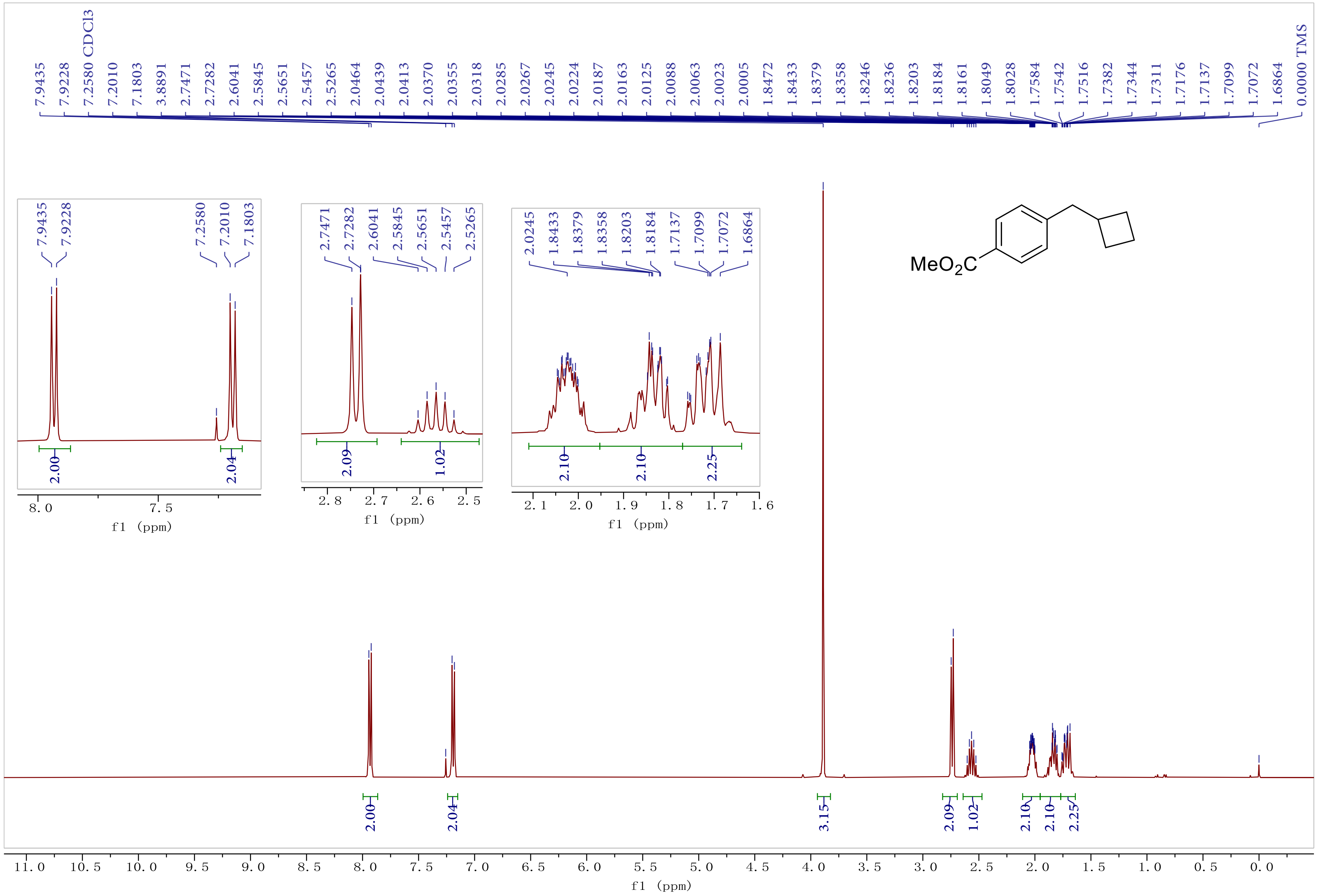


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

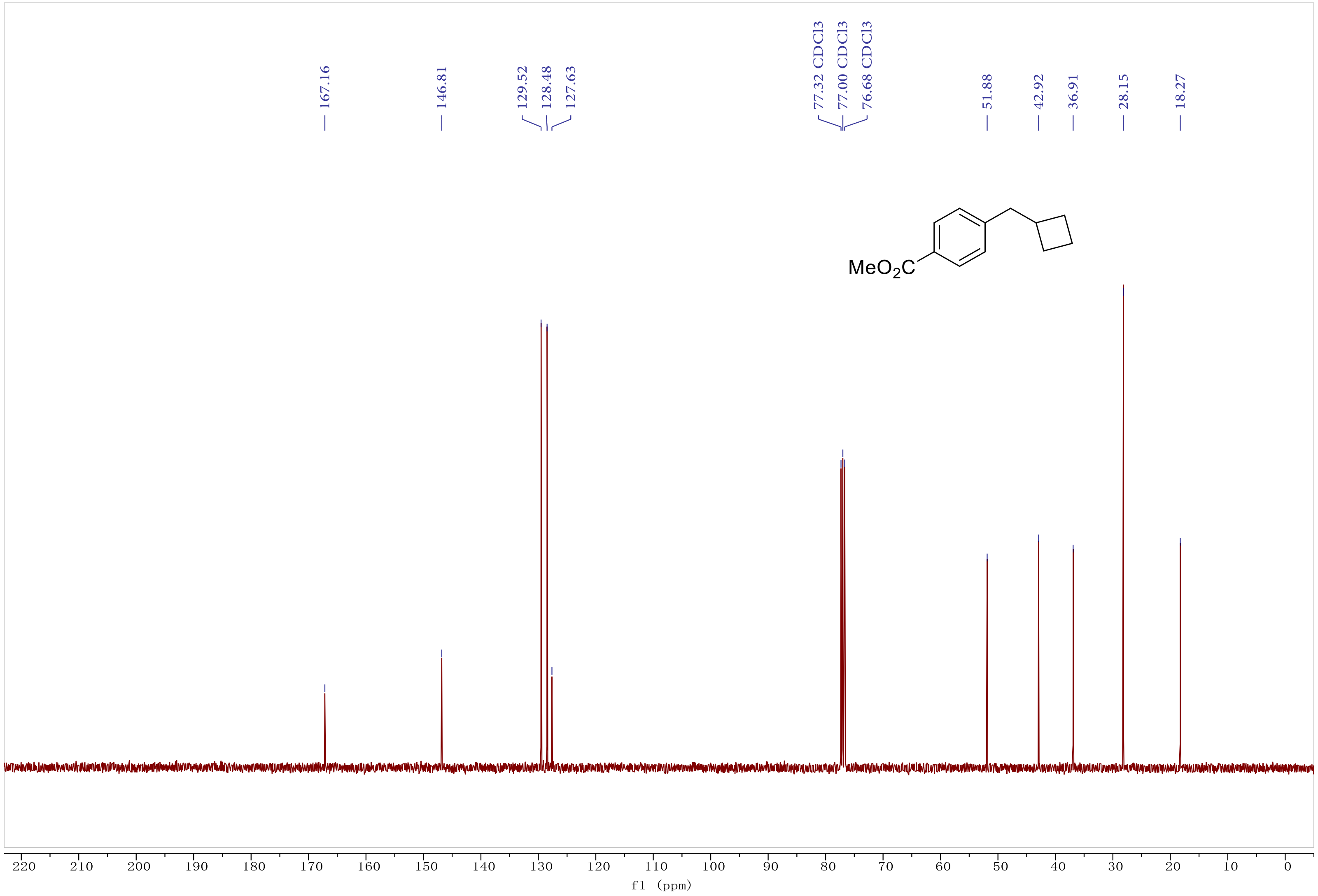


7.23. Methyl 4-(cyclobutylmethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

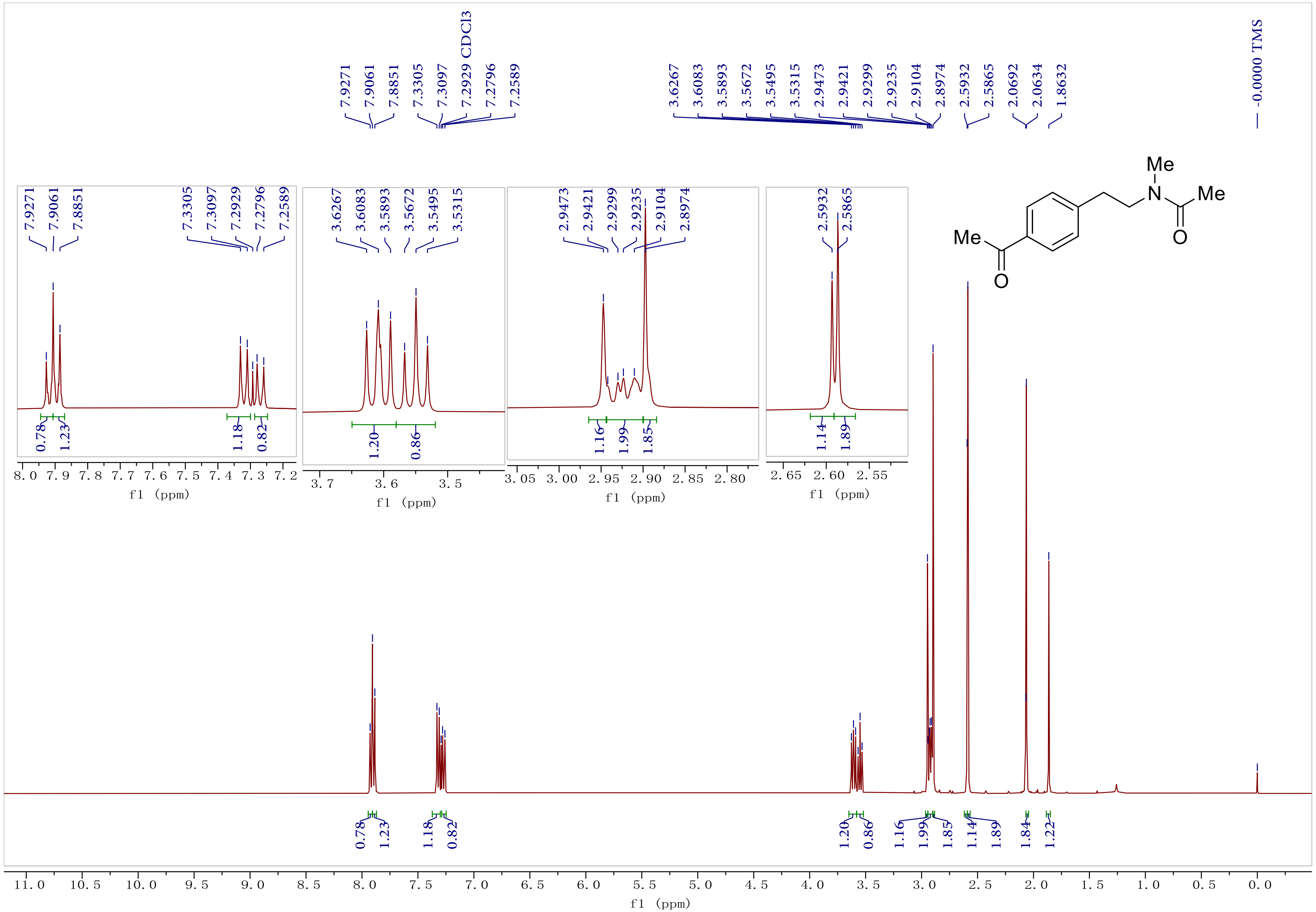


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

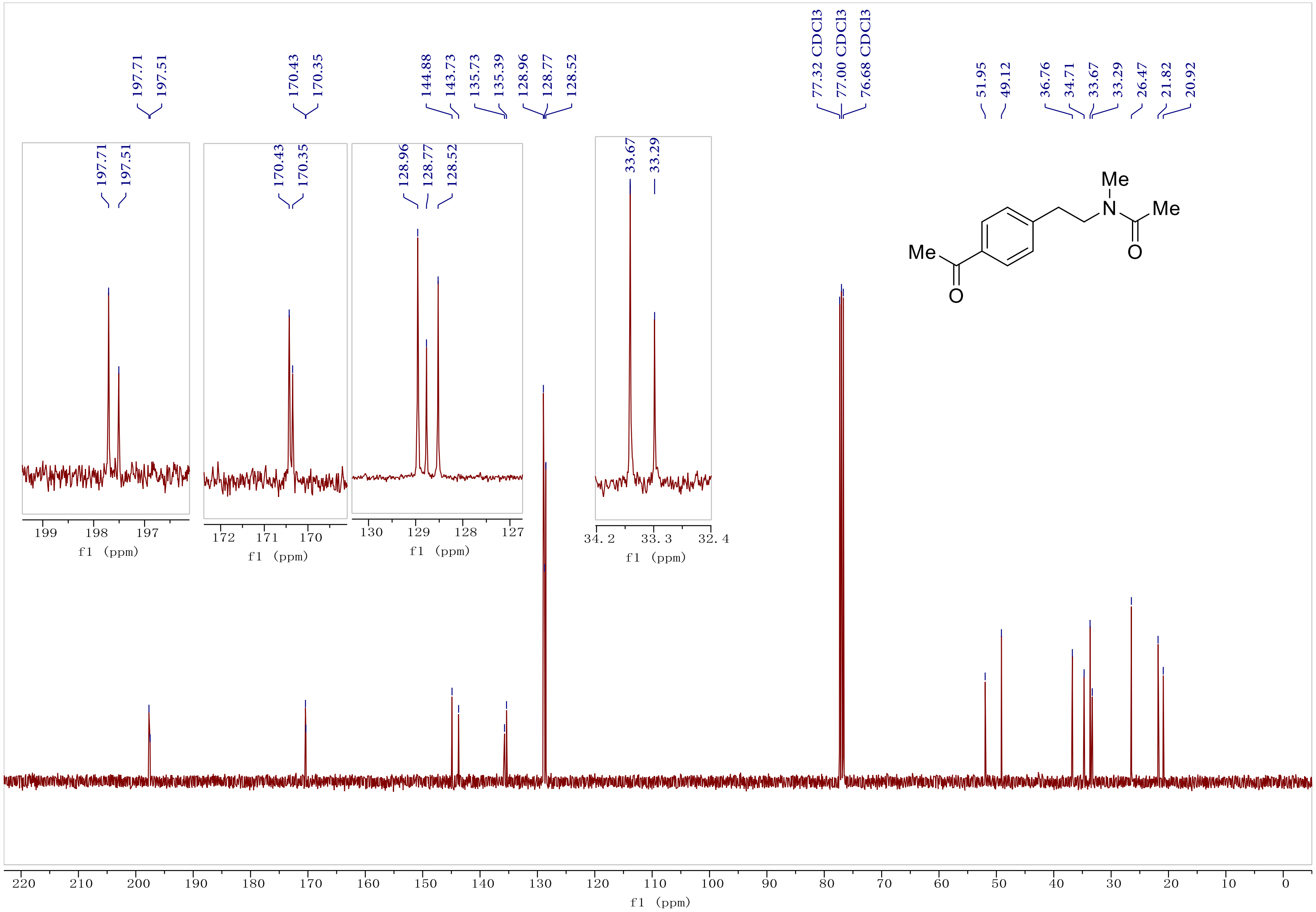


7.24. *N*-(4-Acetylphenethyl)-*N*-methylacetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

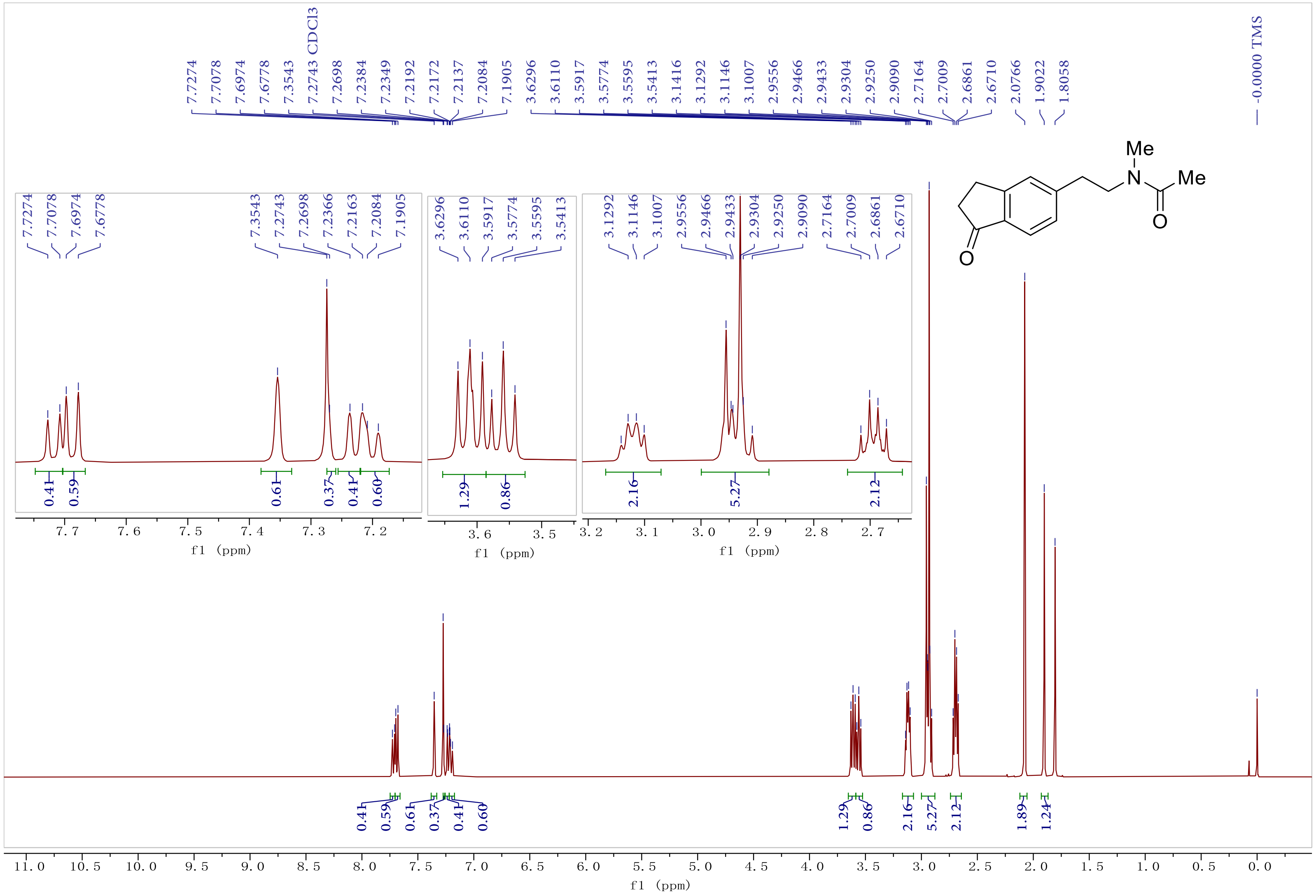


¹³C NMR spectrum (100 MHz) in CDCl$_3$

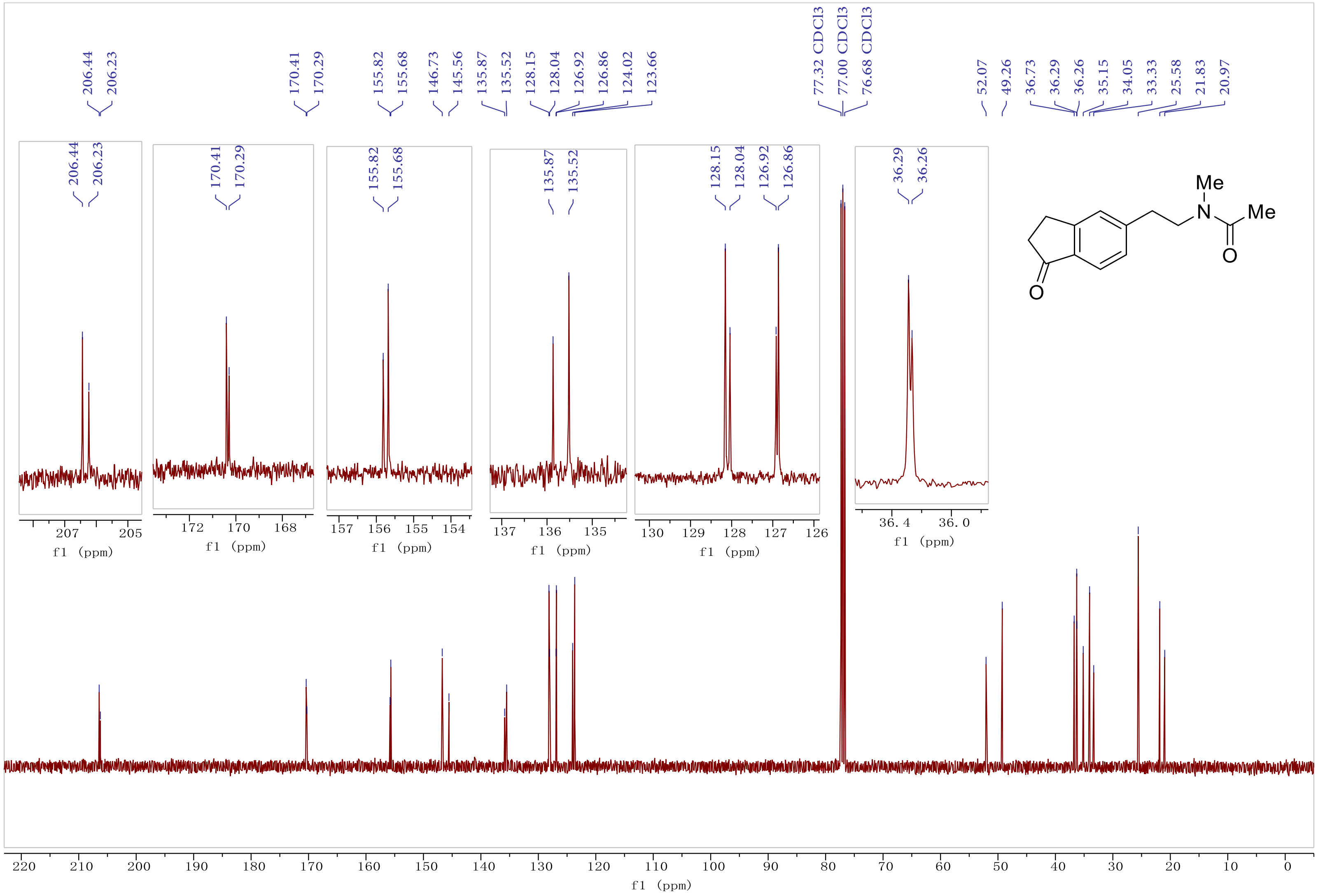


7.25. *N*-Methyl-*N*-(2-(1-oxo-2,3-dihydro-1*H*-inden-5-yl)ethyl)acetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

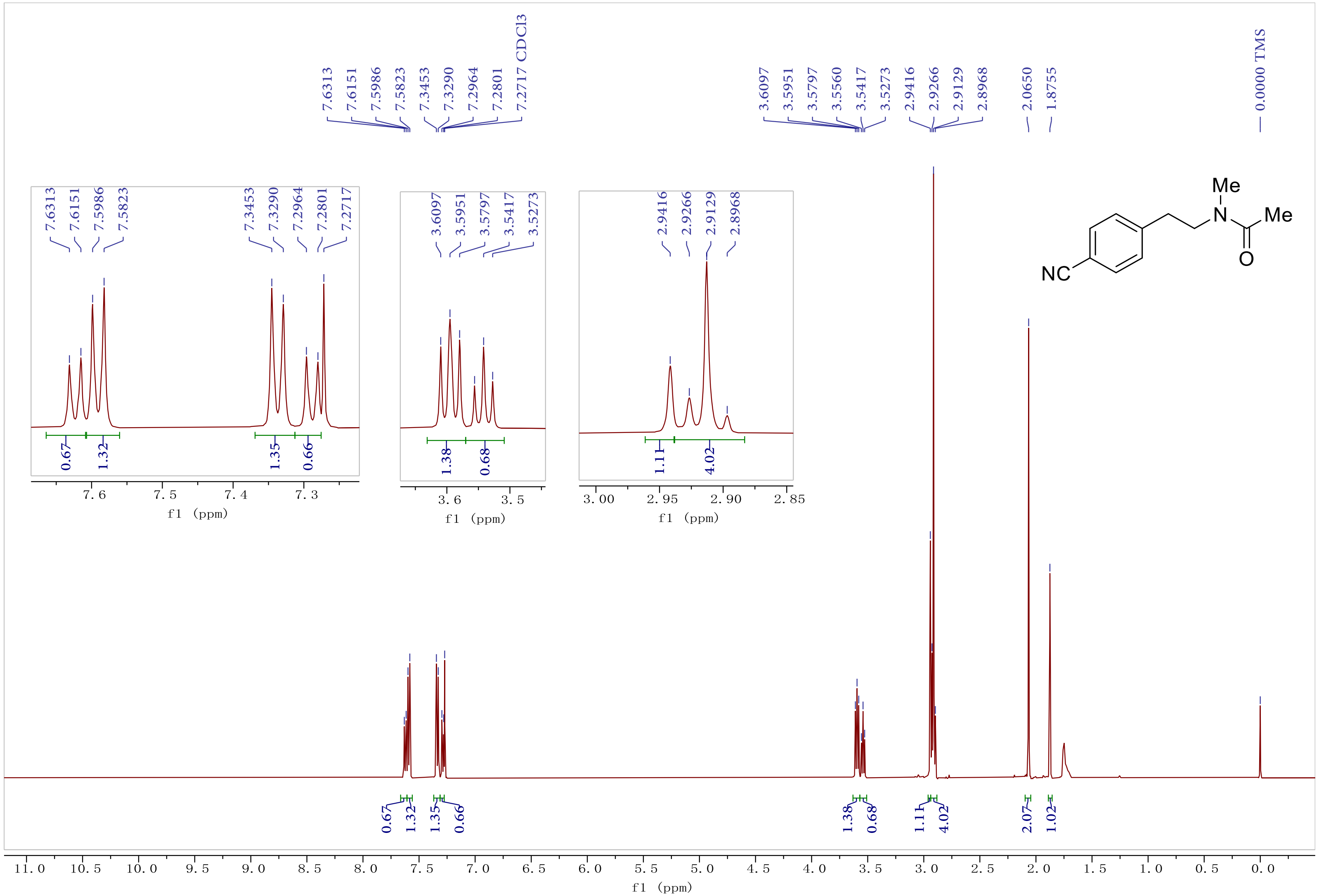


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

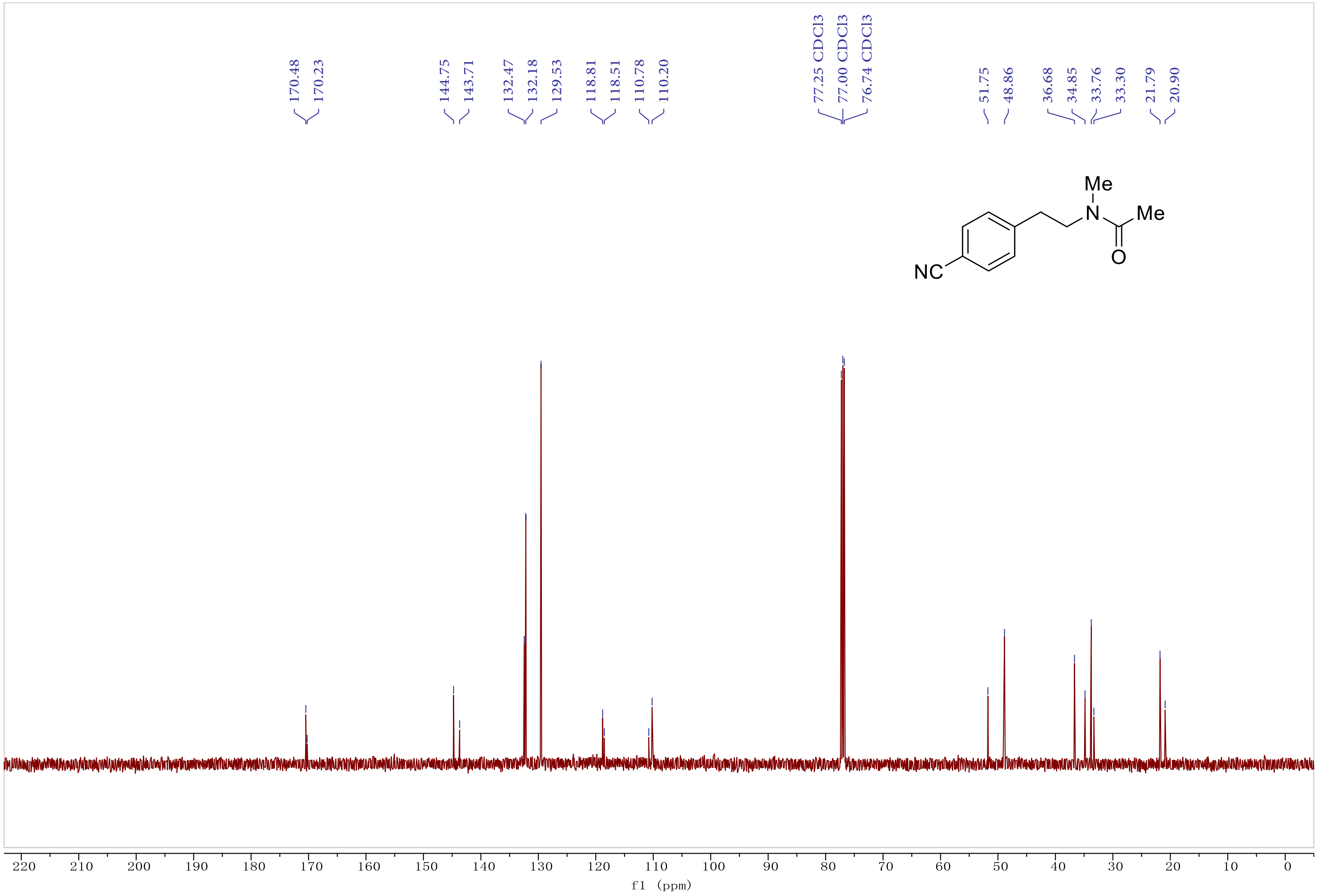


7.26. *N*-(4-Cyanophenethyl)-*N*-methylacetamide

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

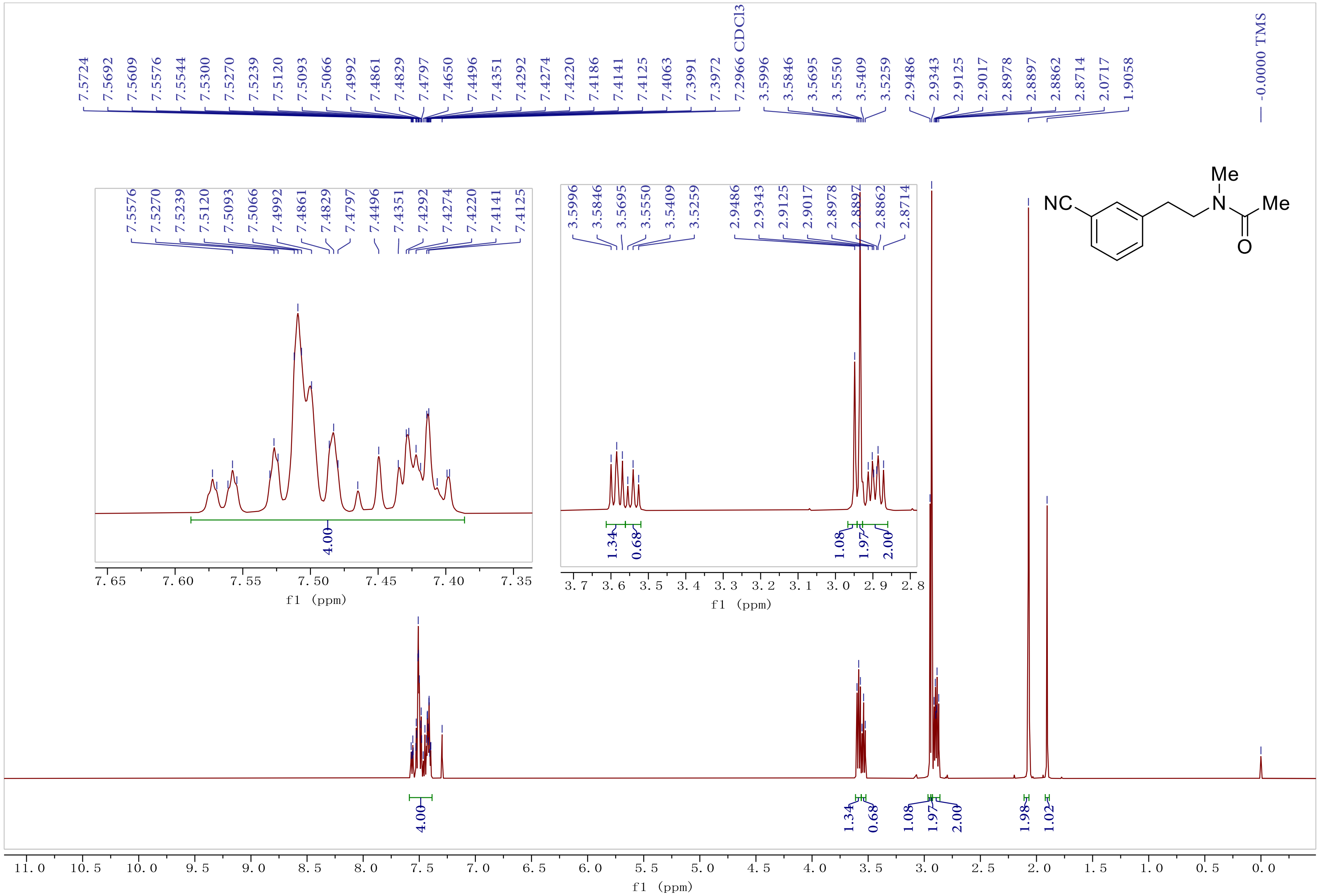


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

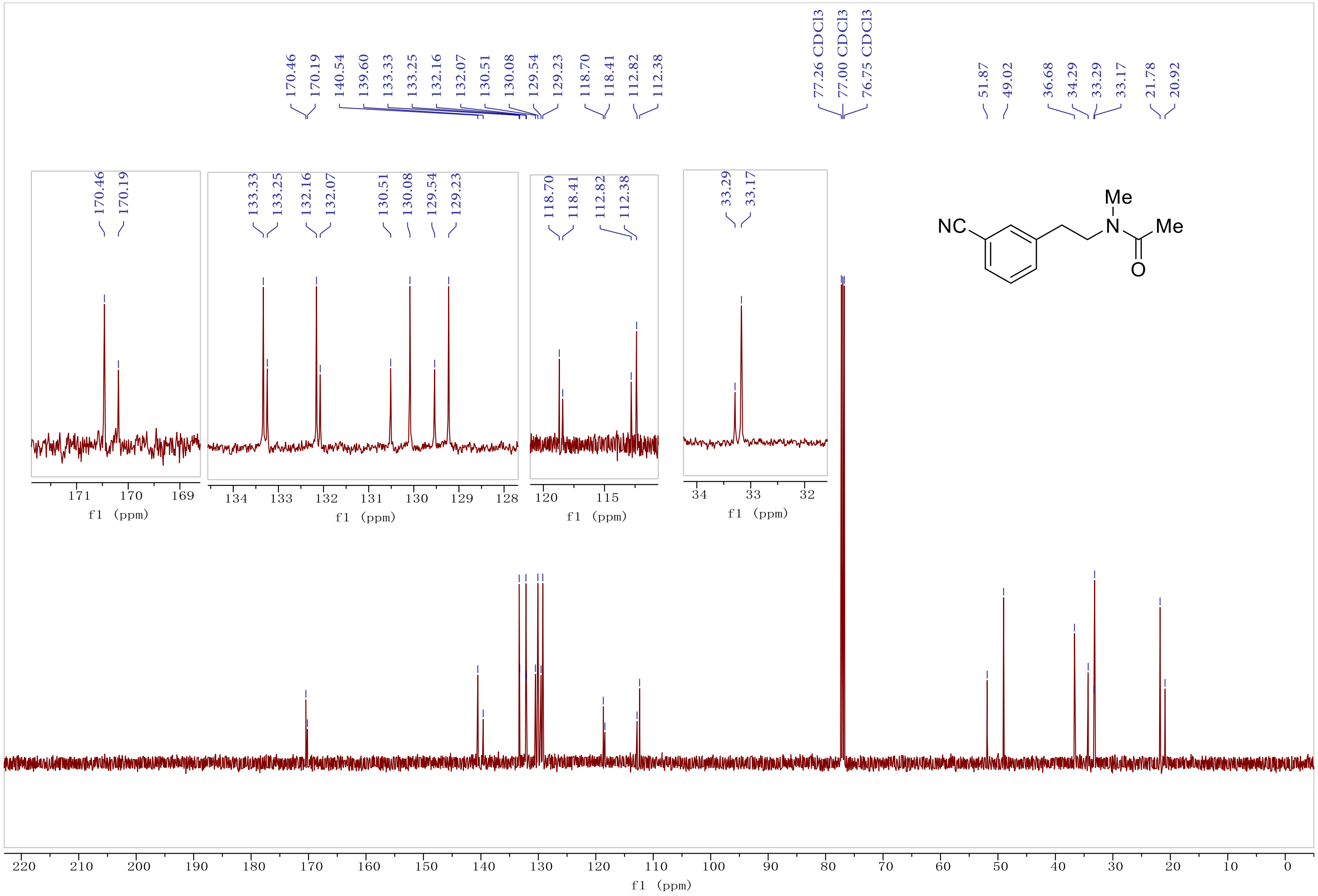


7.27. *N*-(3-Cyanophenethyl)-*N*-methylacetamide

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

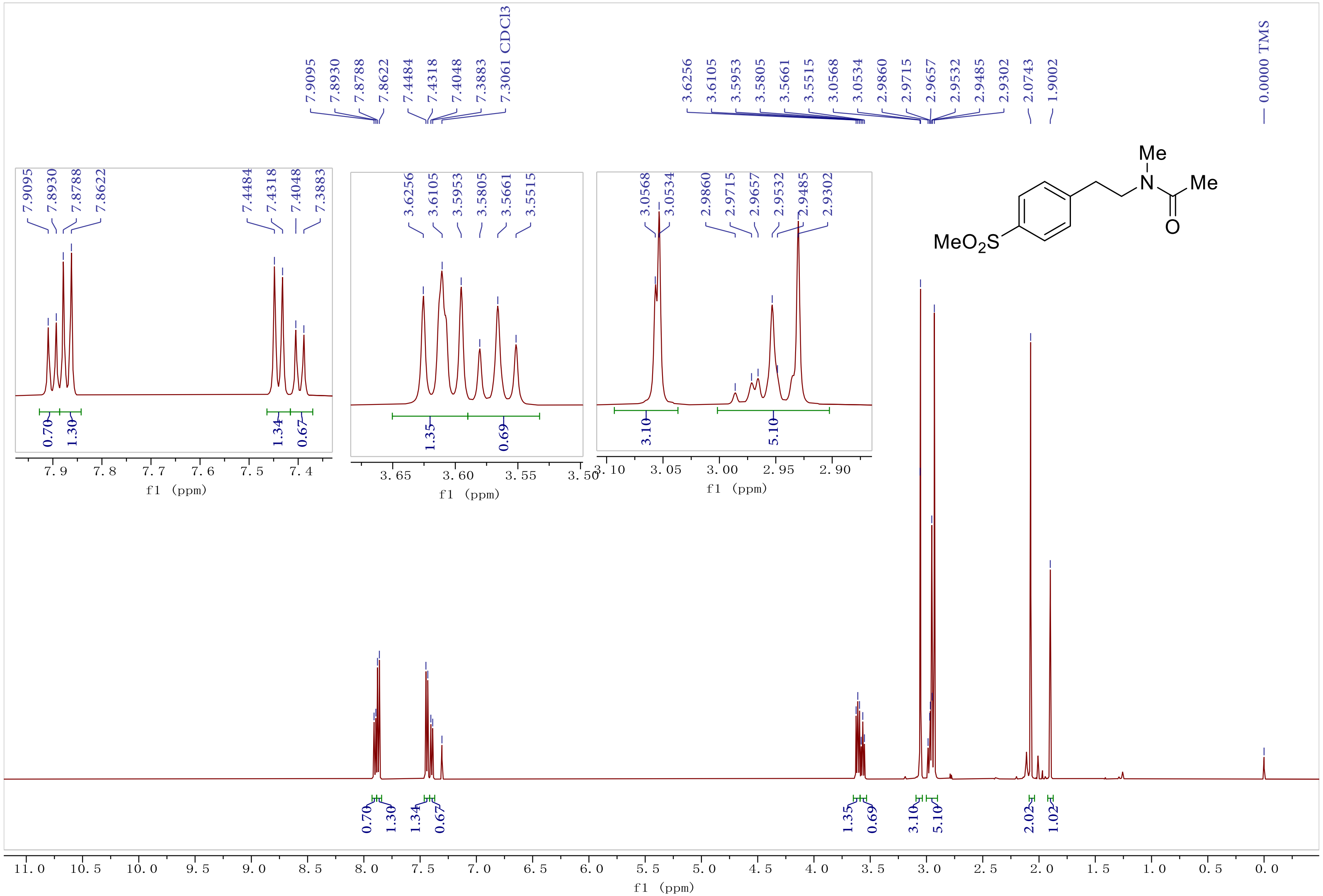


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

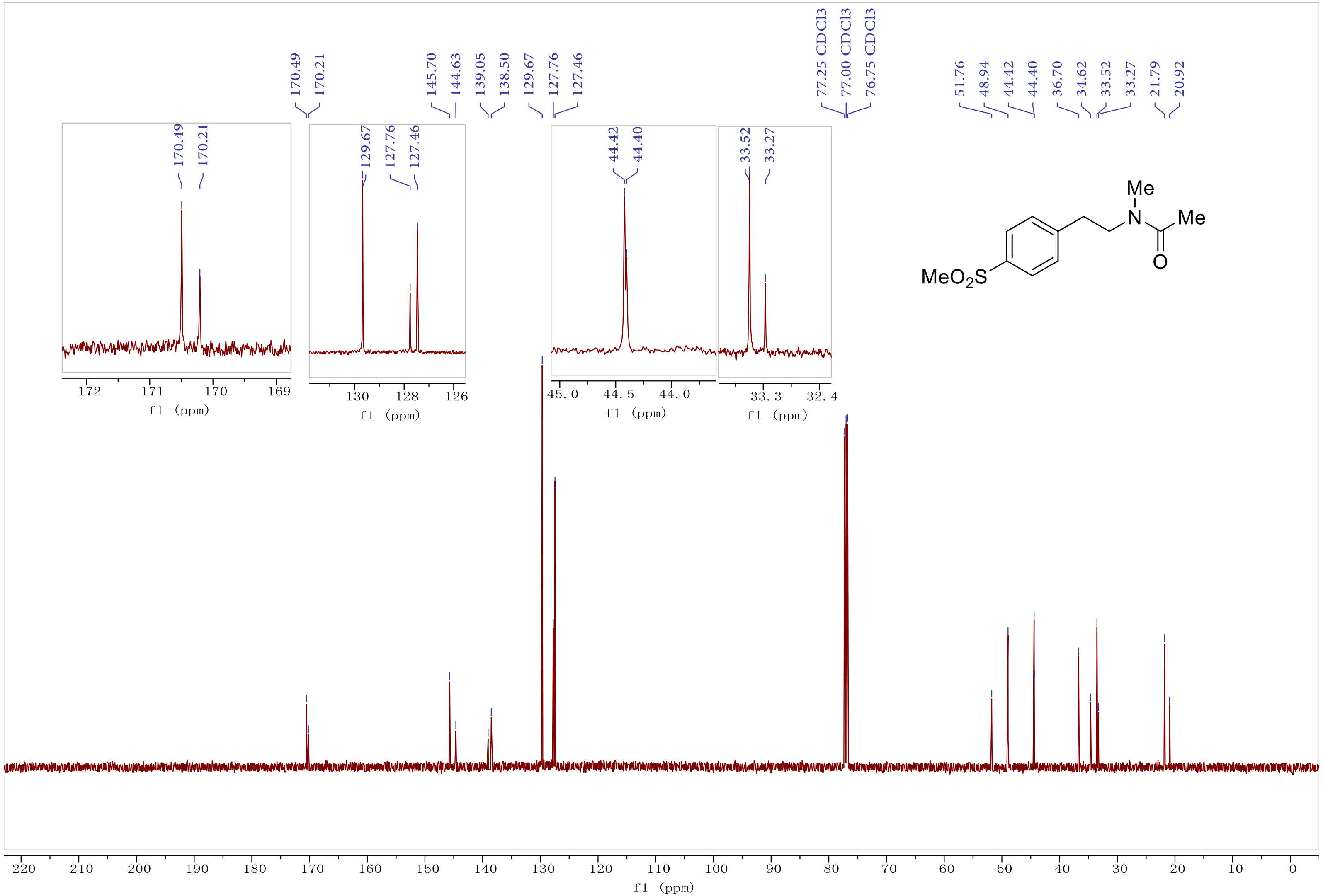


7.28. *N*-Methyl-*N*-(4-(methylsulfonyl)phenethyl)acetamide

^{1}H NMR spectrum (500 MHz) in CDCl$_3$

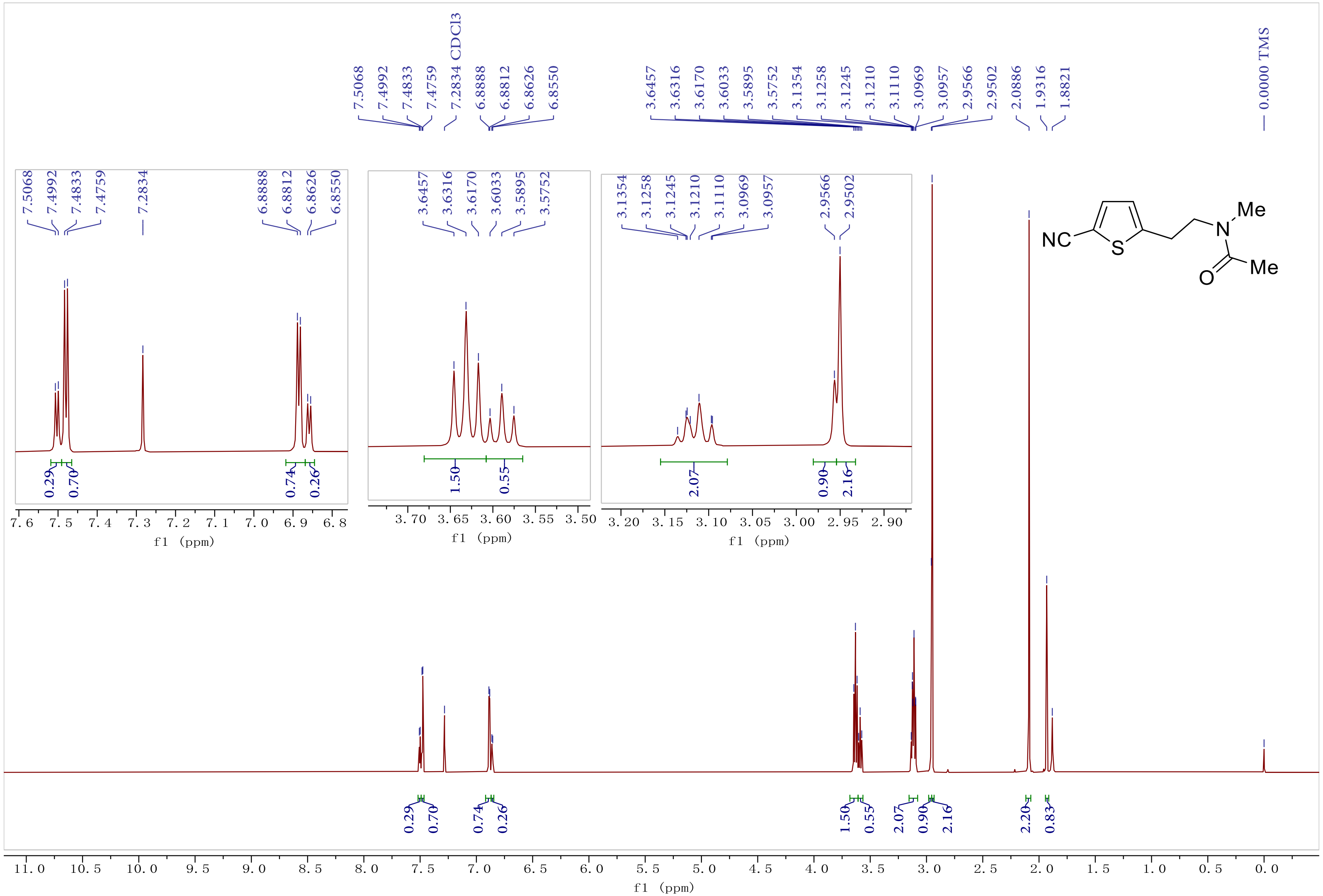


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

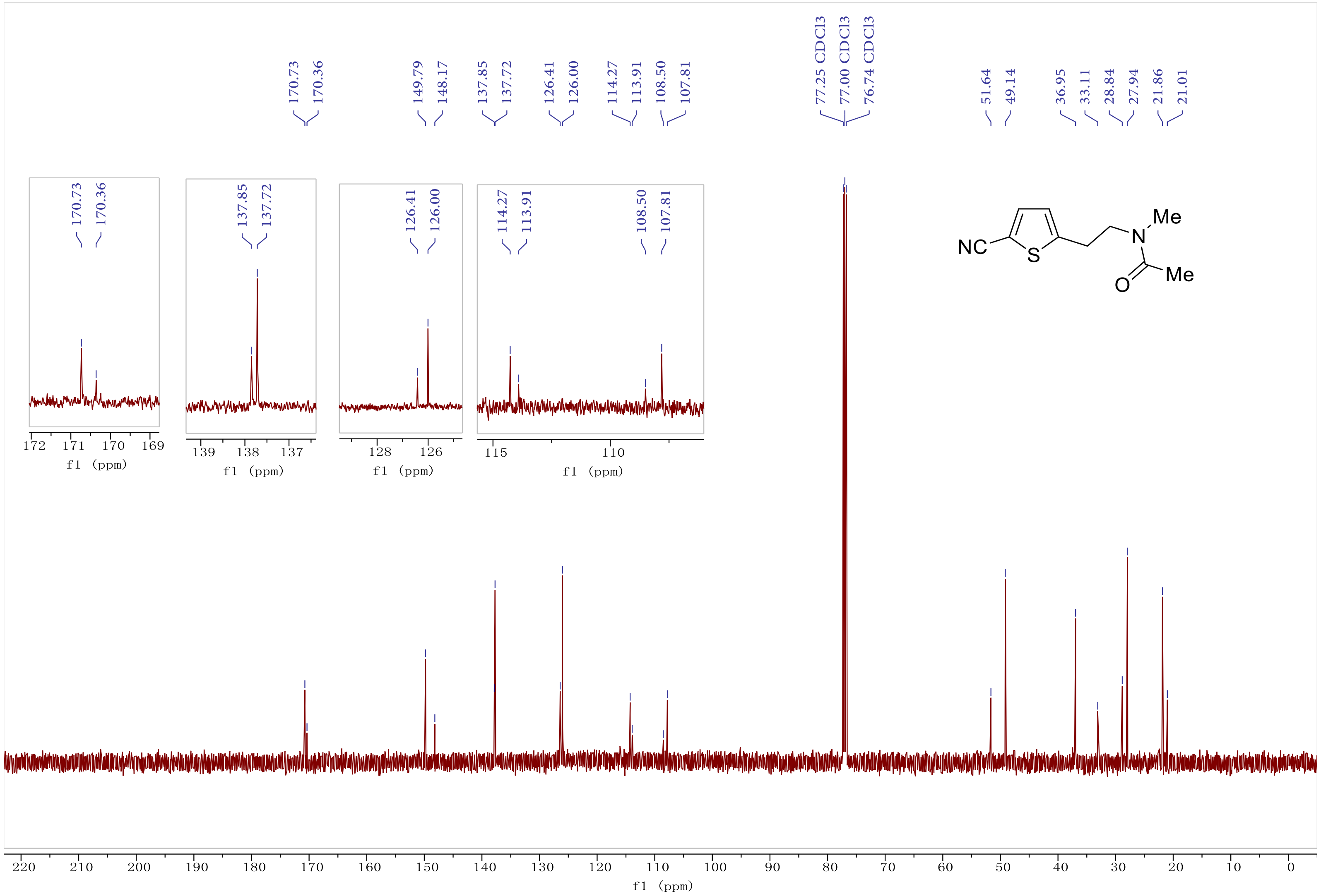


7.29. *N*-(2-(5-Cyanothiophen-2-yl)ethyl)-*N*-methylacetamide

^{1}H NMR spectrum (500 MHz) in CDCl$_3$

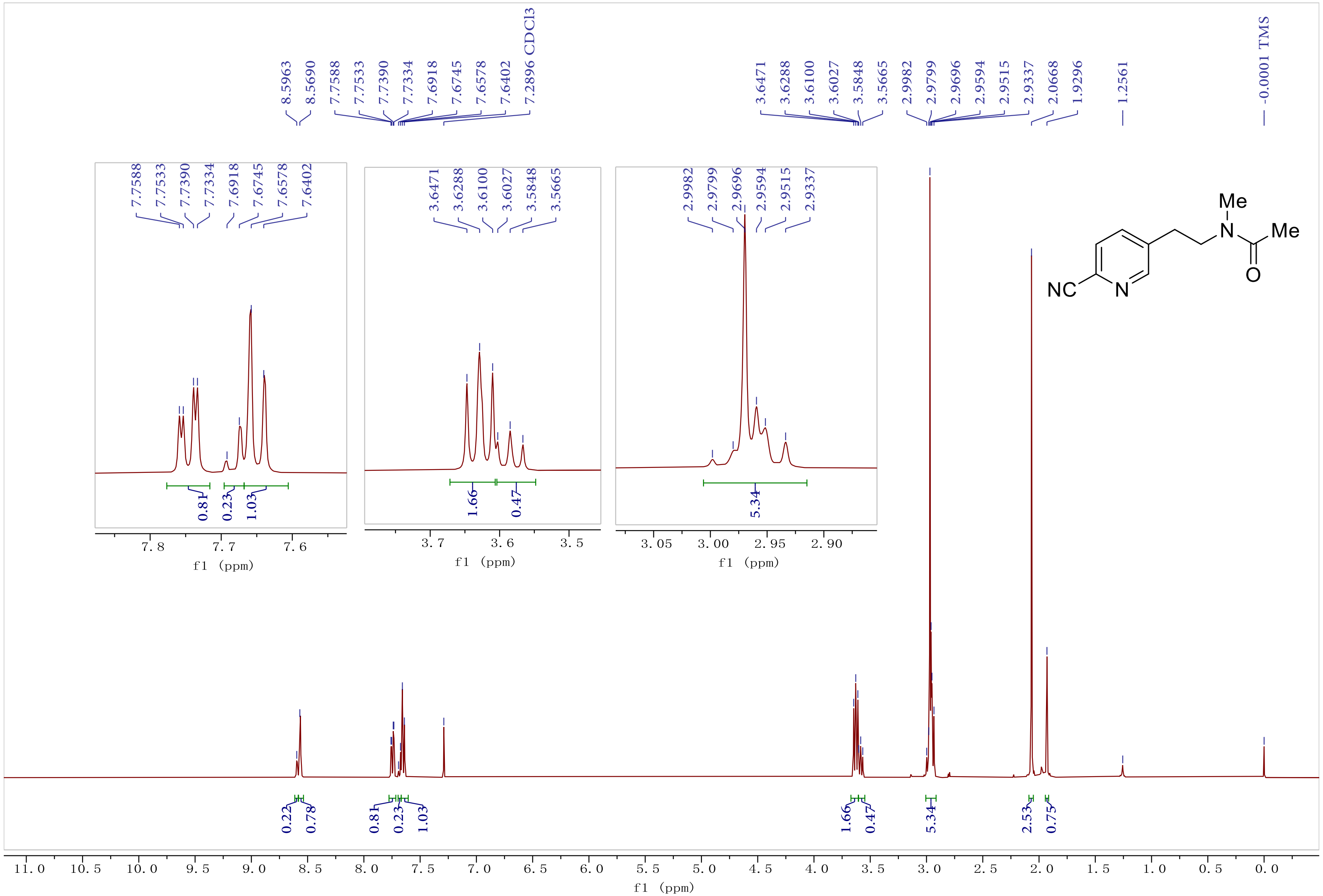


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

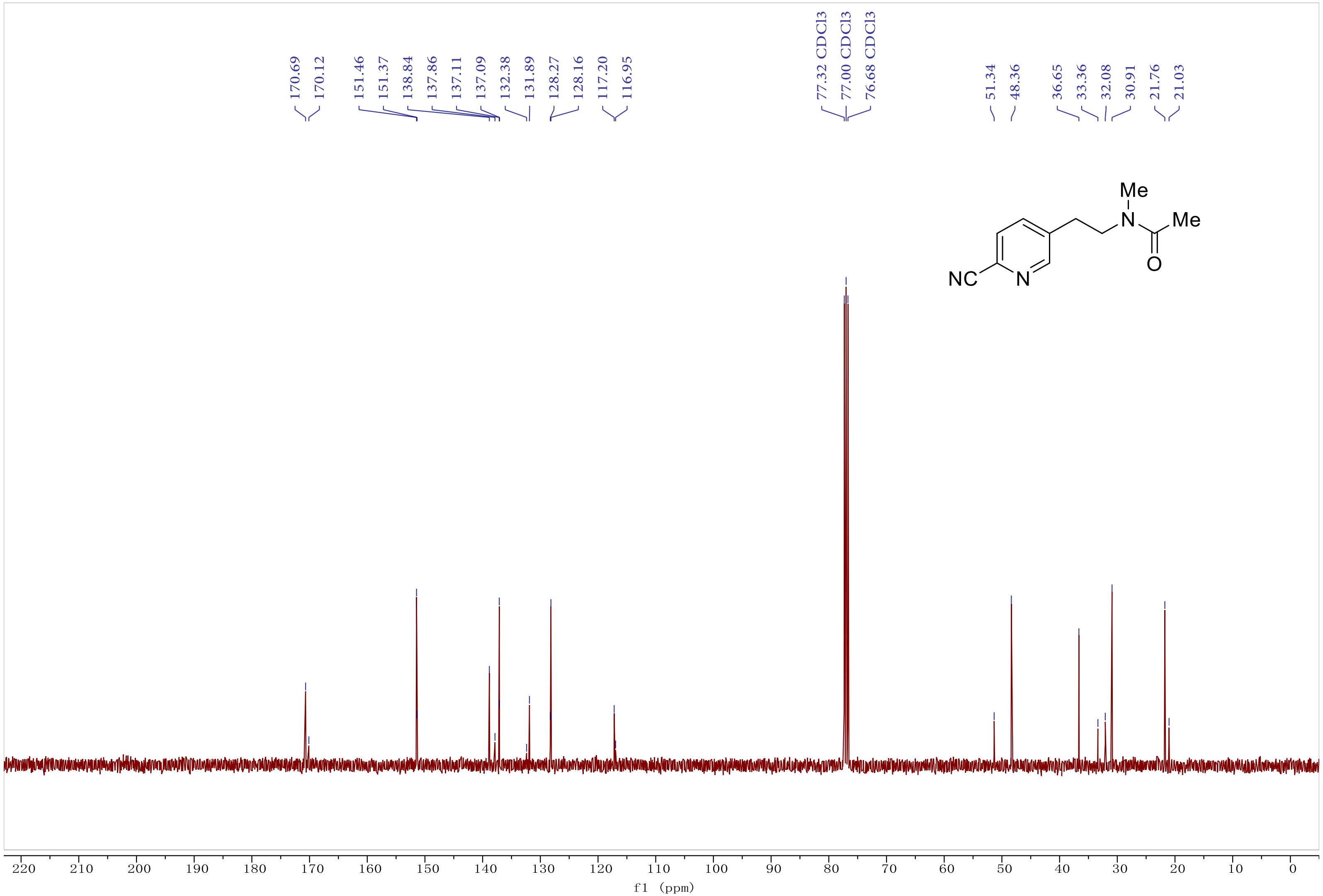


7.30. *N*-(2-(6-Cyanopyridin-3-yl)ethyl)-*N*-methylacetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

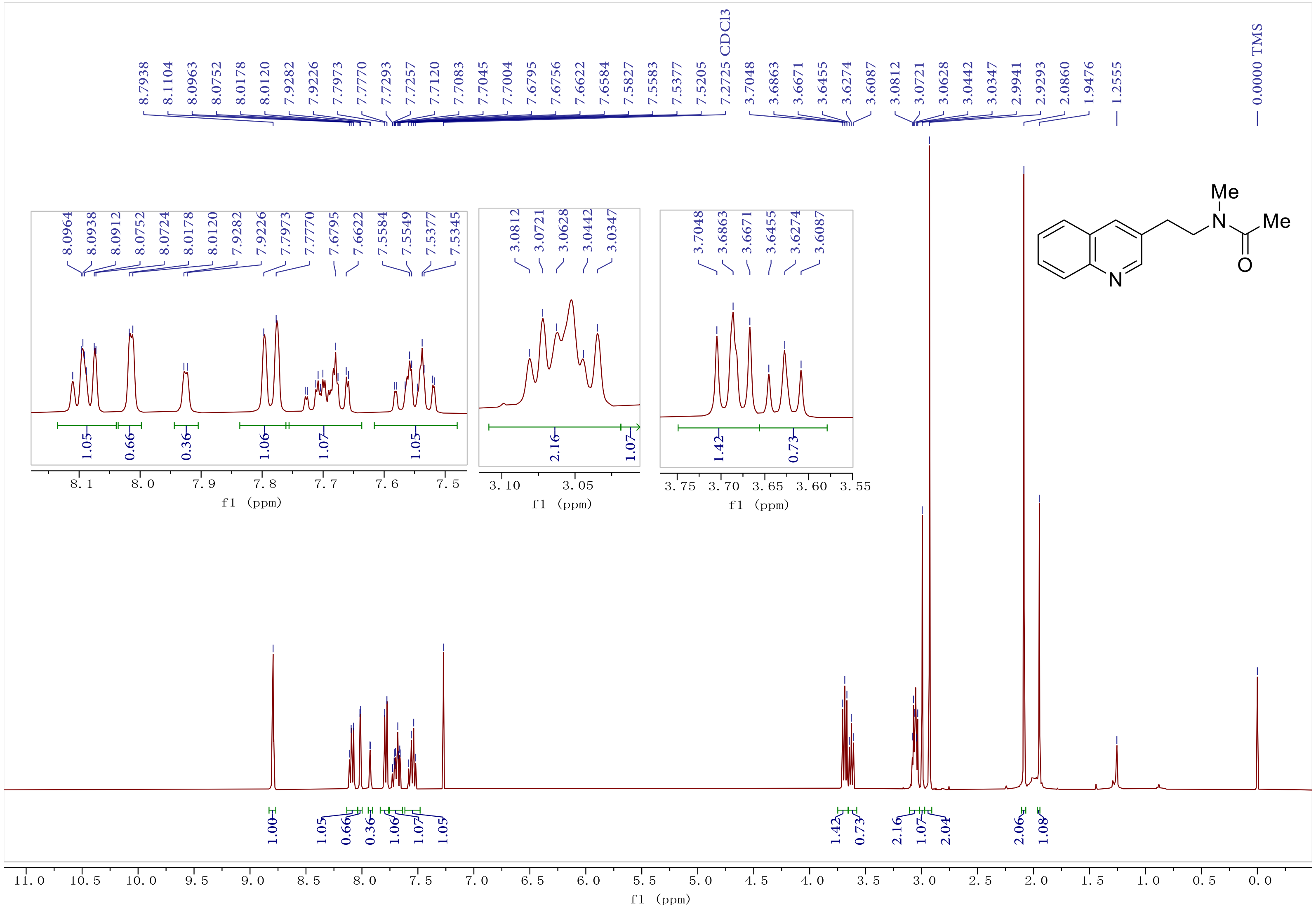


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

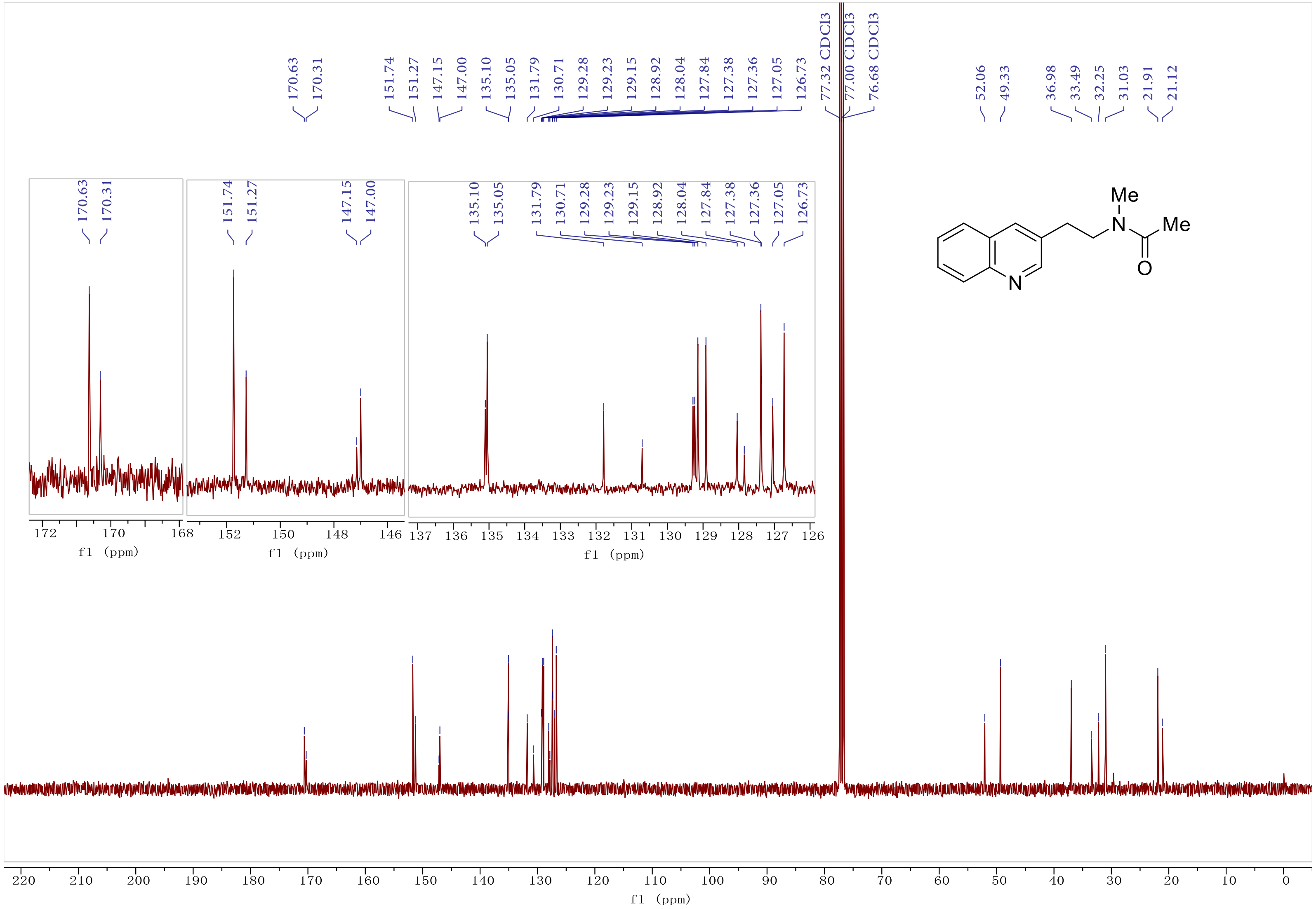


7.31. *N*-Methyl-*N*-(2-(quinolin-3-yl)ethyl)acetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

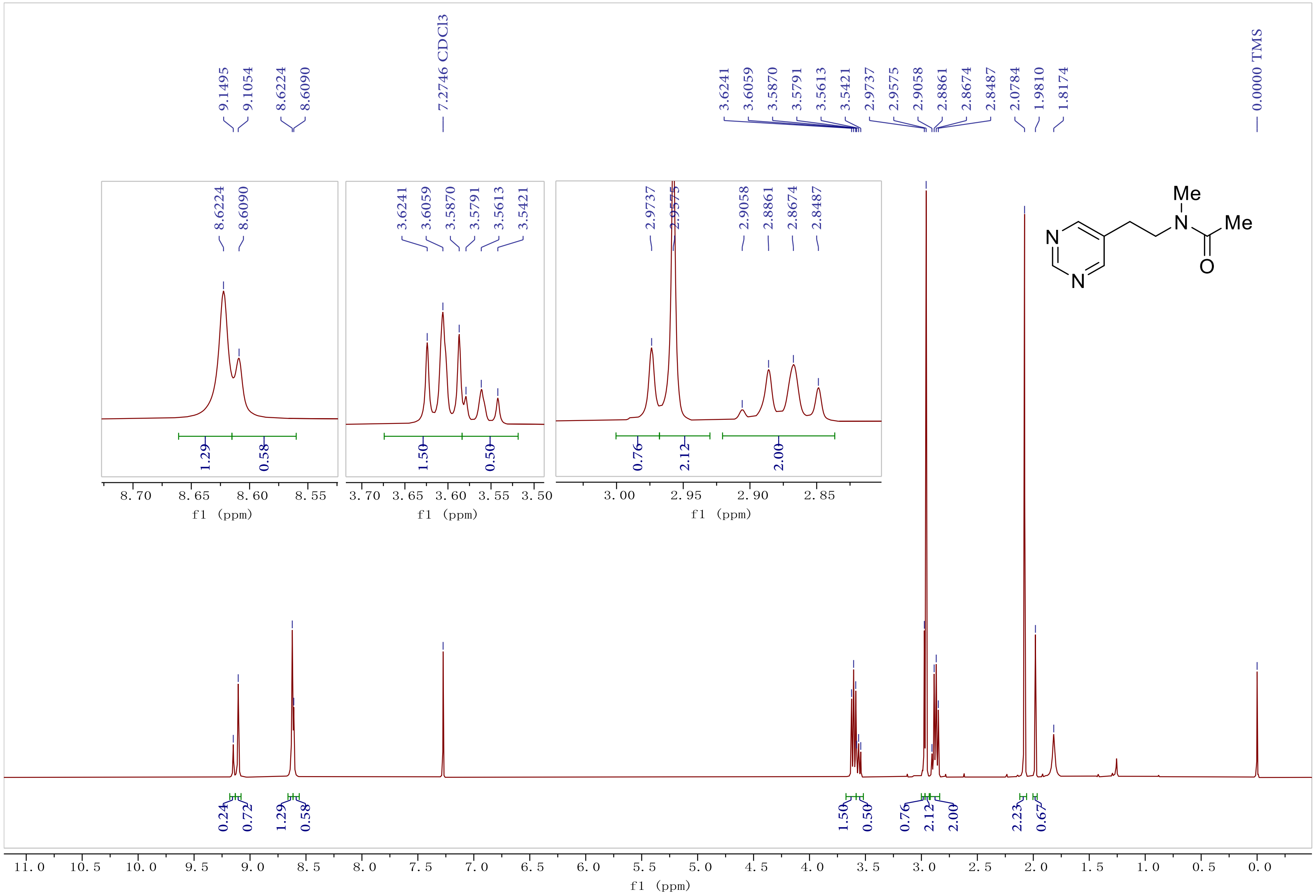


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

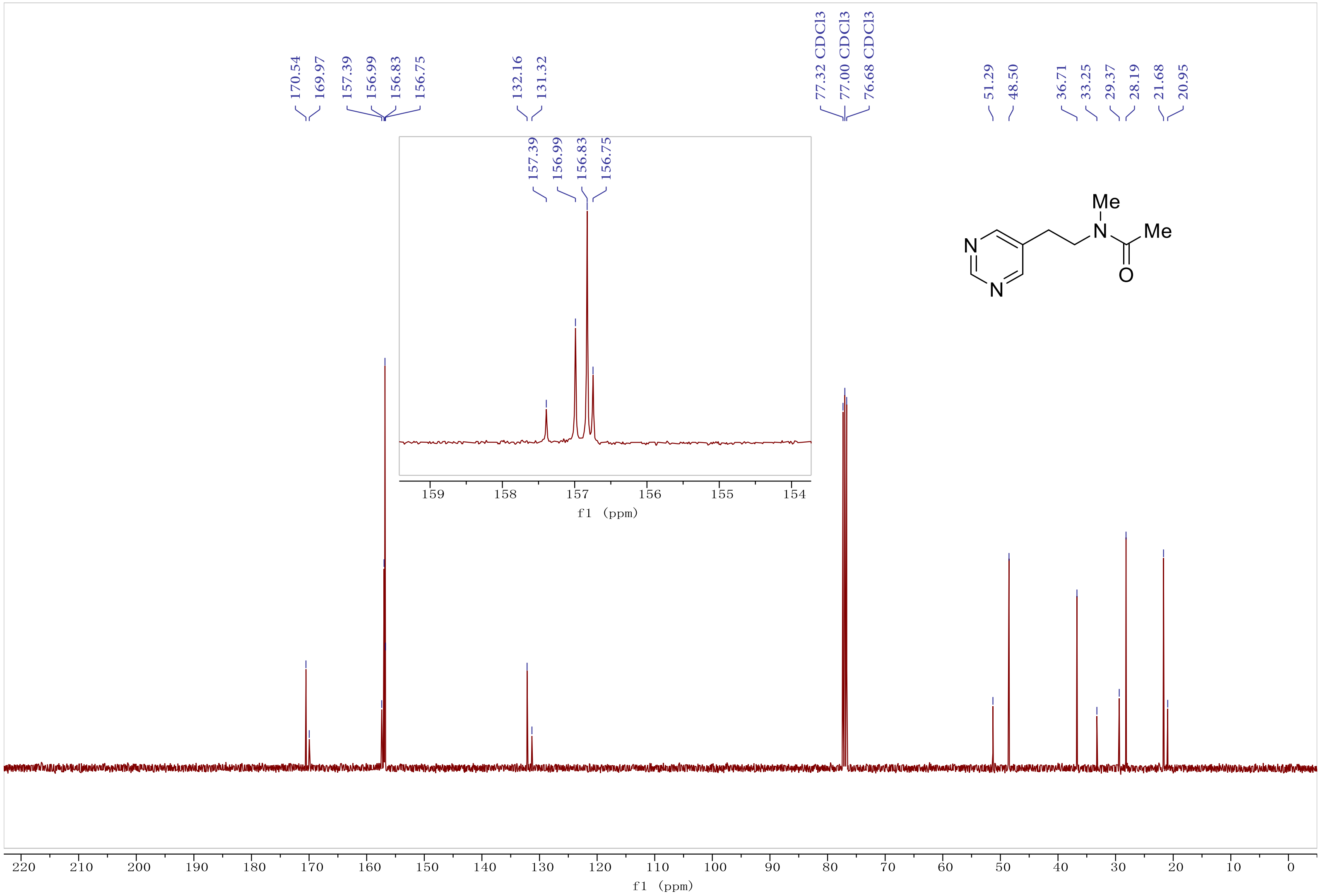


7.32. *N*-Methyl-*N*-(2-(pyrimidin-5-yl)ethyl)acetamide

^{1}H NMR spectrum (400 MHz) in CDCl$_3$

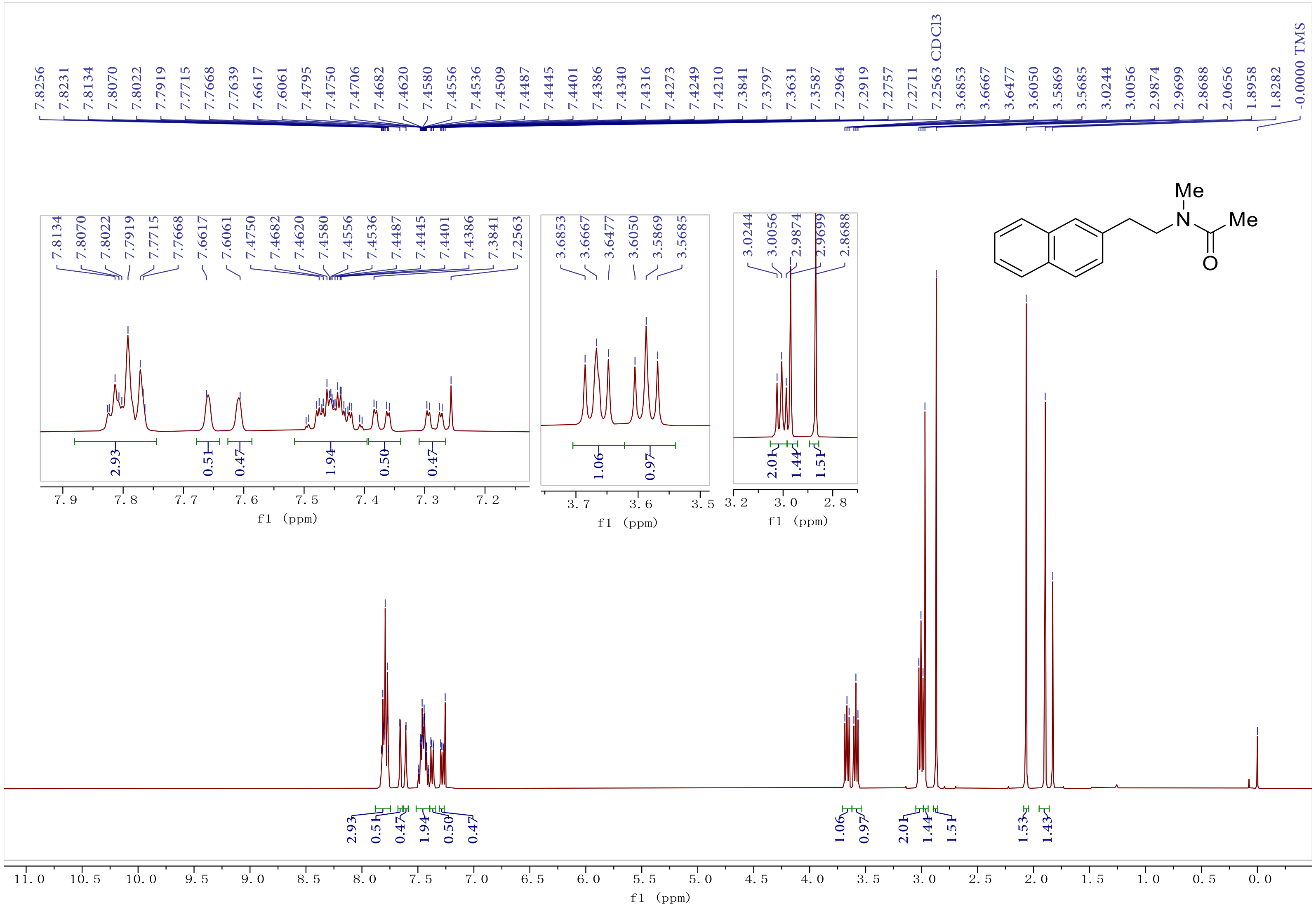


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

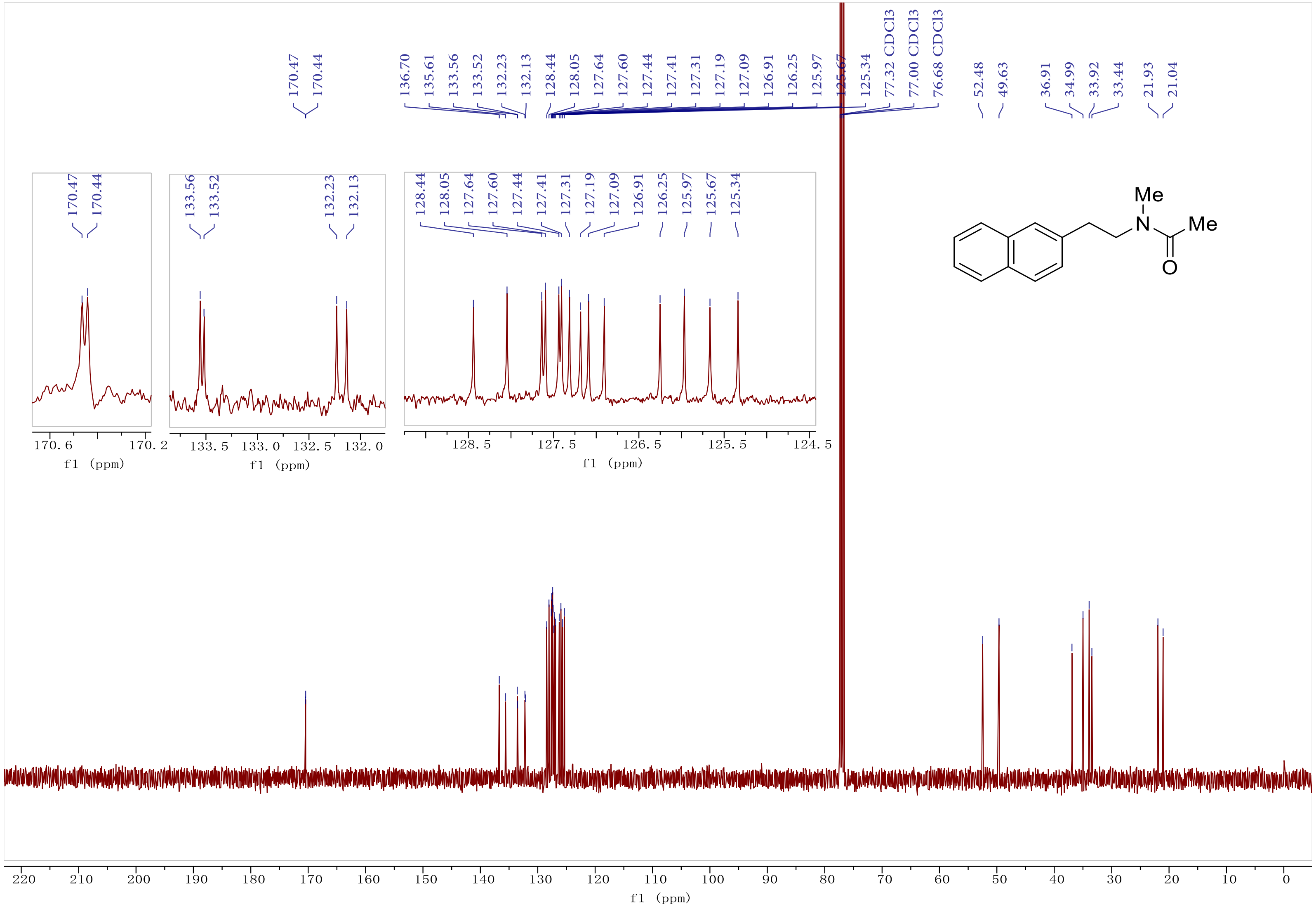


7.33. *N*-Methyl-*N*-(2-(naphthalen-2-yl)ethyl)acetamide

^{1}H NMR Spectrum (400 MHz) in $CDCl_3$

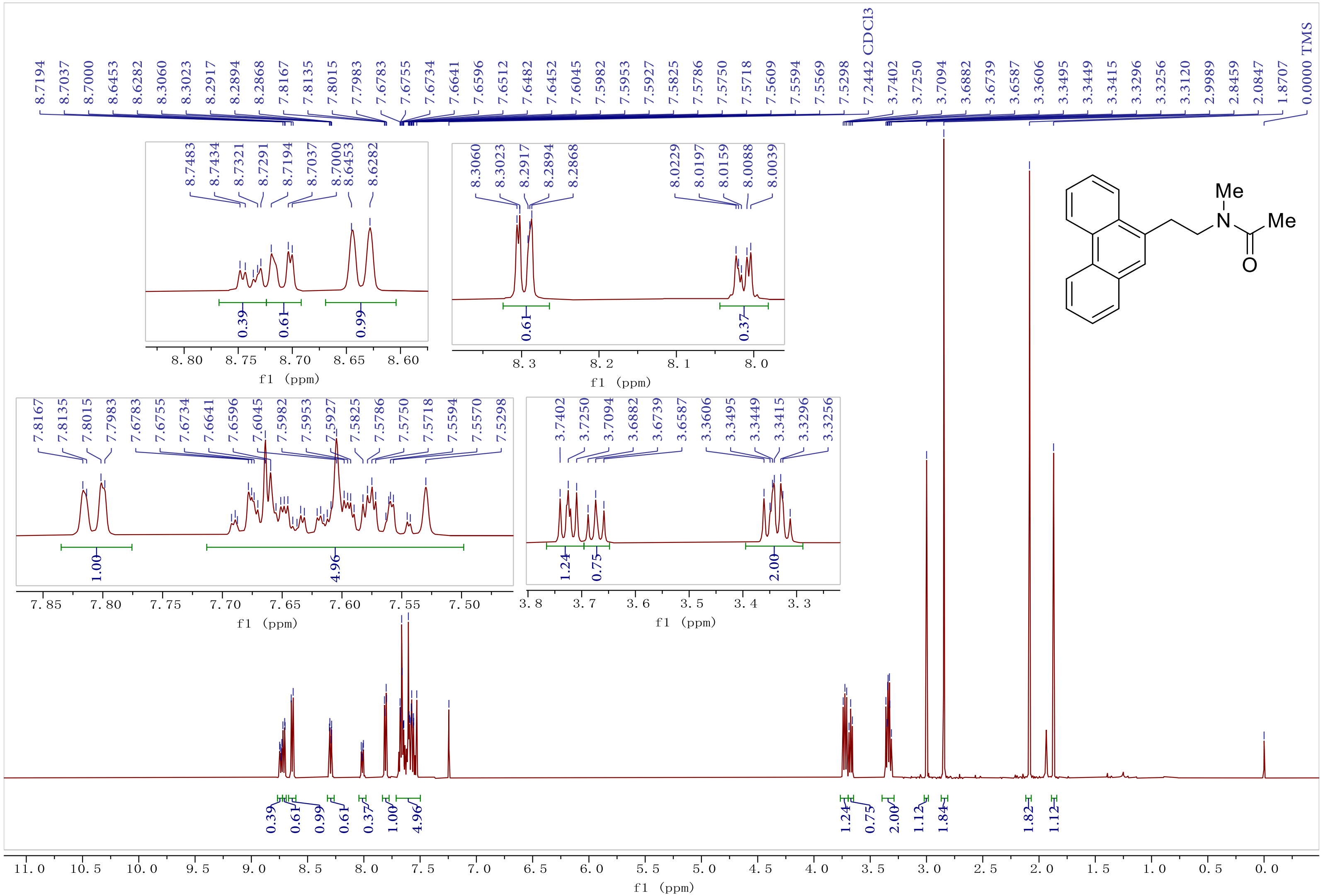


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

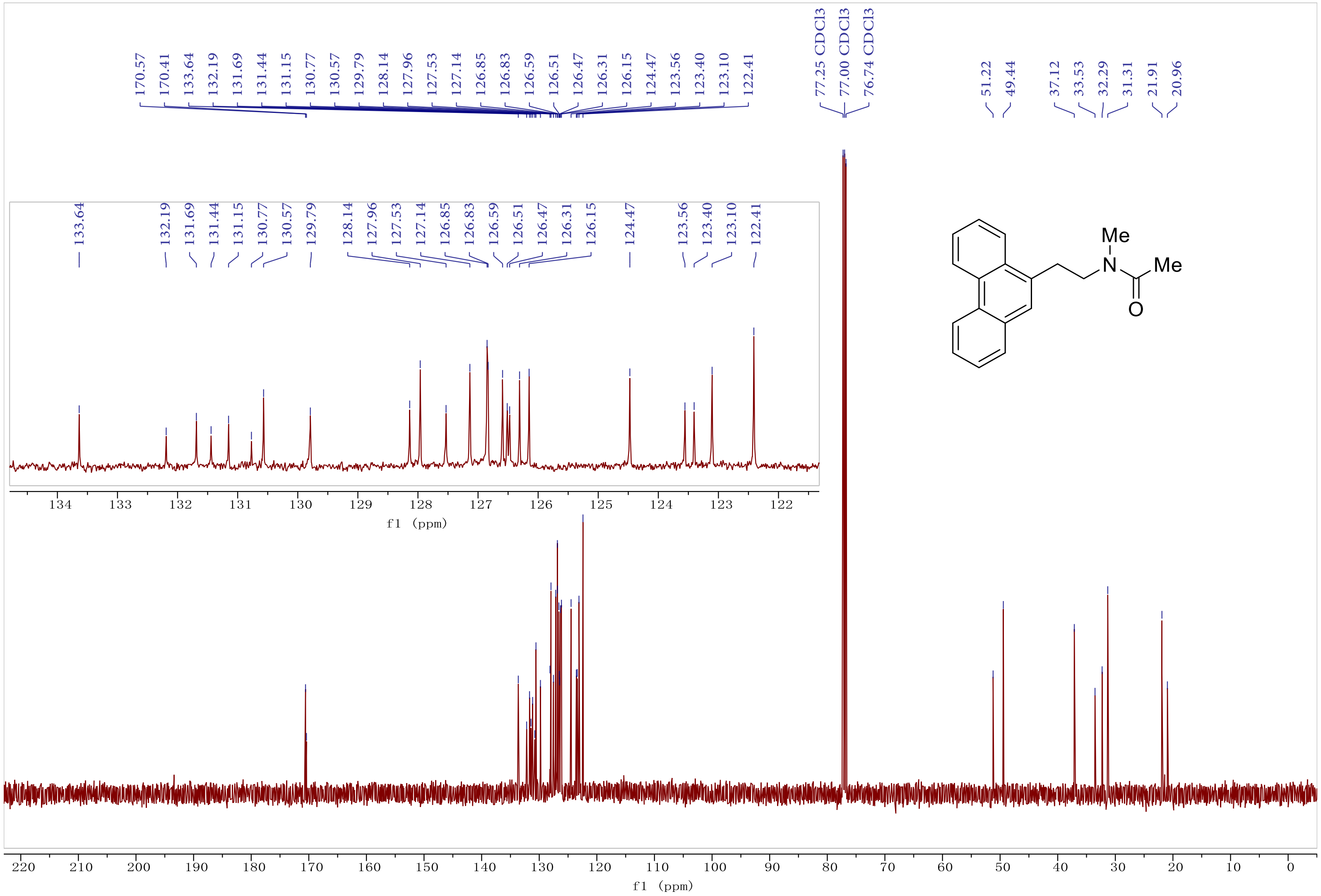


7.34. *N*-Methyl-*N*-(2-(phenanthren-9-yl)ethyl)acetamide

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

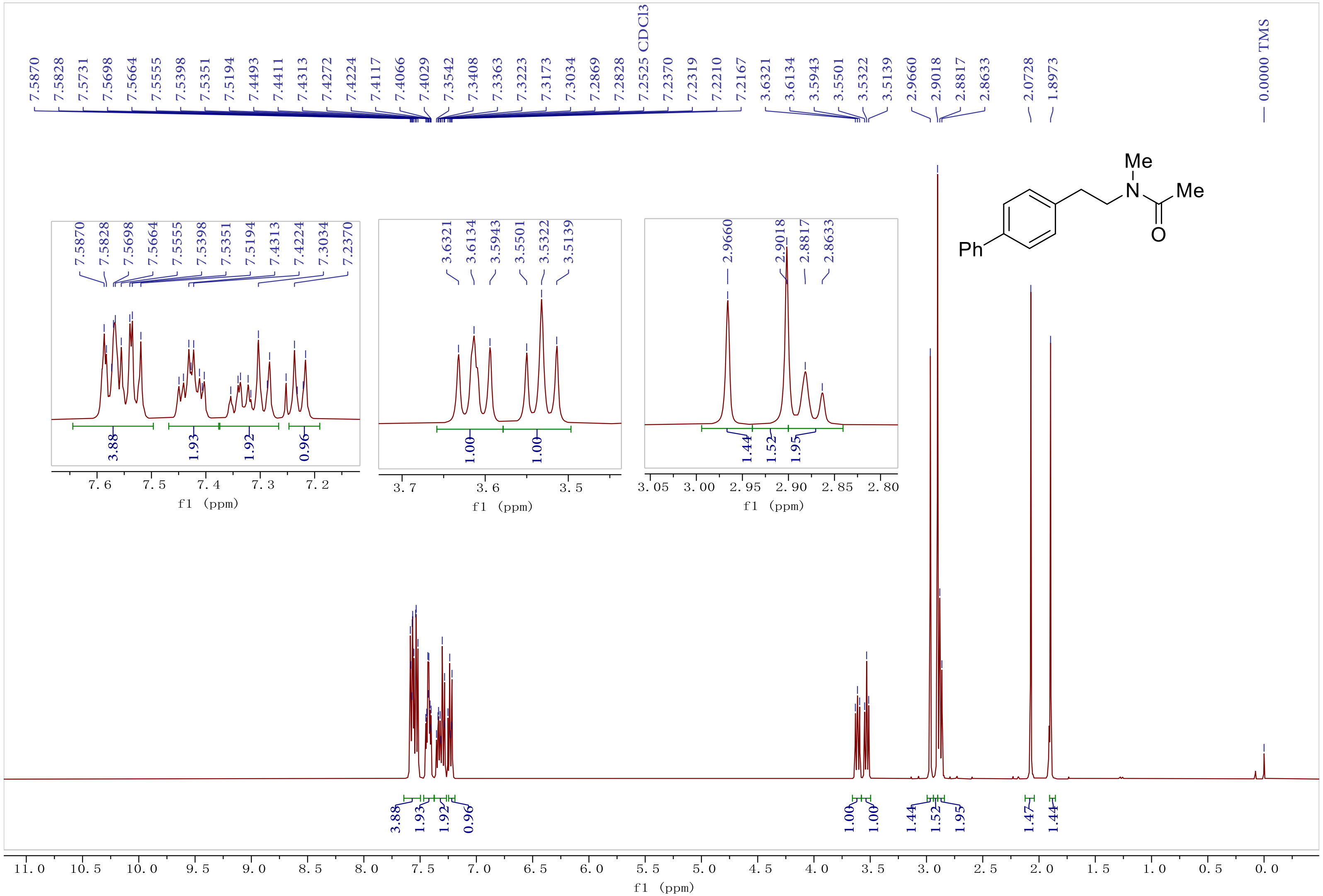


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

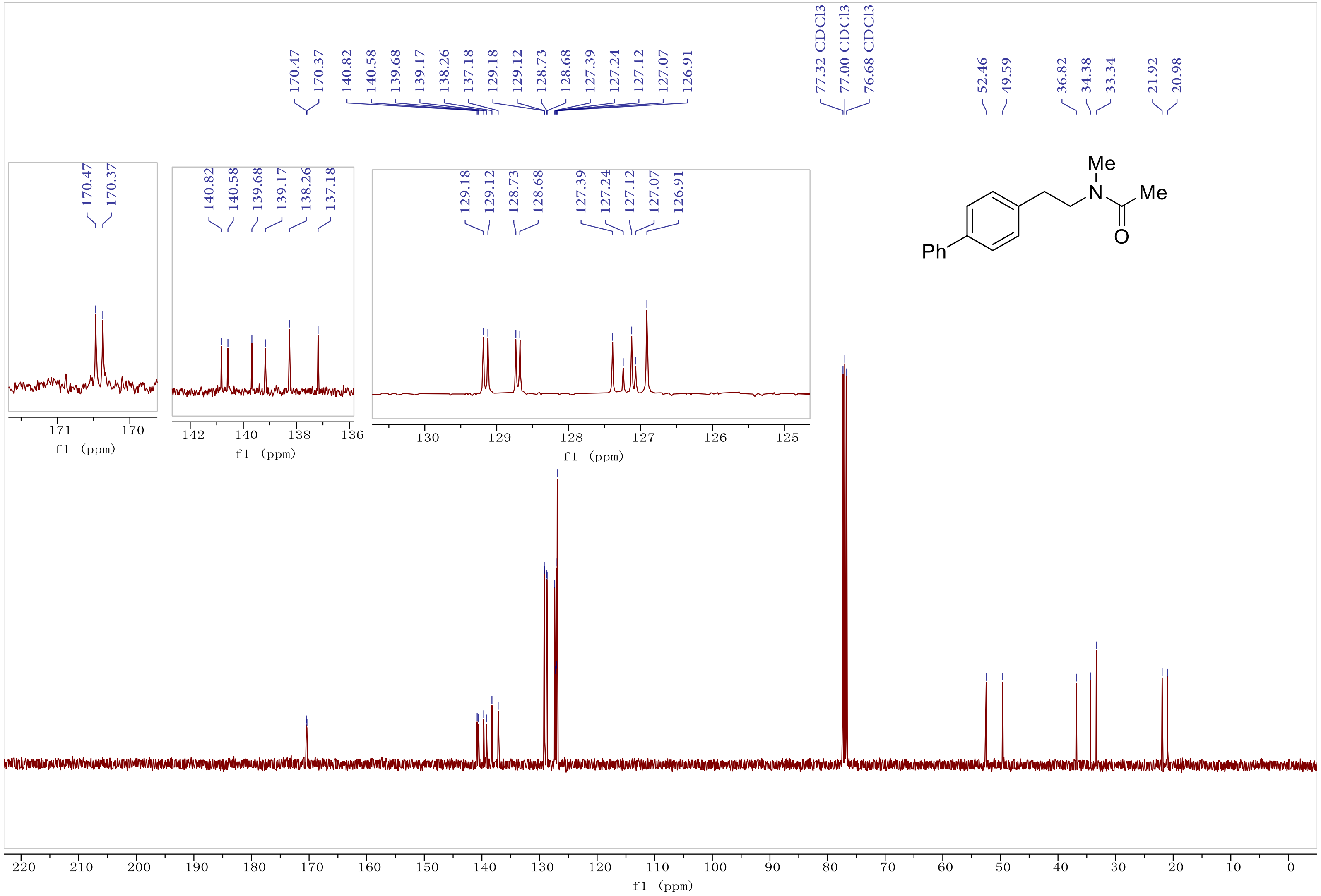


7.35. *N*-(2-([1,1'-Biphenyl]-4-yl)ethyl)-*N*-methylacetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

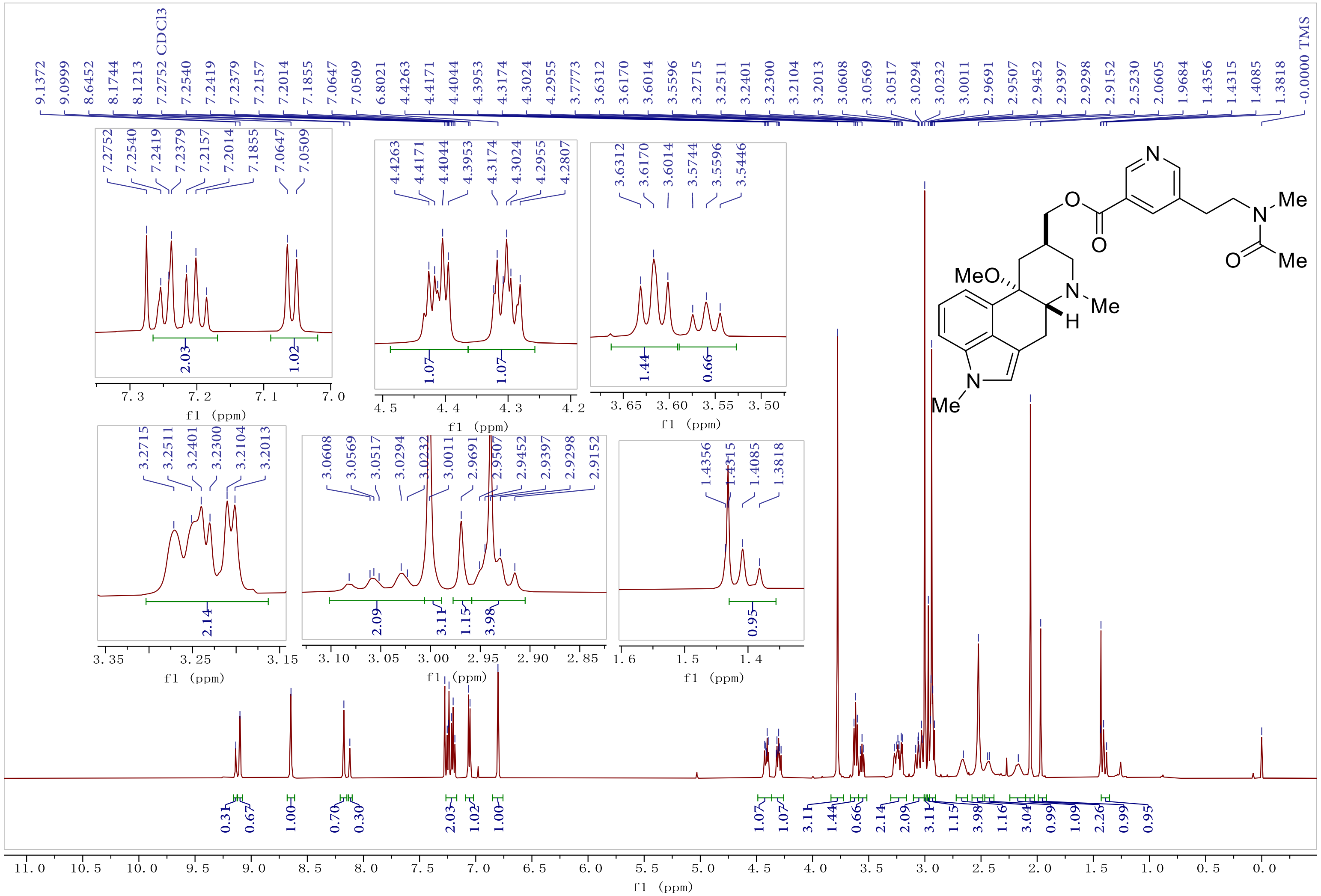


^{13}C NMR spectrum (100 MHz) in CDCl$_3$

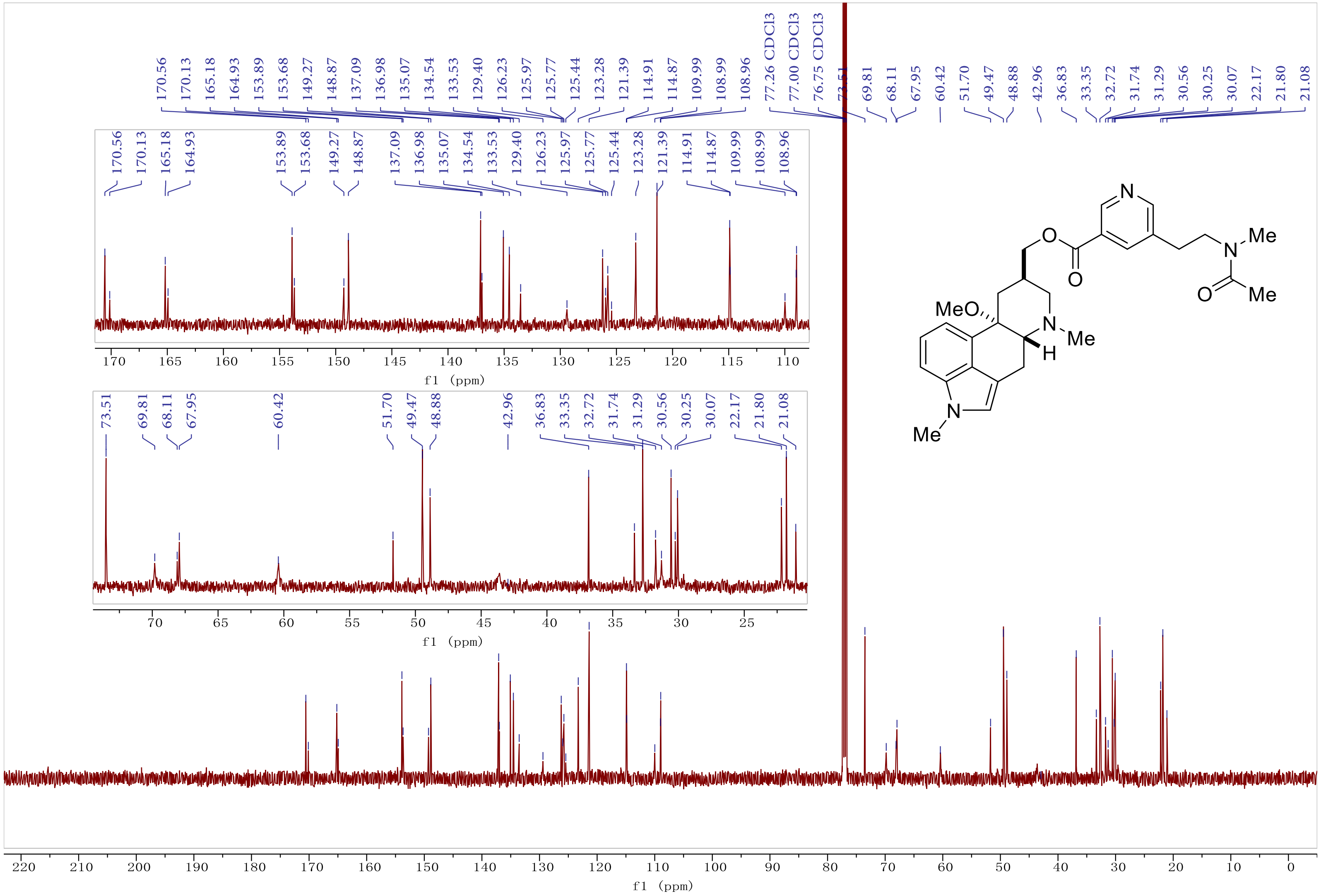


7.36. ((6aR,9R,10aS)-10a-Methoxy-4,7-dimethyl-4,6,6a,7,8,9,10,10a-octahydroindolo[4,3-*fg*]quinolin-9-yl)methyl 5-(2-(*N*-methylacetamido)ethyl)nicotinate

^{1}H NMR spectrum (500 MHz) in CDCl$_3$

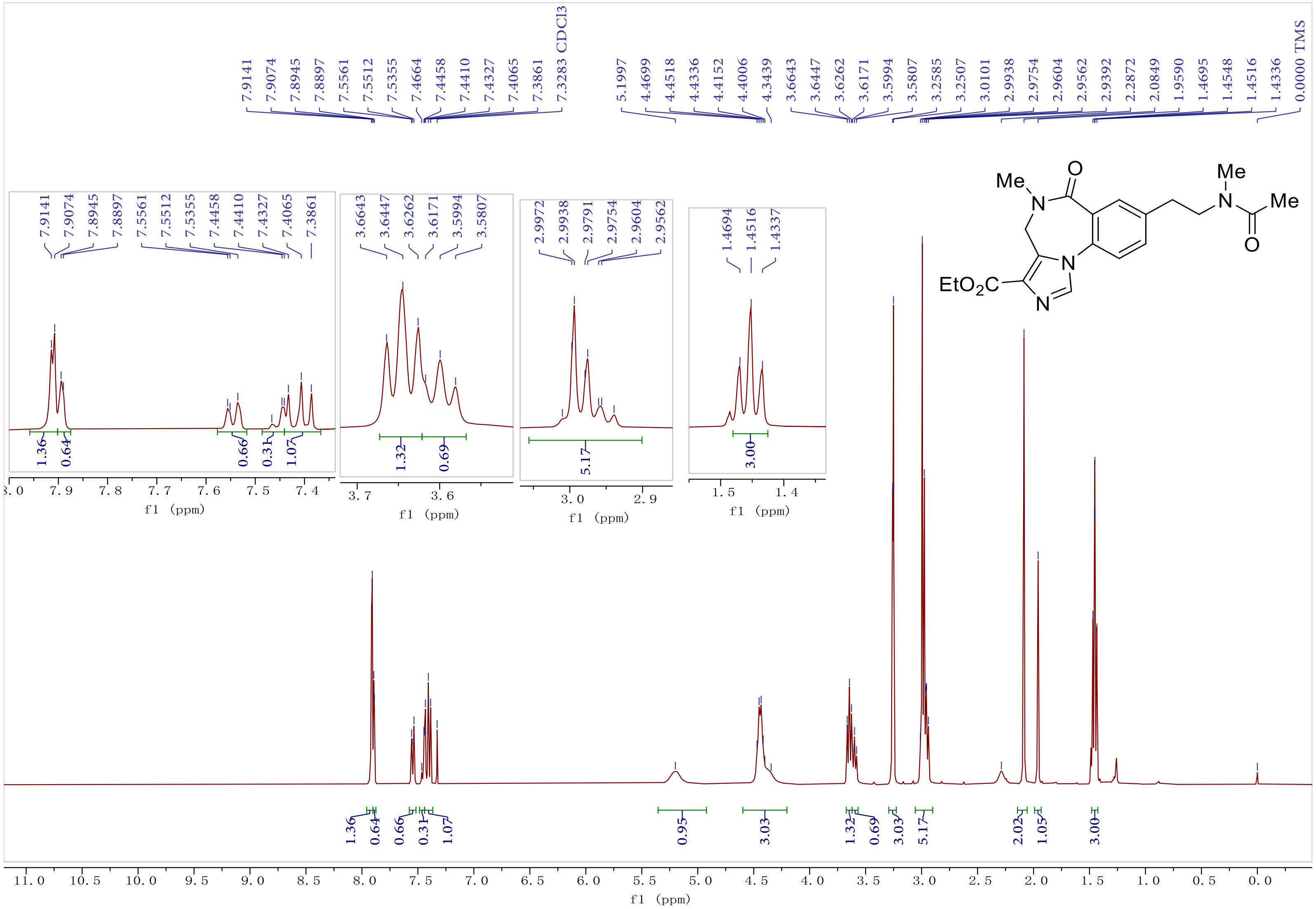


^{13}C NMR spectrum (125 MHz) in CDCl$_3$

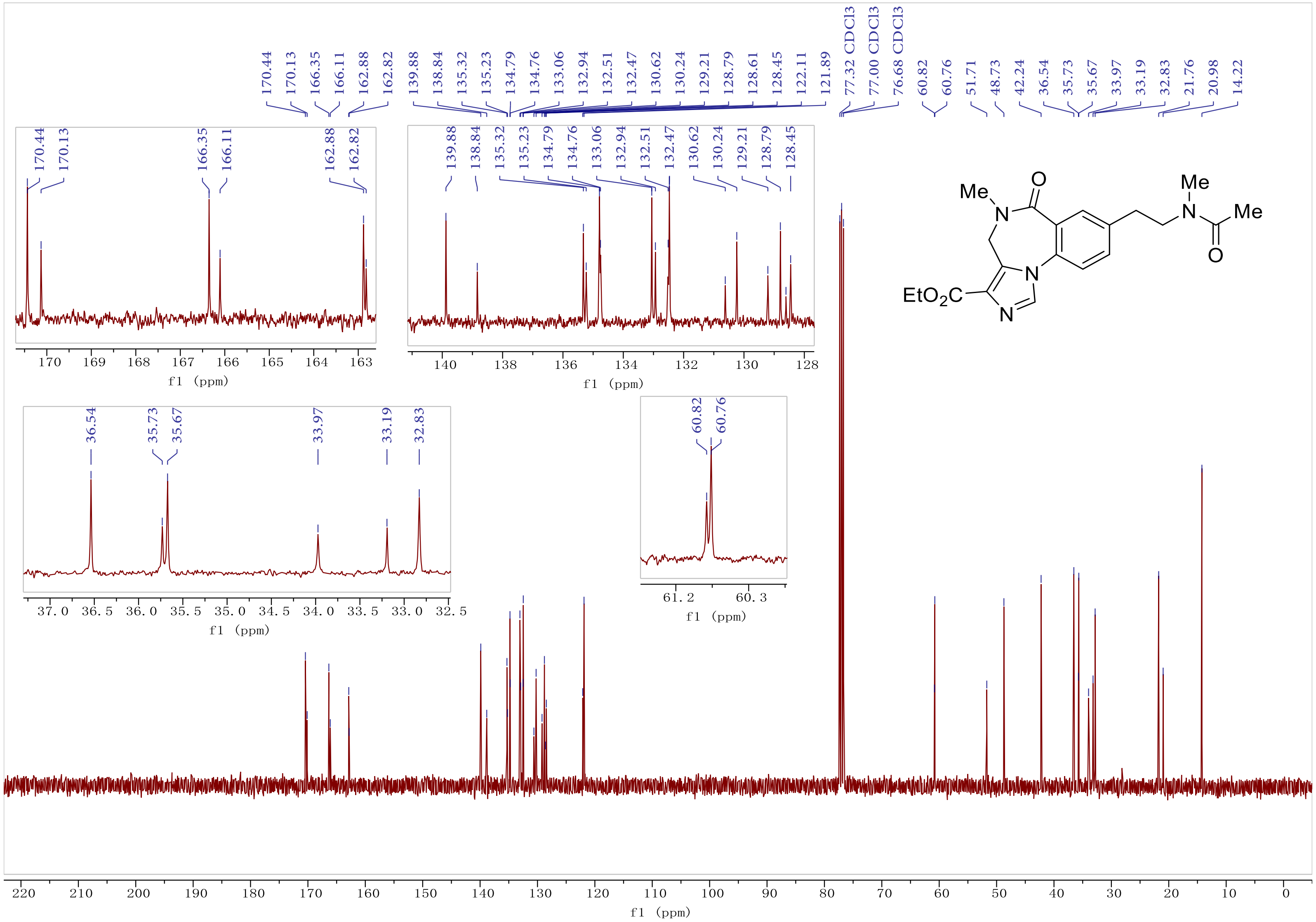


7.37. Ethyl 5-methyl-8-(2-(*N*-methylacetamido)ethyl)-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

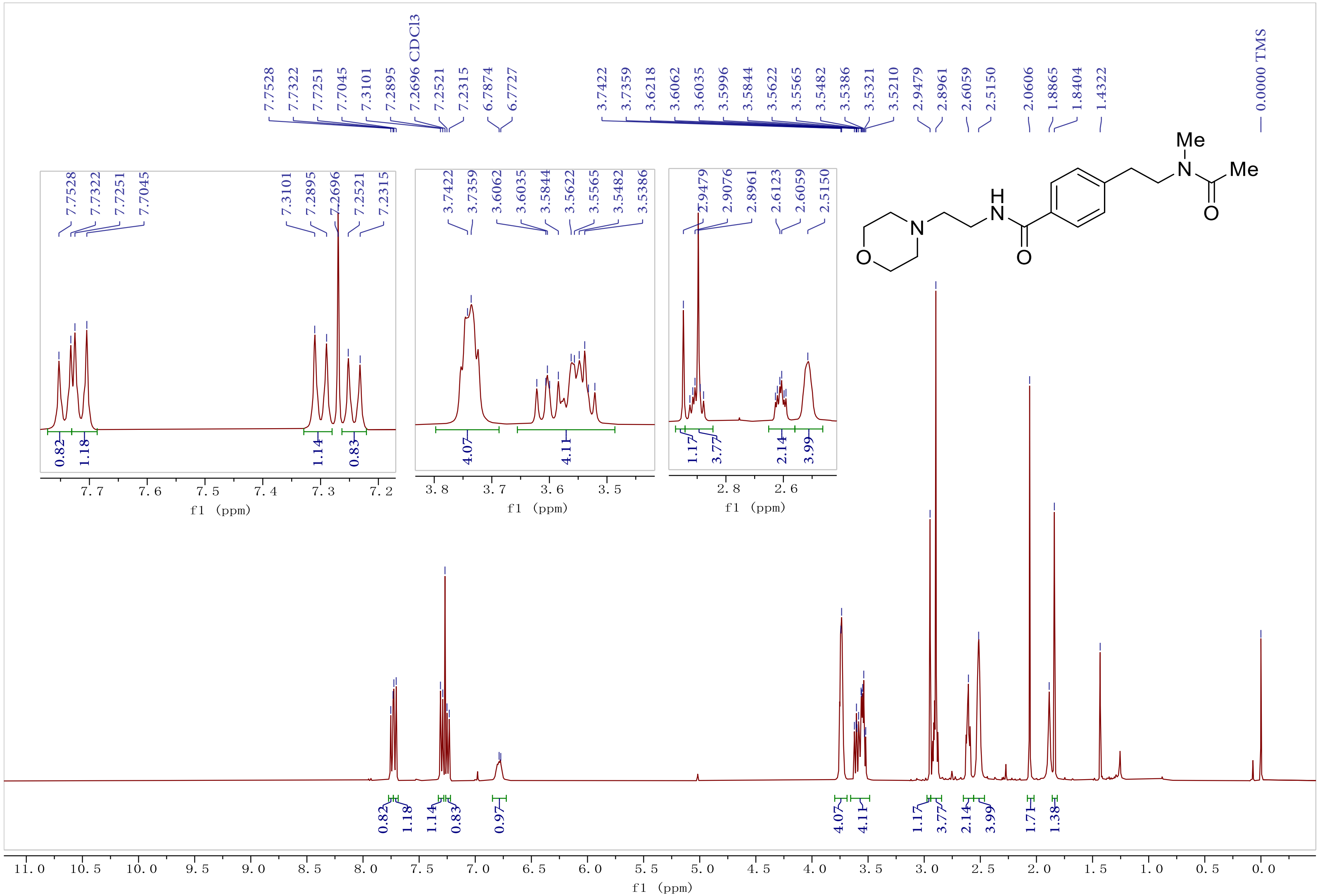


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

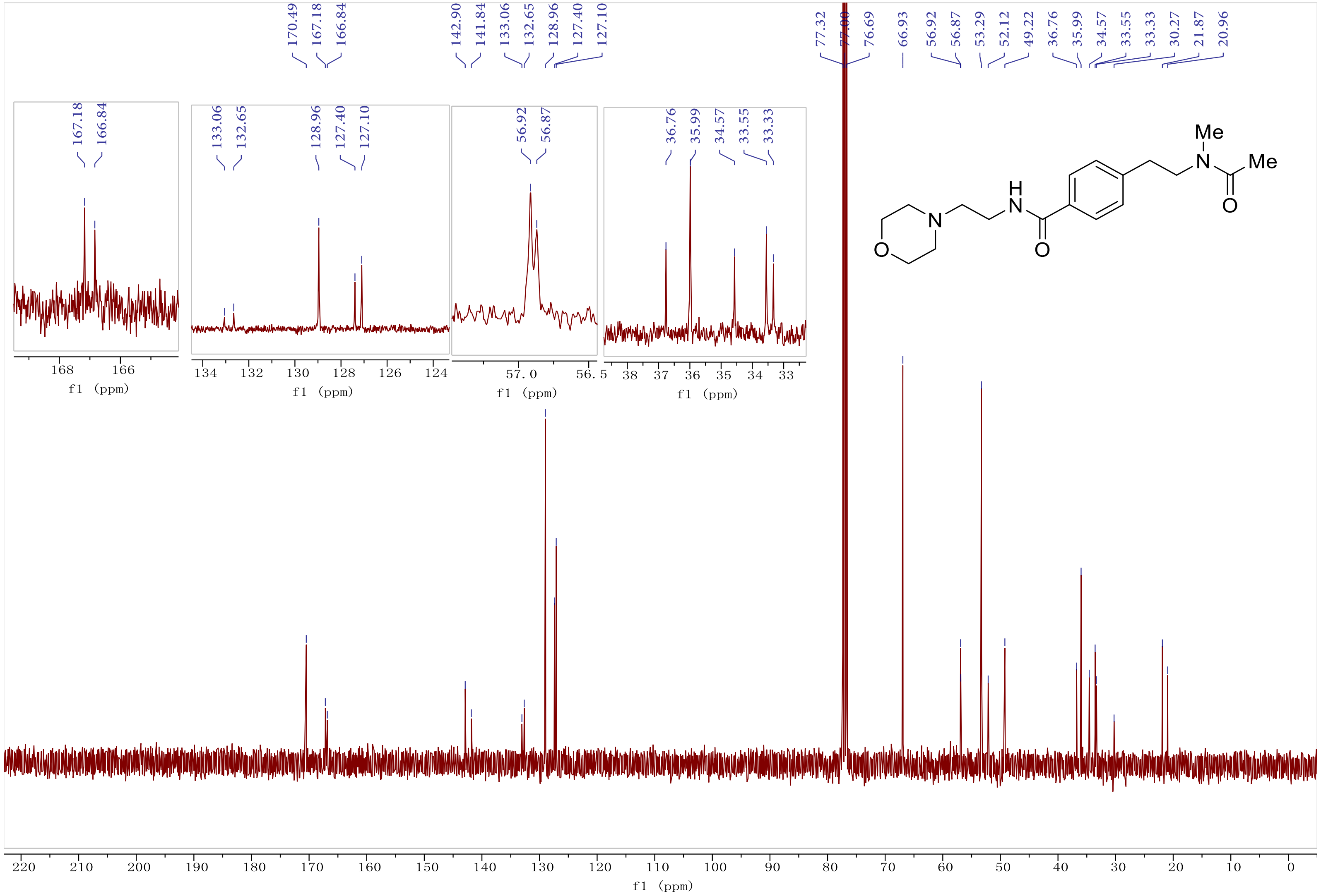


7.38. 4-(2-(*N*-Methylacetamido)ethyl)-*N*-(2-morpholinoethyl)benzamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

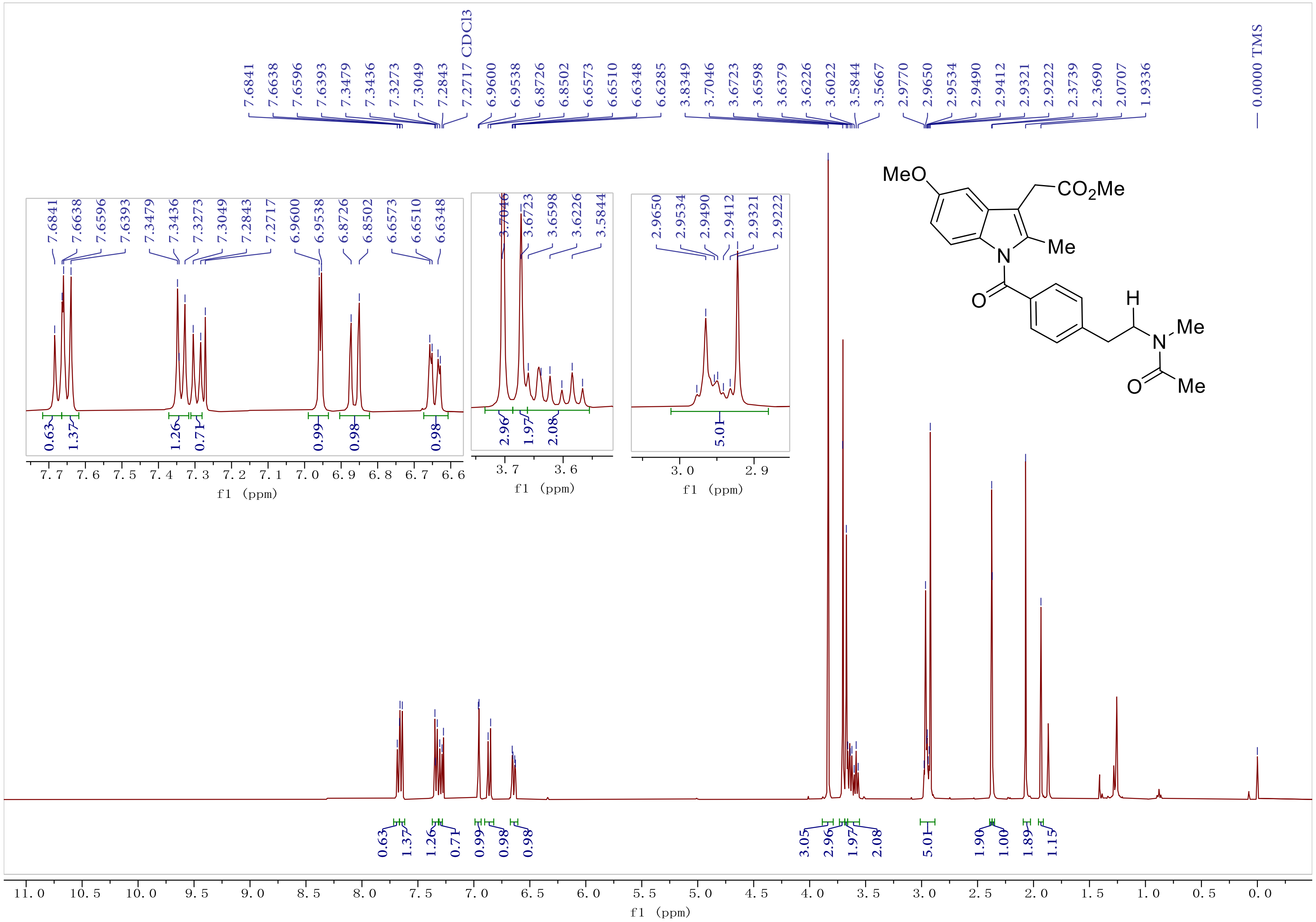


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

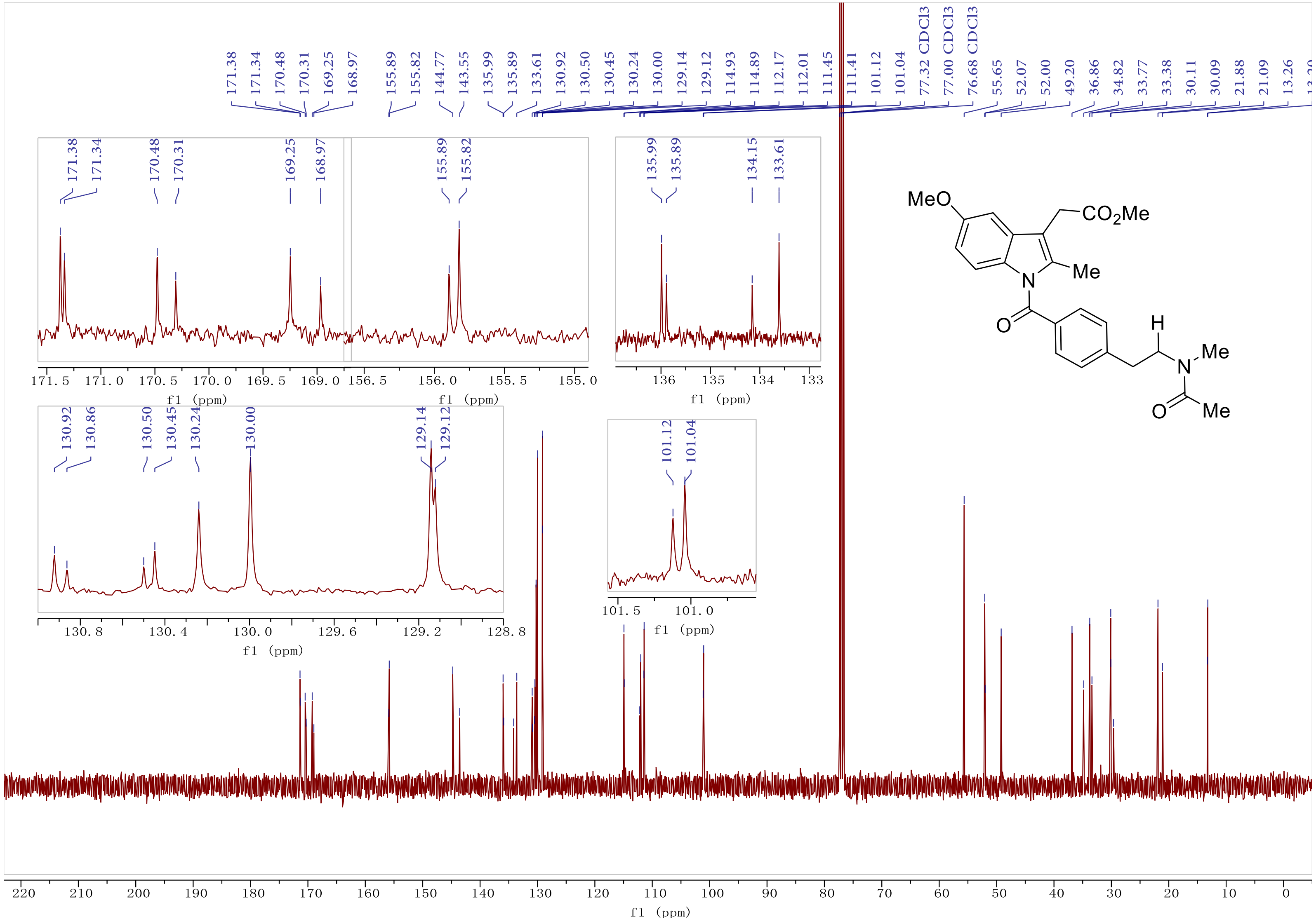


7.39. Methyl 2-(5-methoxy-2-methyl-1-(4-(2-(*N*-methylacetamido)ethyl)benzoyl)-1*H*-indol-3-yl)acetate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

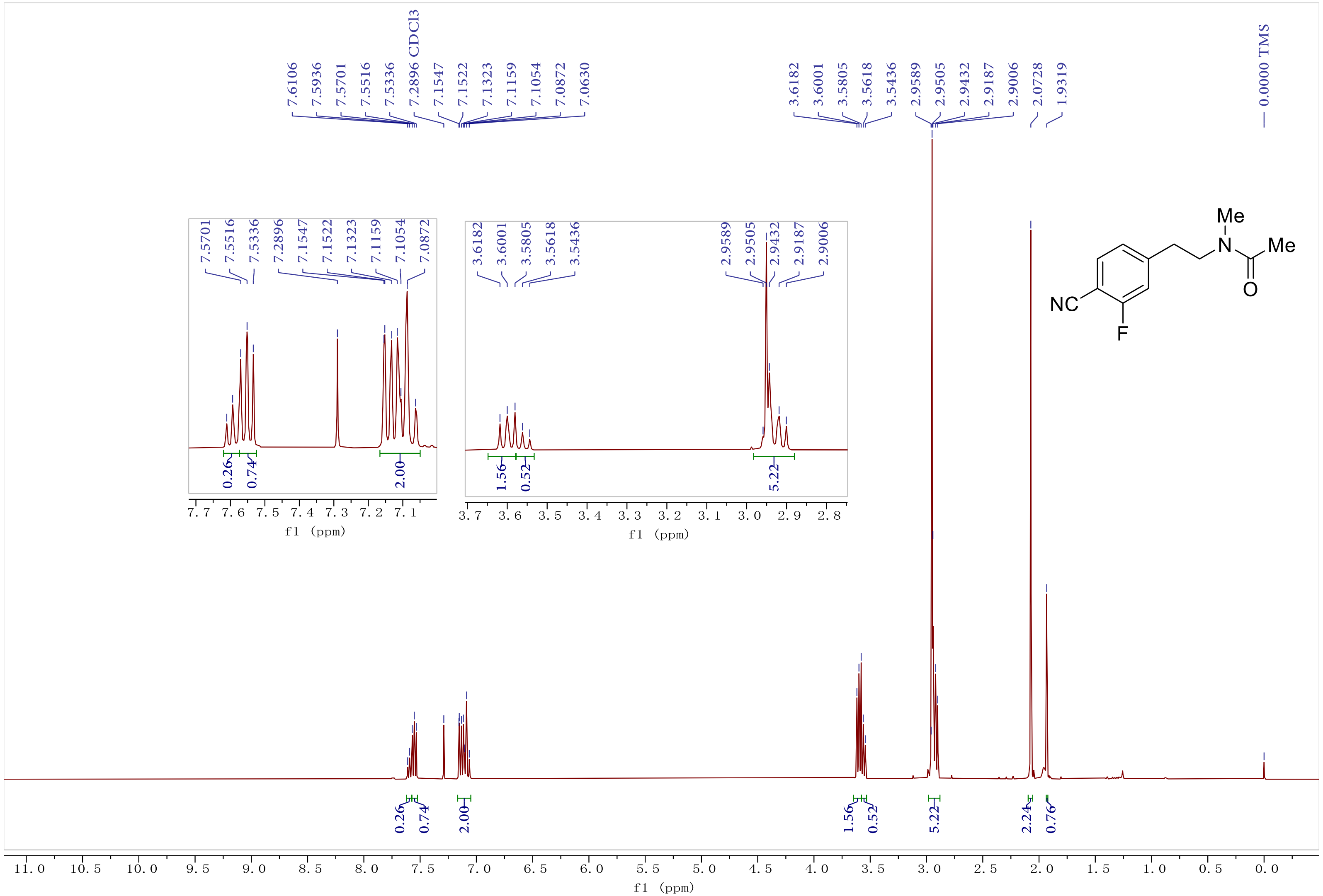


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

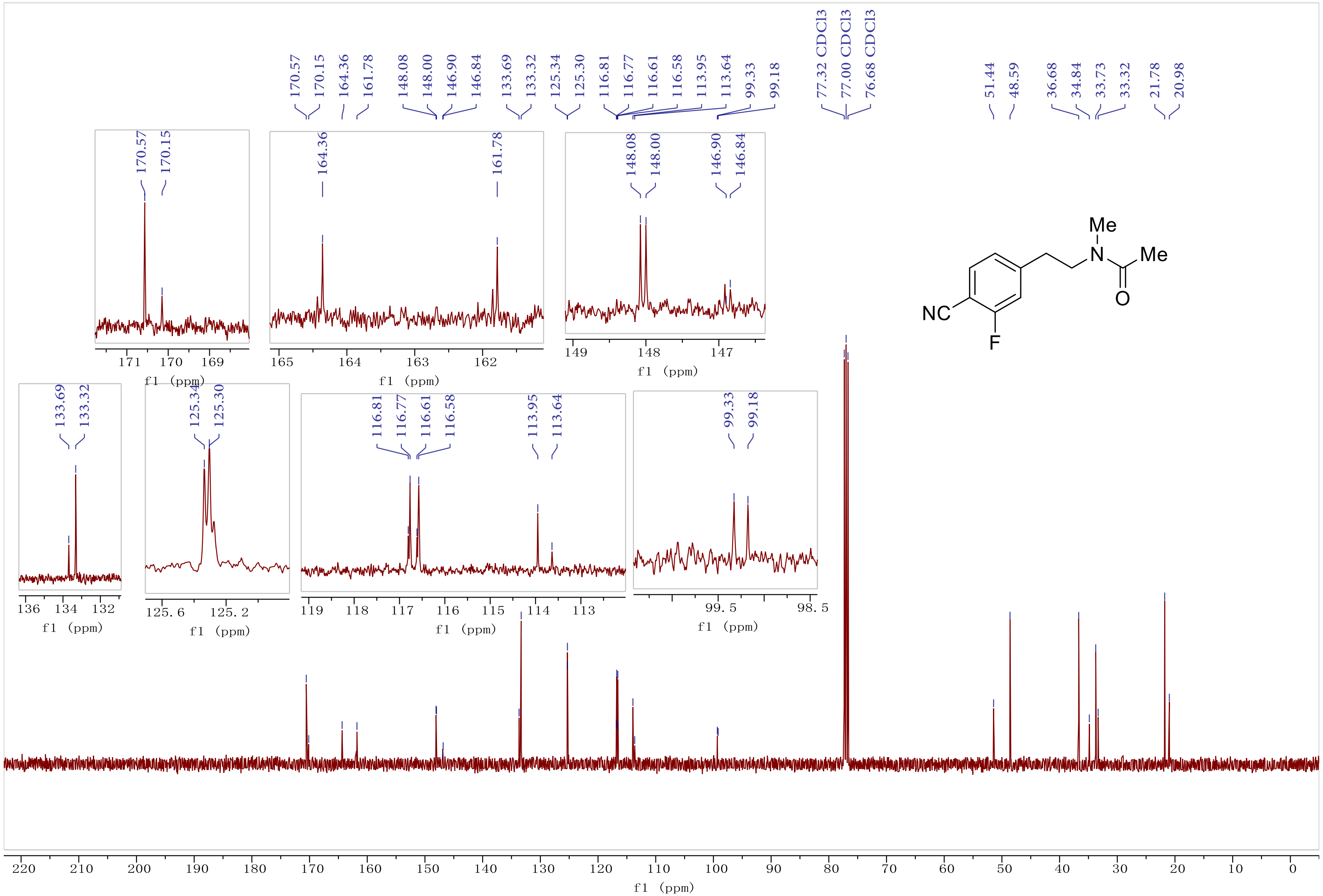


7.40. *N*-(4-Cyano-3-fluorophenethyl)-*N*-methylacetamide

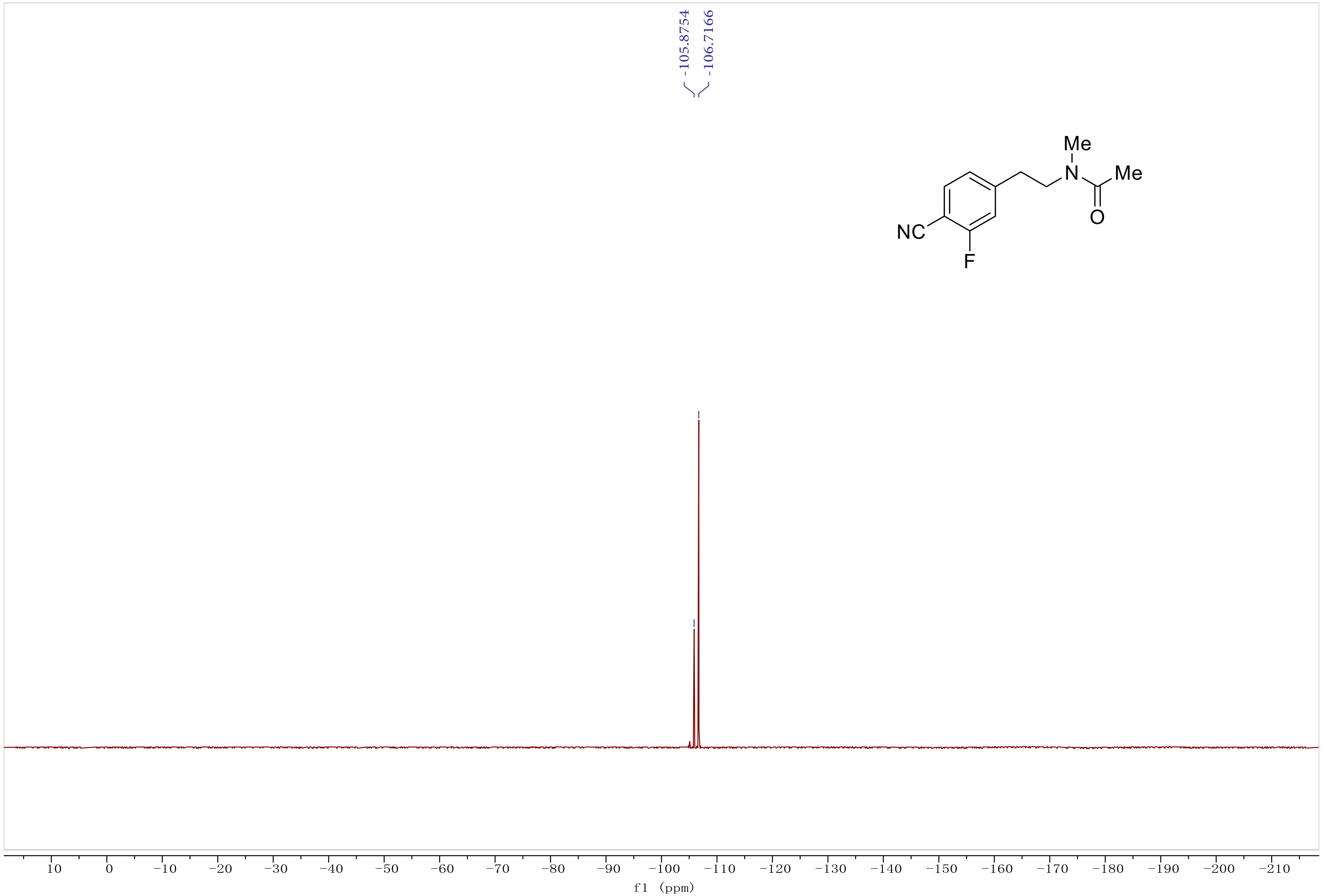
^{1}H NMR spectrum (400 MHz) in $CDCl_3$



^{13}C NMR spectrum (100 MHz) in $CDCl_3$

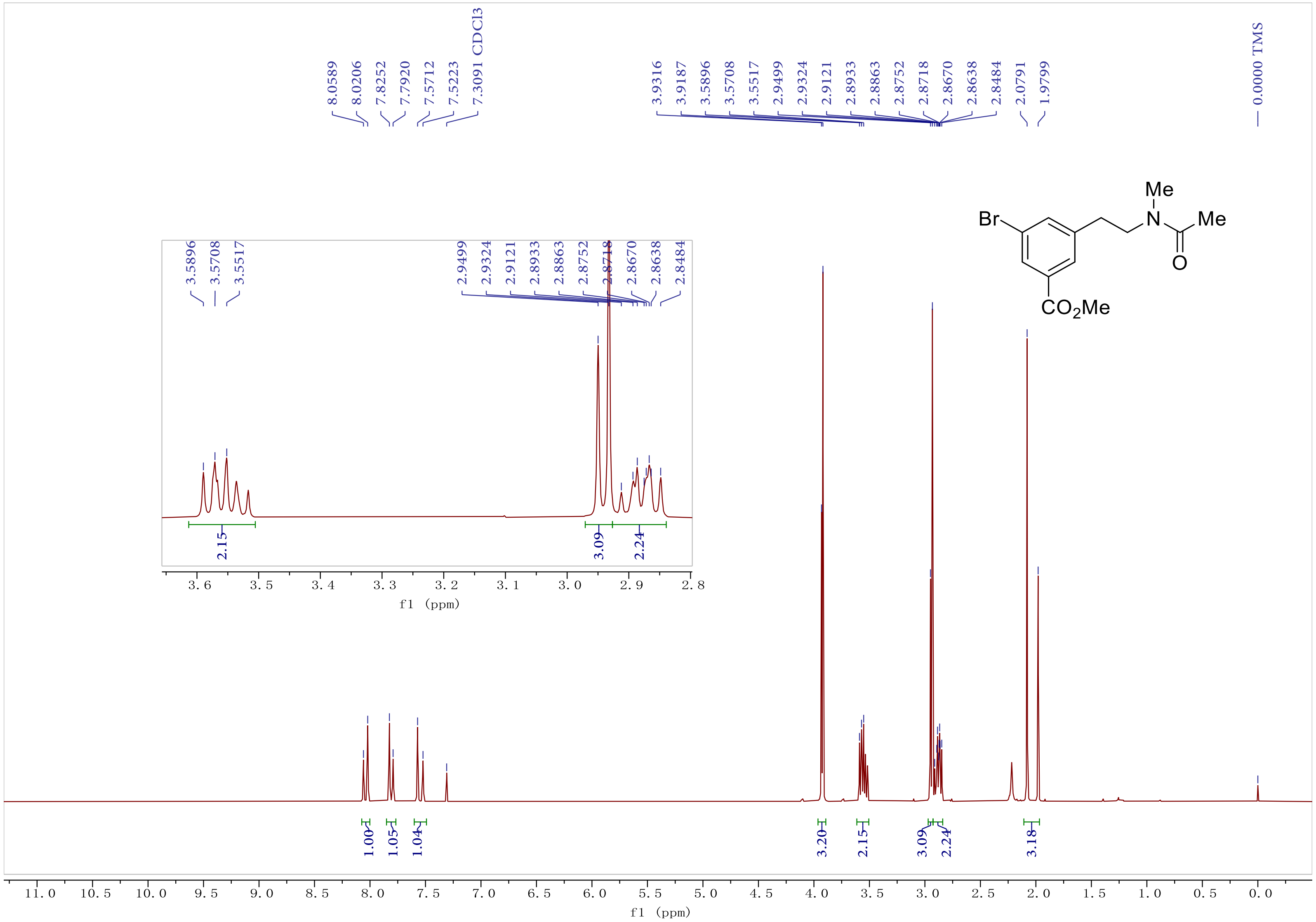


^{19}F NMR spectrum (376 MHz) in $CDCl_3$

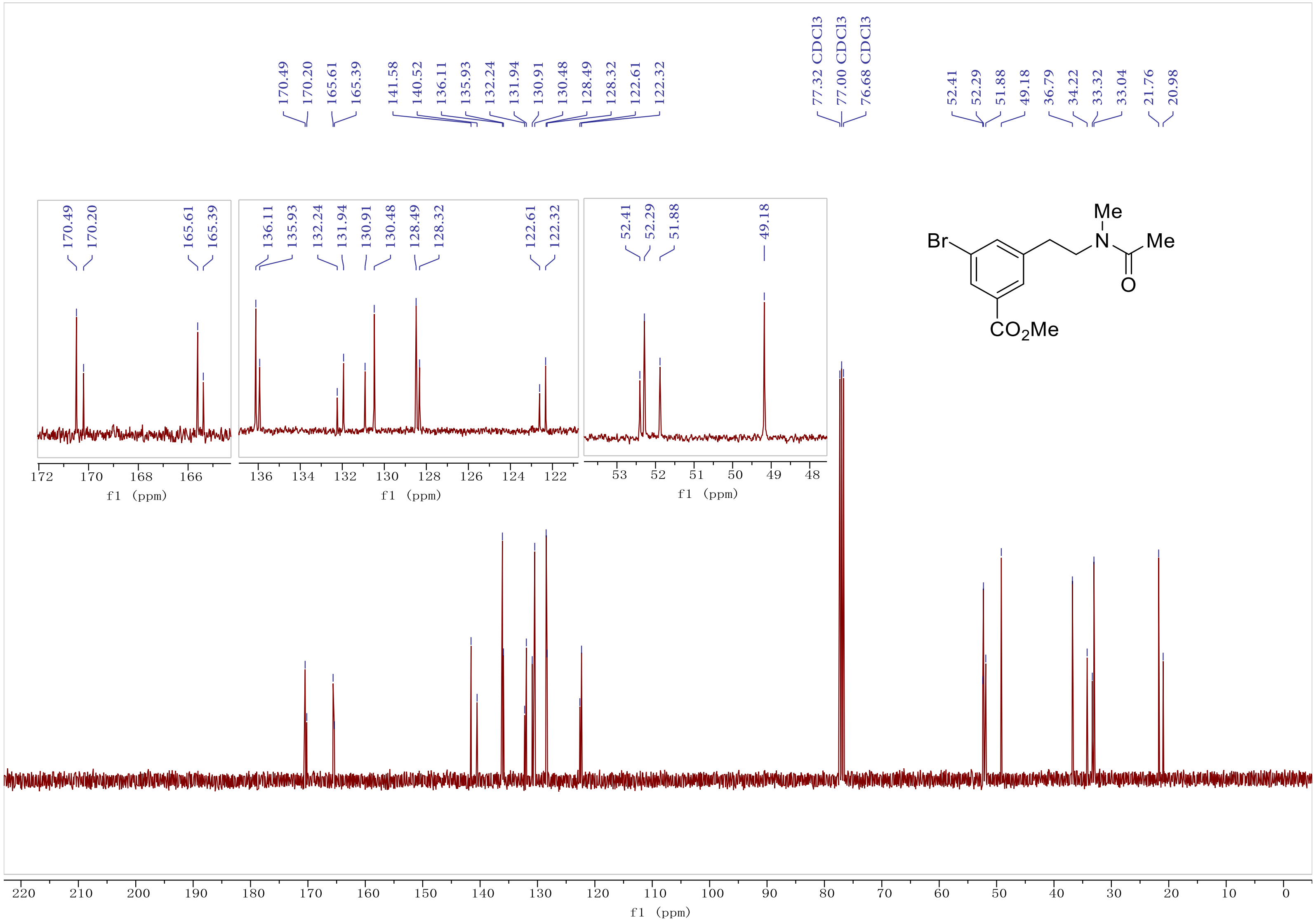


7.41. Methyl 3-bromo-5-(2-(*N*-methylacetamido)ethyl)benzoate

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

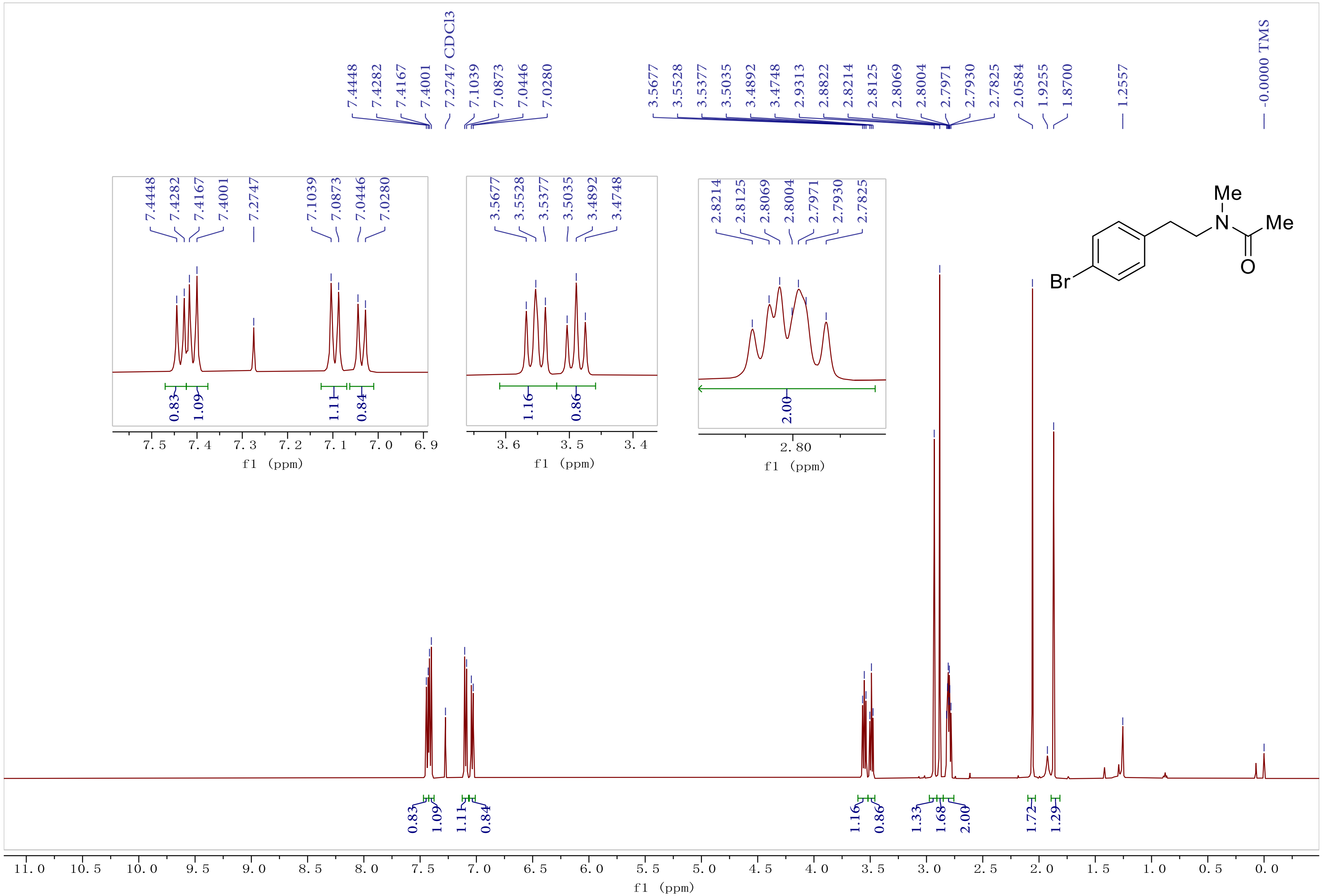


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

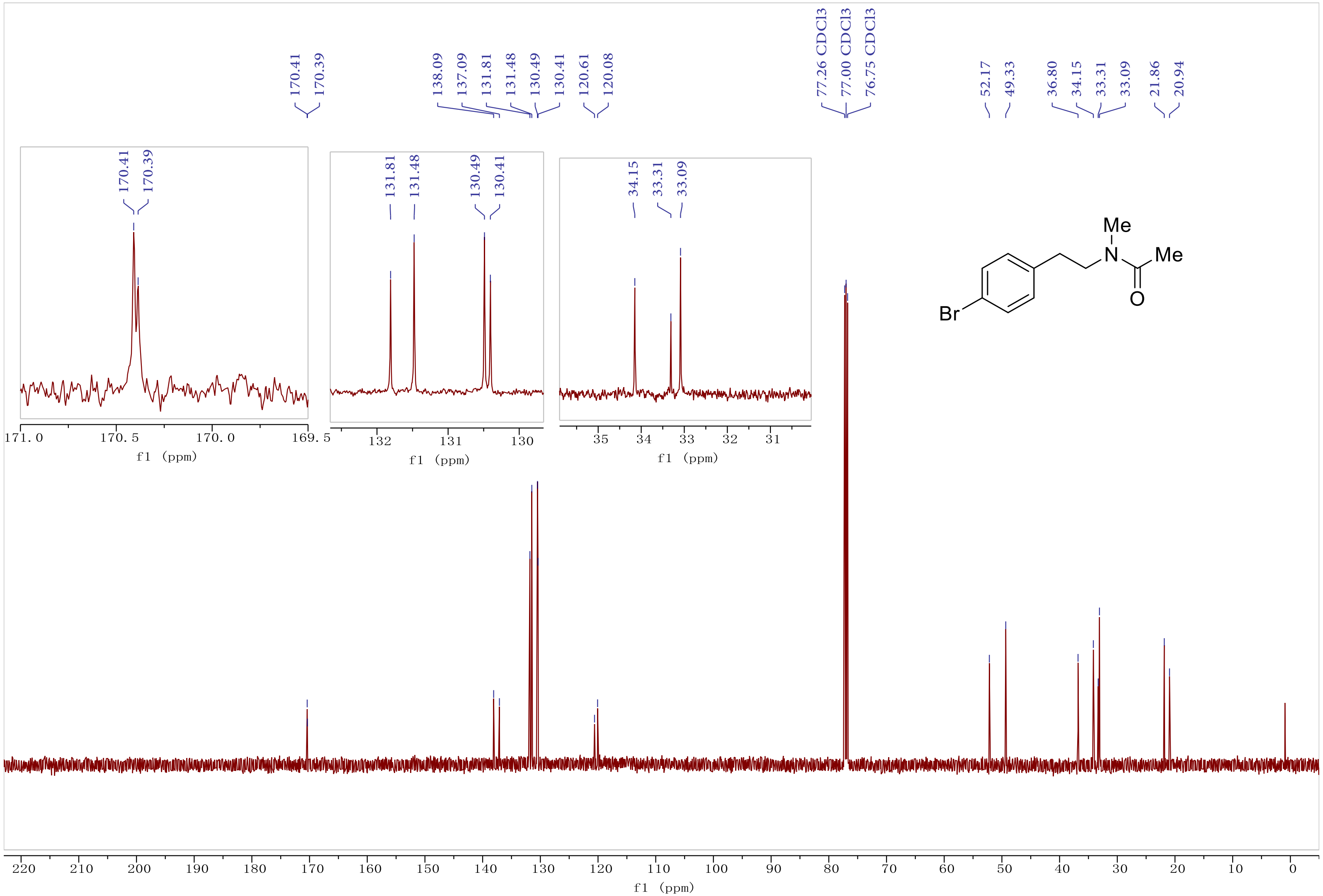


7.42. *N*-(4-Bromophenethyl)-*N*-methylacetamide

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

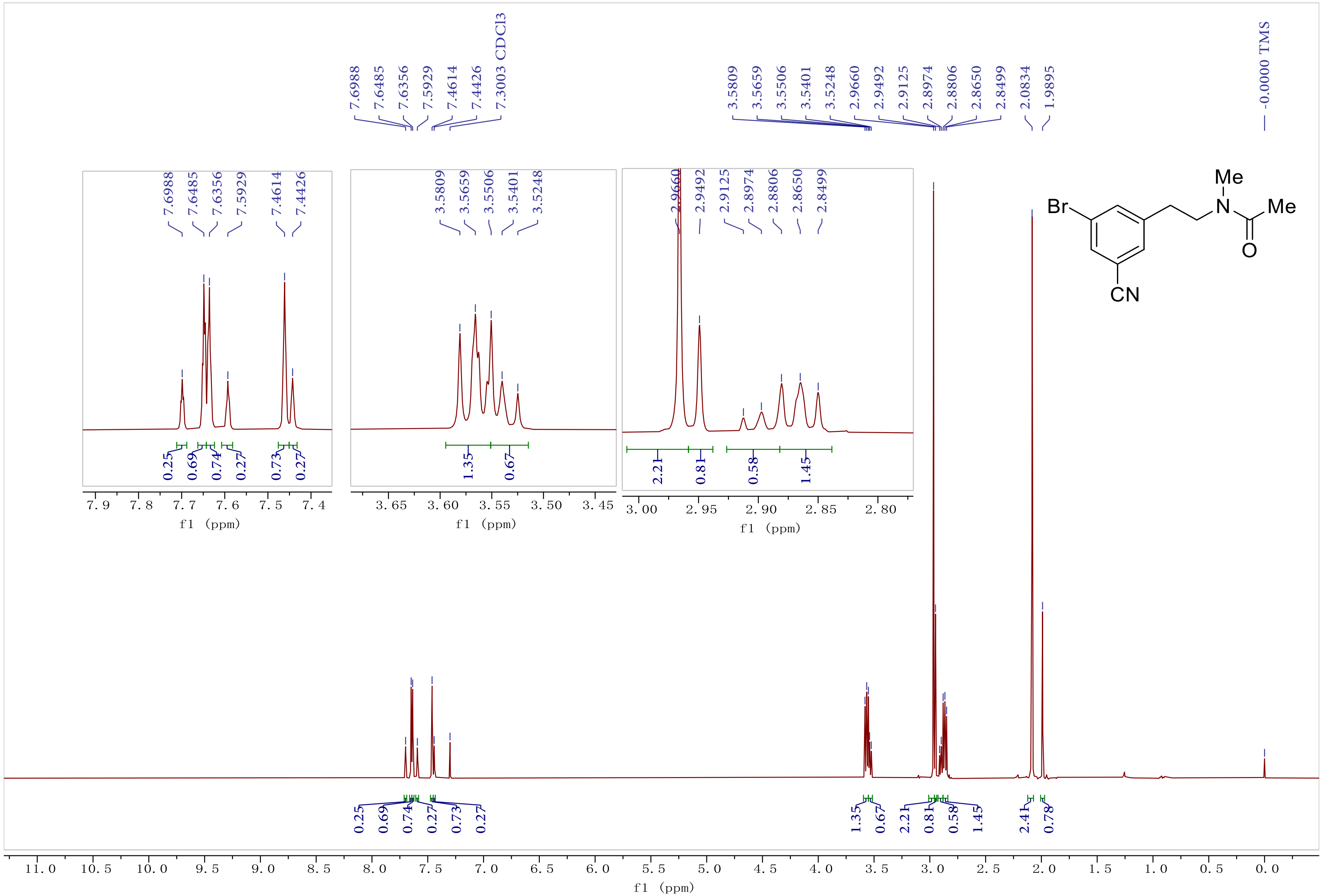


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

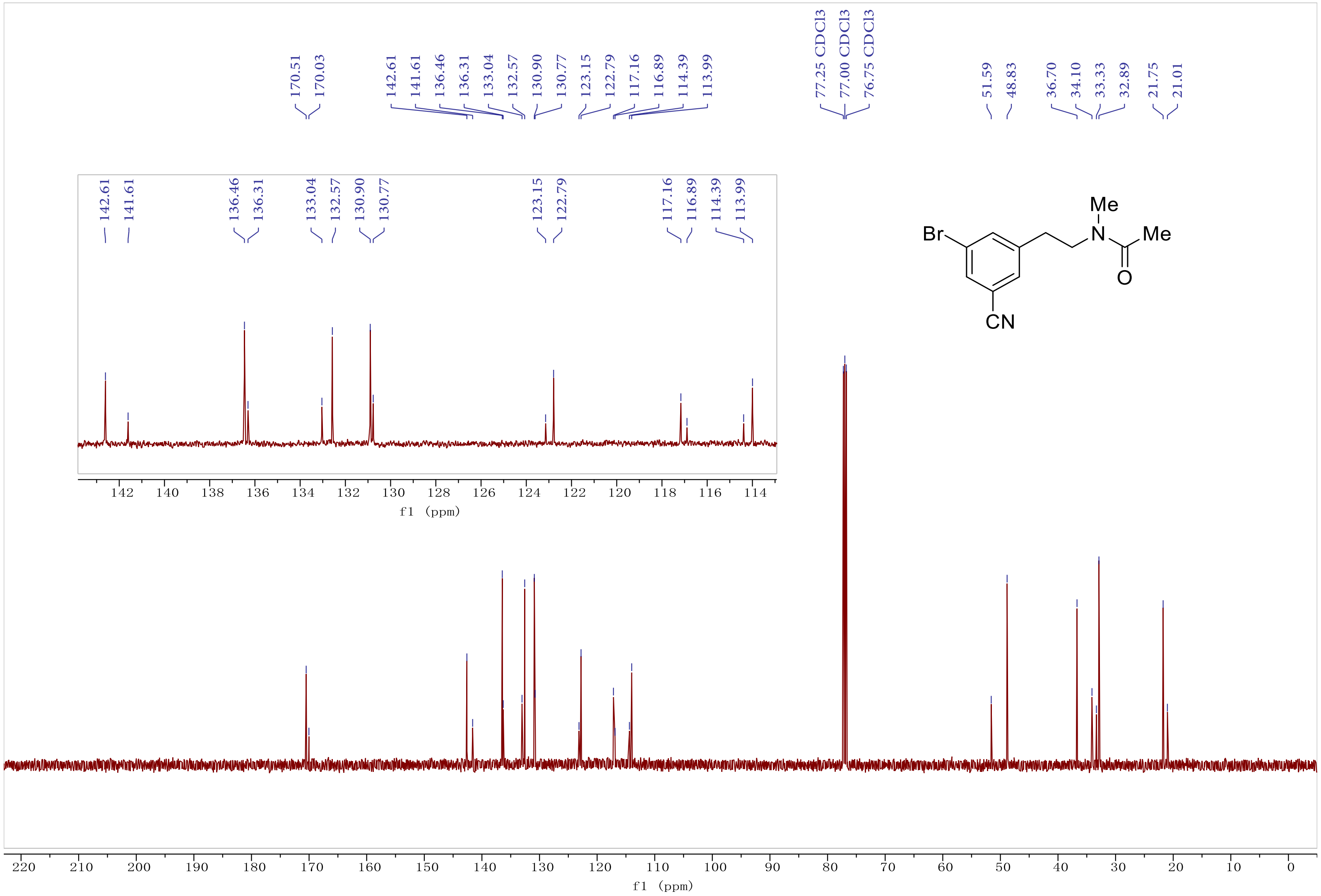


7.43. ***N*-(3-Bromo-5-cyanophenethyl)-*N*-methylacetamide**

^{1}H NMR spectrum (500 MHz) in $CDCl_3$

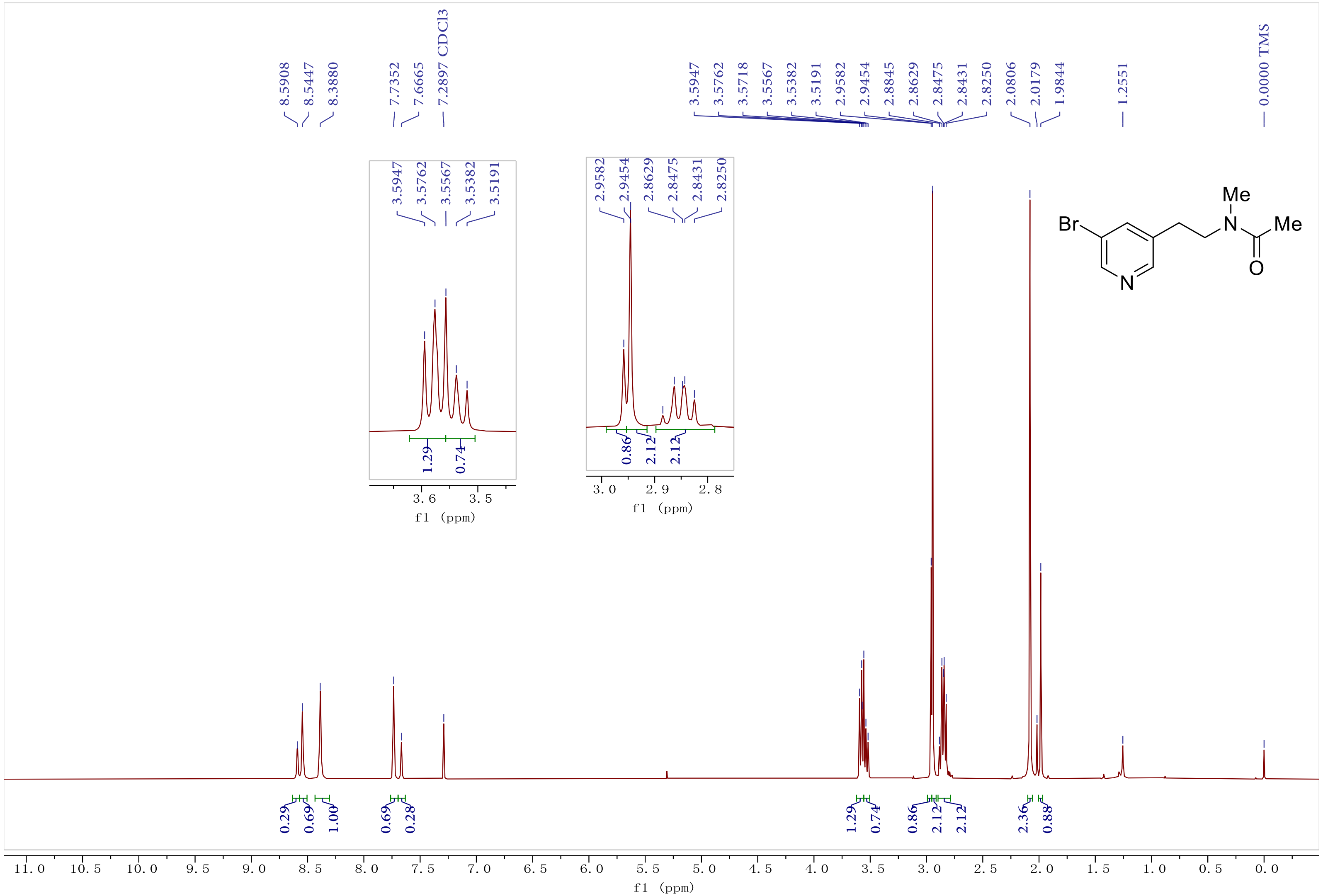


^{13}C NMR spectrum (125 MHz) in $CDCl_3$

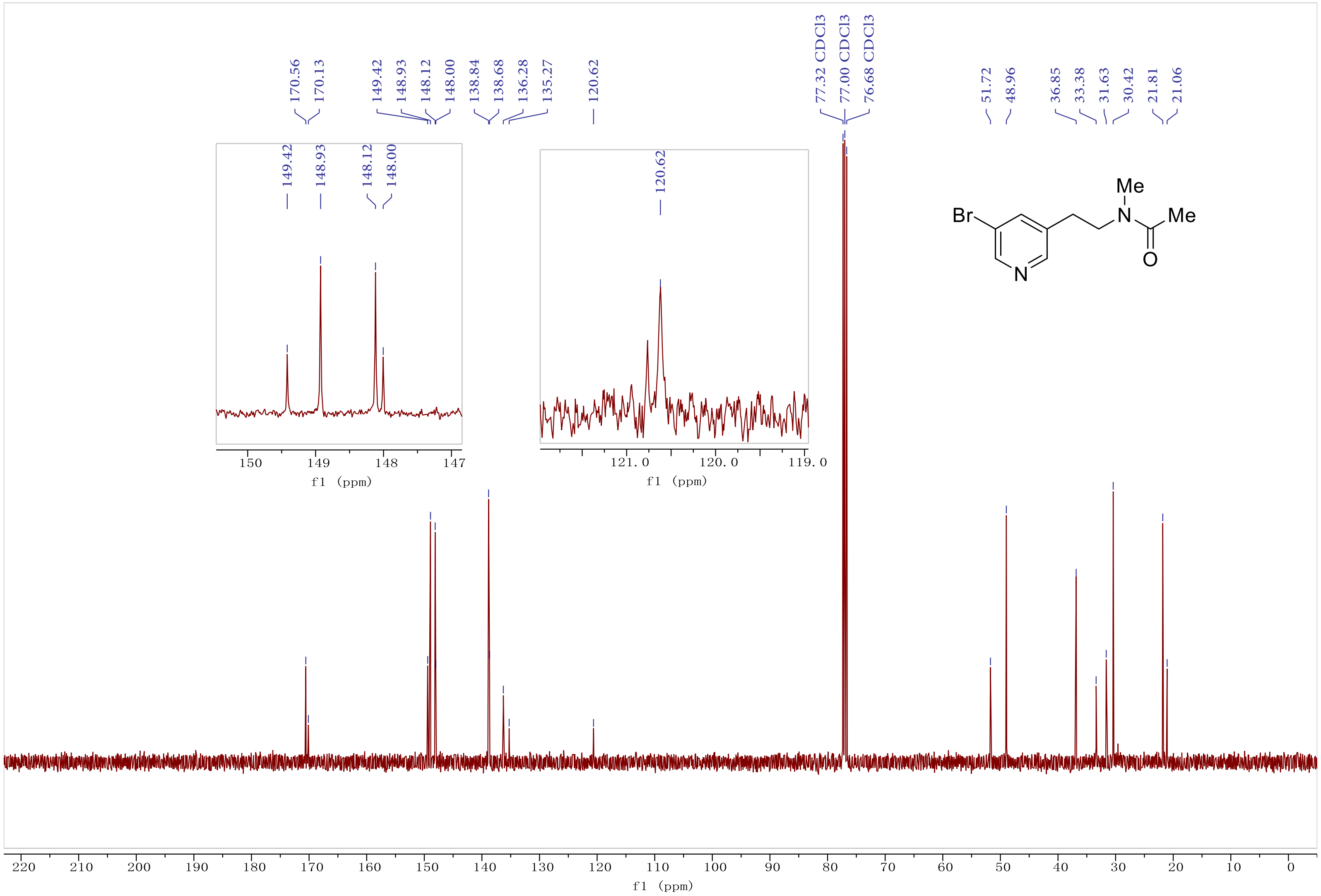


7.44. *N*-(2-(5-Bromopyridin-3-yl)ethyl)-*N*-methylacetamide

^{1}H NMR spectrum (400 MHz) in $CDCl_3$

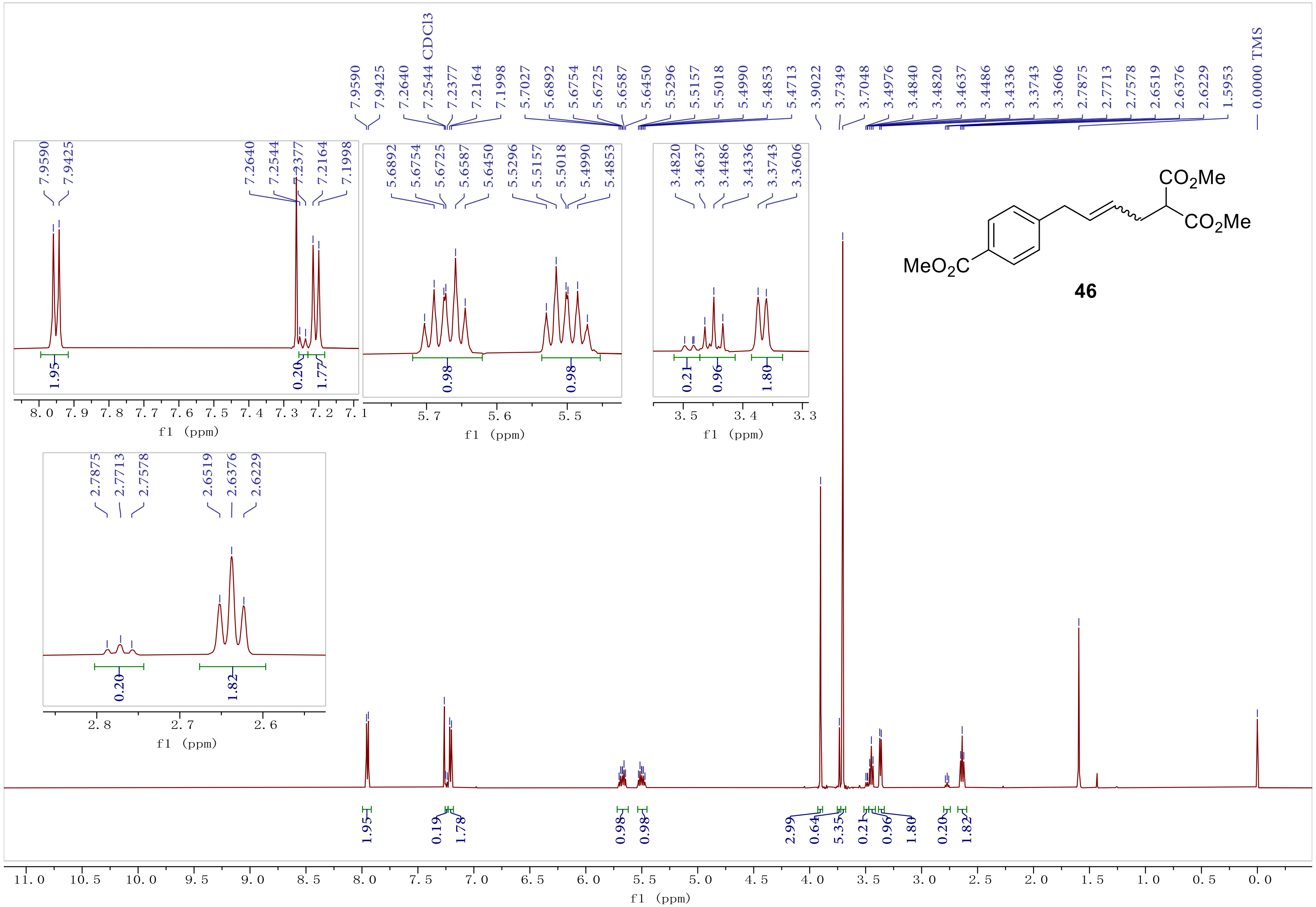


^{13}C NMR spectrum (100 MHz) in $CDCl_3$

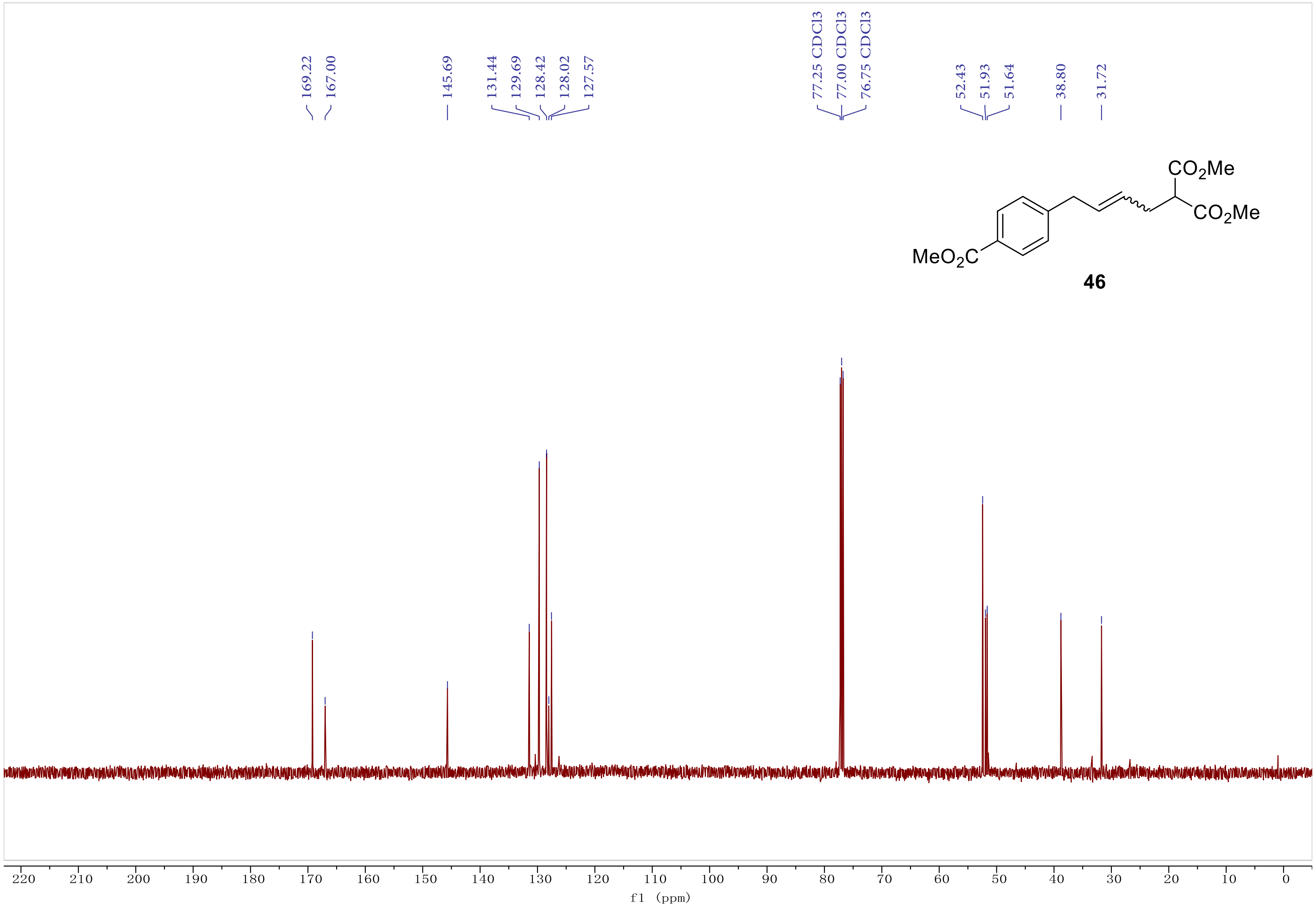


7.45. Dimethyl 2-(4-(4-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate (46)

^{1}H NMR spectrum (500 MHz) in CDCl$_3$



^{13}C NMR spectrum (125 MHz) in $CDCl_3$



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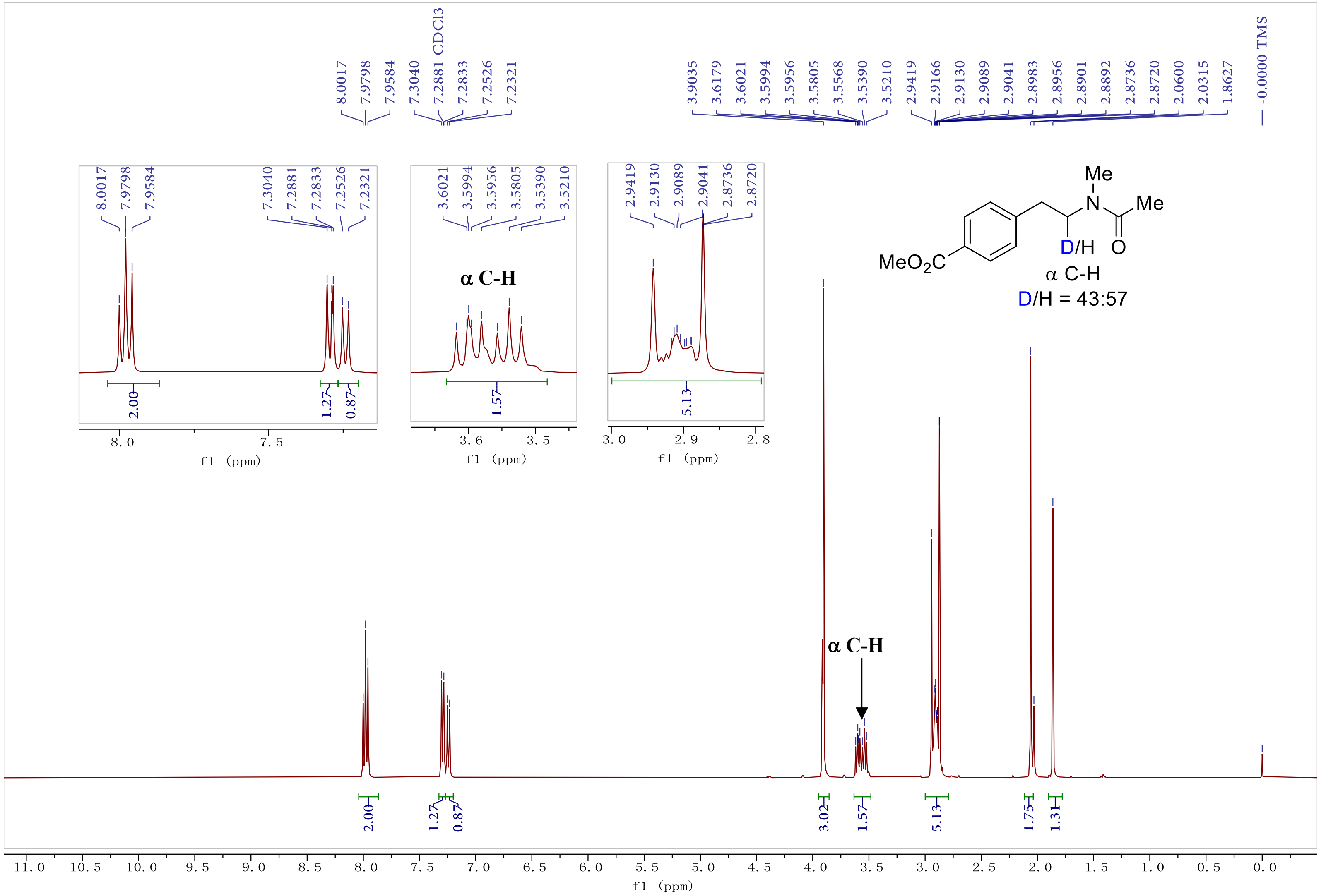
7.46. Deuterium labelling experiments with D₂O

Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

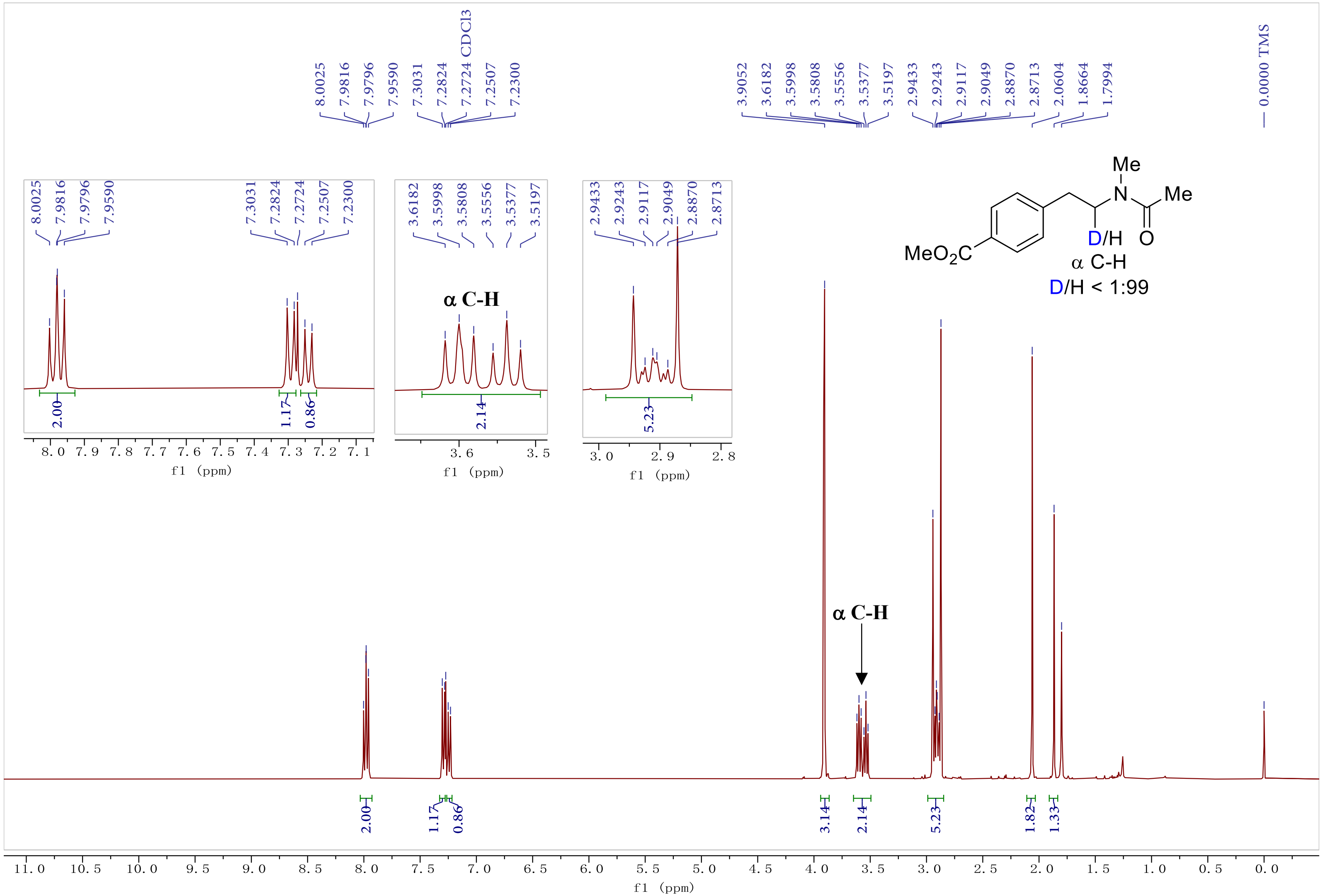
^{1}H NMR spectrum (400 MHz) in $CDCl_3$



7.47. Deuterium labelling experiments using Hantzsch ester (3-*d*$_2$)

Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

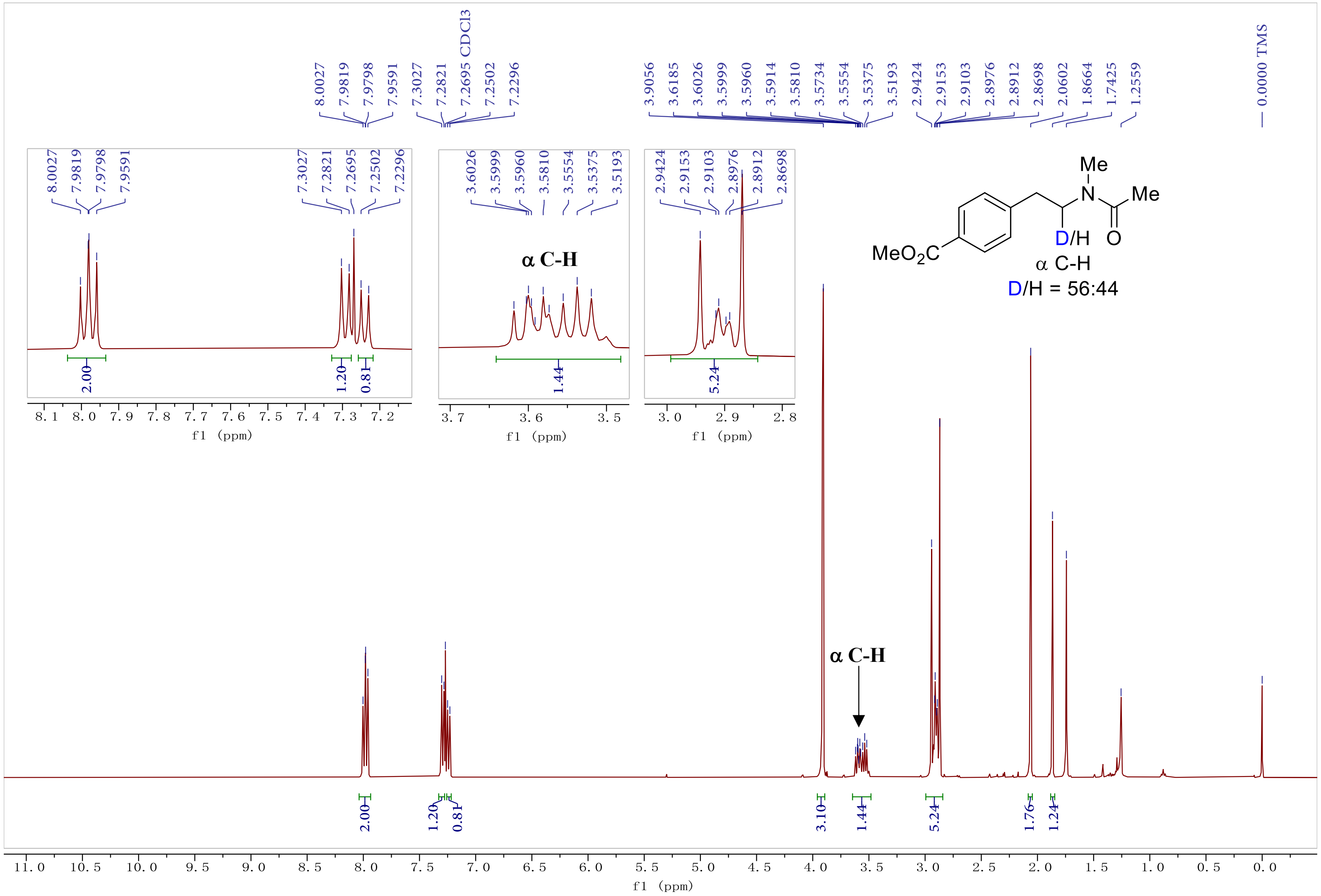
^{1}H NMR Spectrum (400 MHz) in CDCl$_3$



7.48. Deuterium labelling experiments using Hantzsch ester (3-d_2) and D_2O

Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

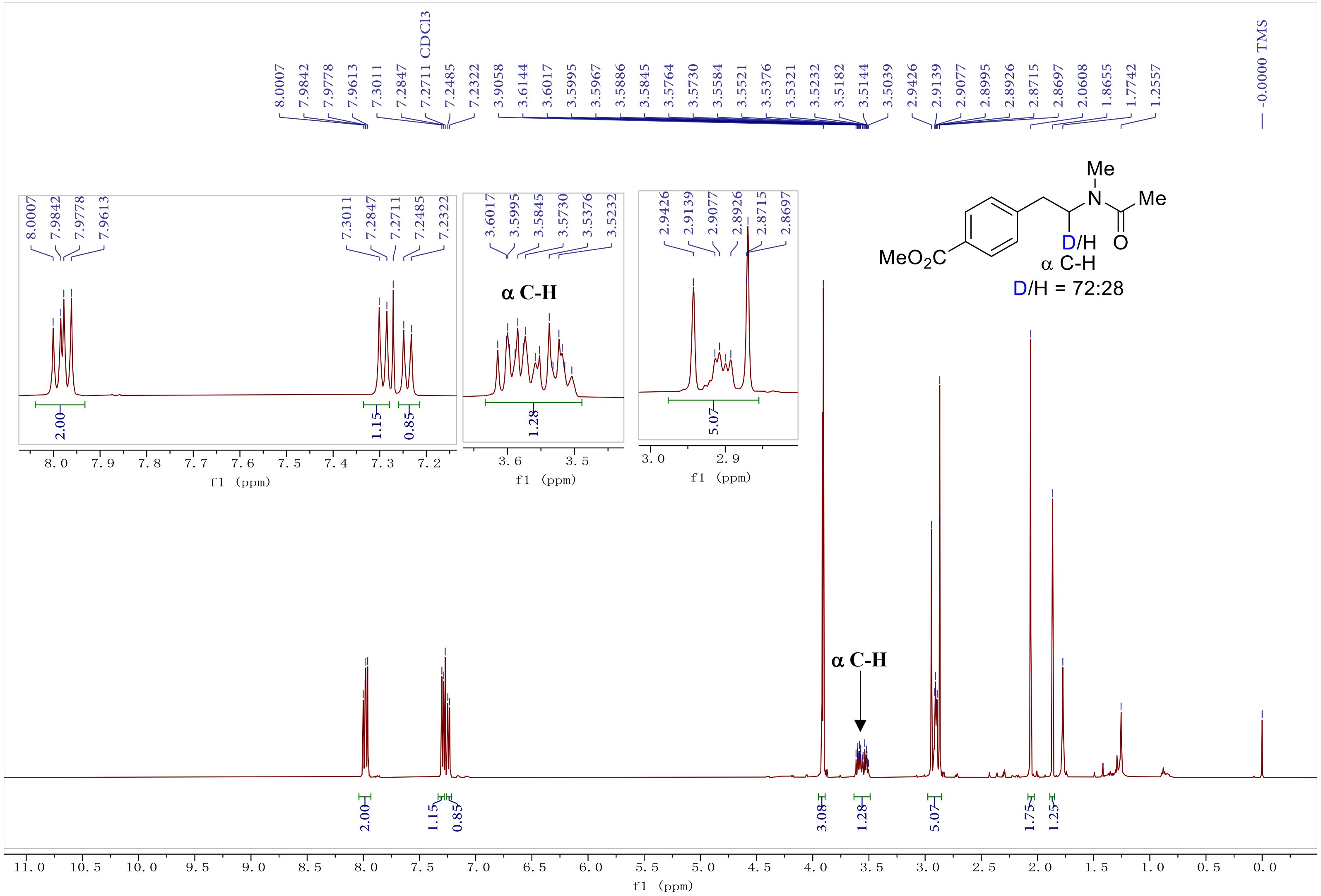
^{1}H NMR Spectrum (400 MHz) in $CDCl_3$



7.49. Deuterium labelling experiments using Hantzsch ester (3-d_3) and D_2O

Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

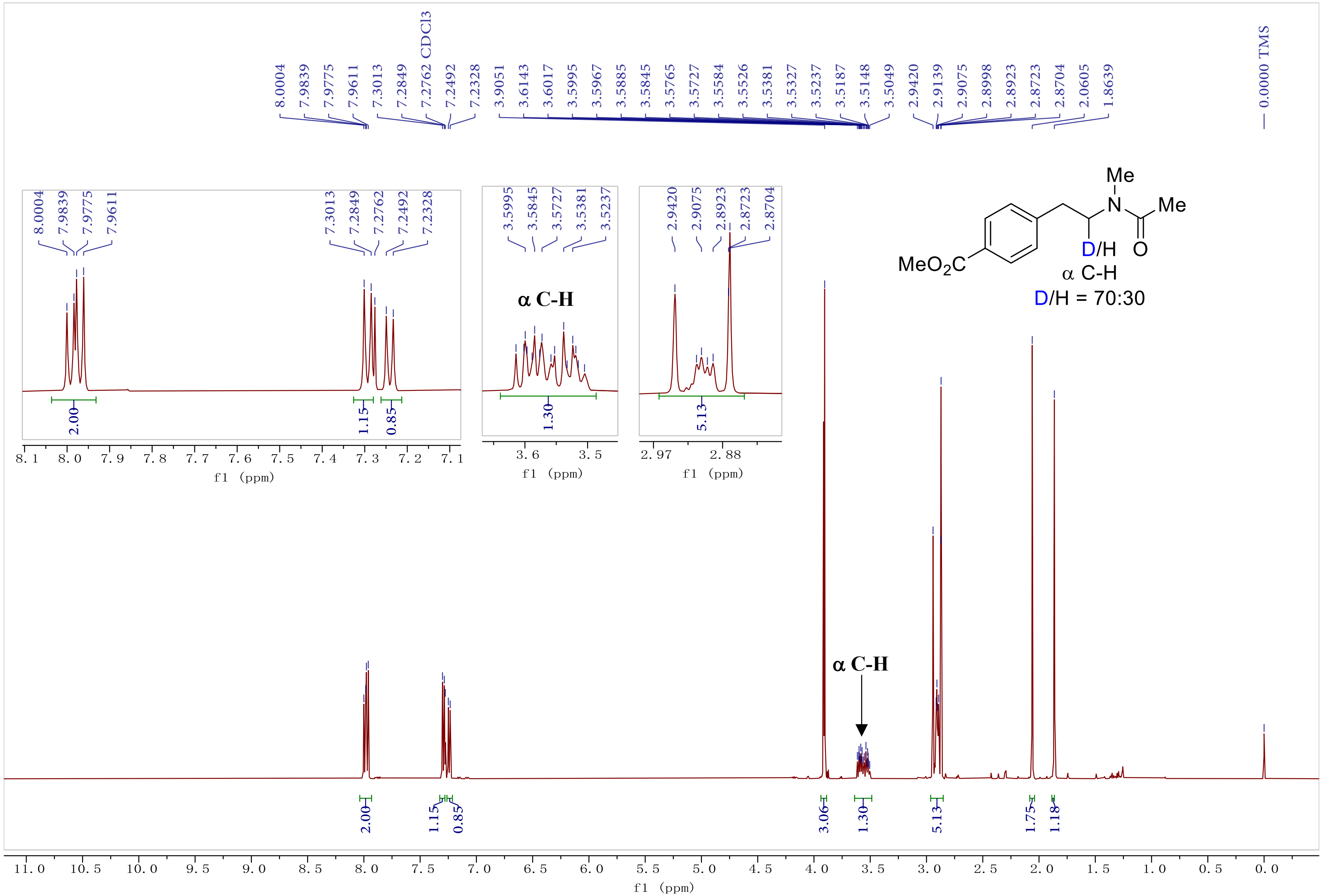
^{1}H NMR Spectrum (500 MHz) in $CDCl_3$



7.50. Deuterium labelling experiments using Hantzsch ester (3-d_3), D_2O and CD_3CN

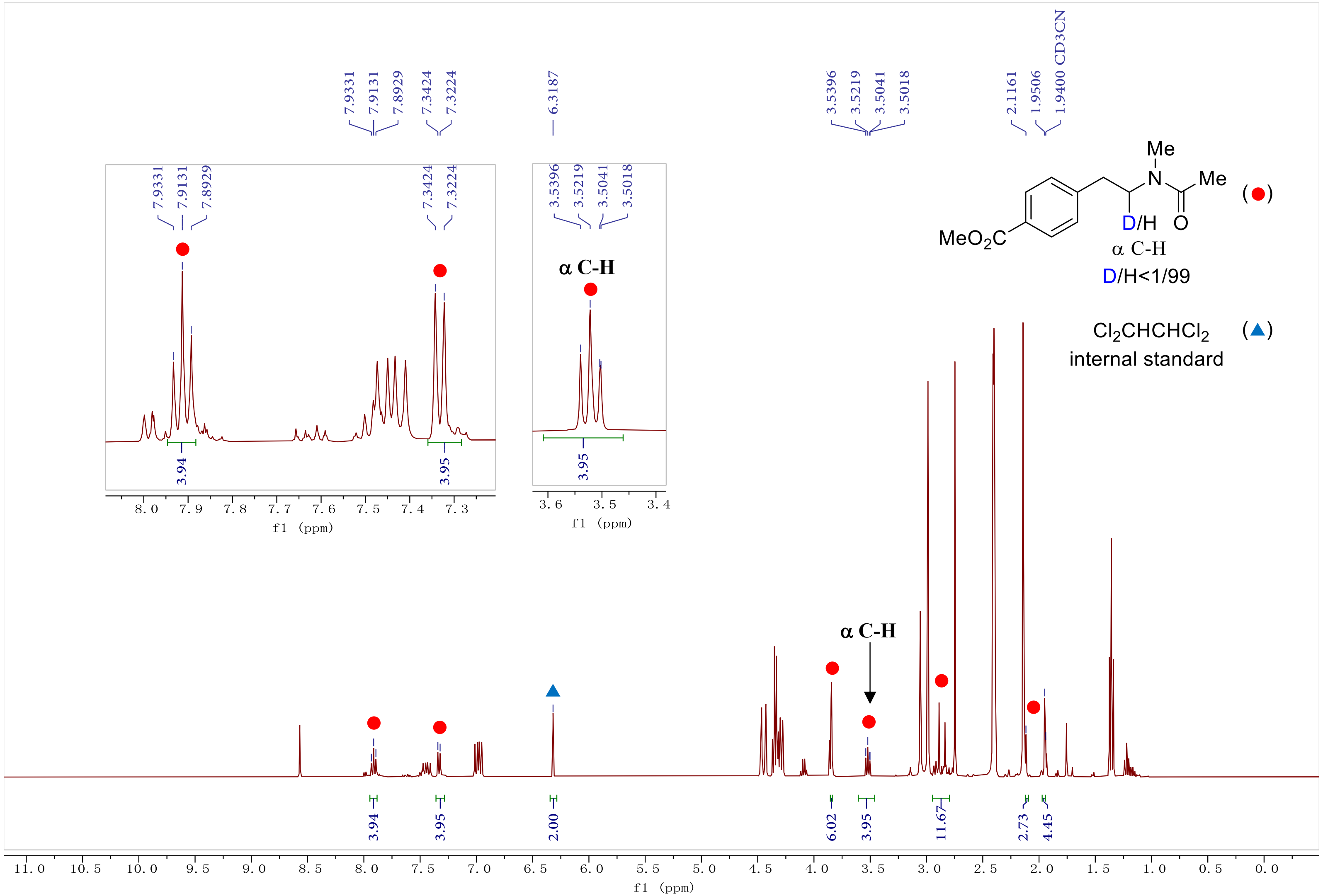
Methyl 4-(2-(*N*-methylacetamido)ethyl)benzoate (4)

^{1}H NMR Spectrum (500 MHz) in $CDCl_3$



7.51. Deuterium labelling experiments with CD3CN

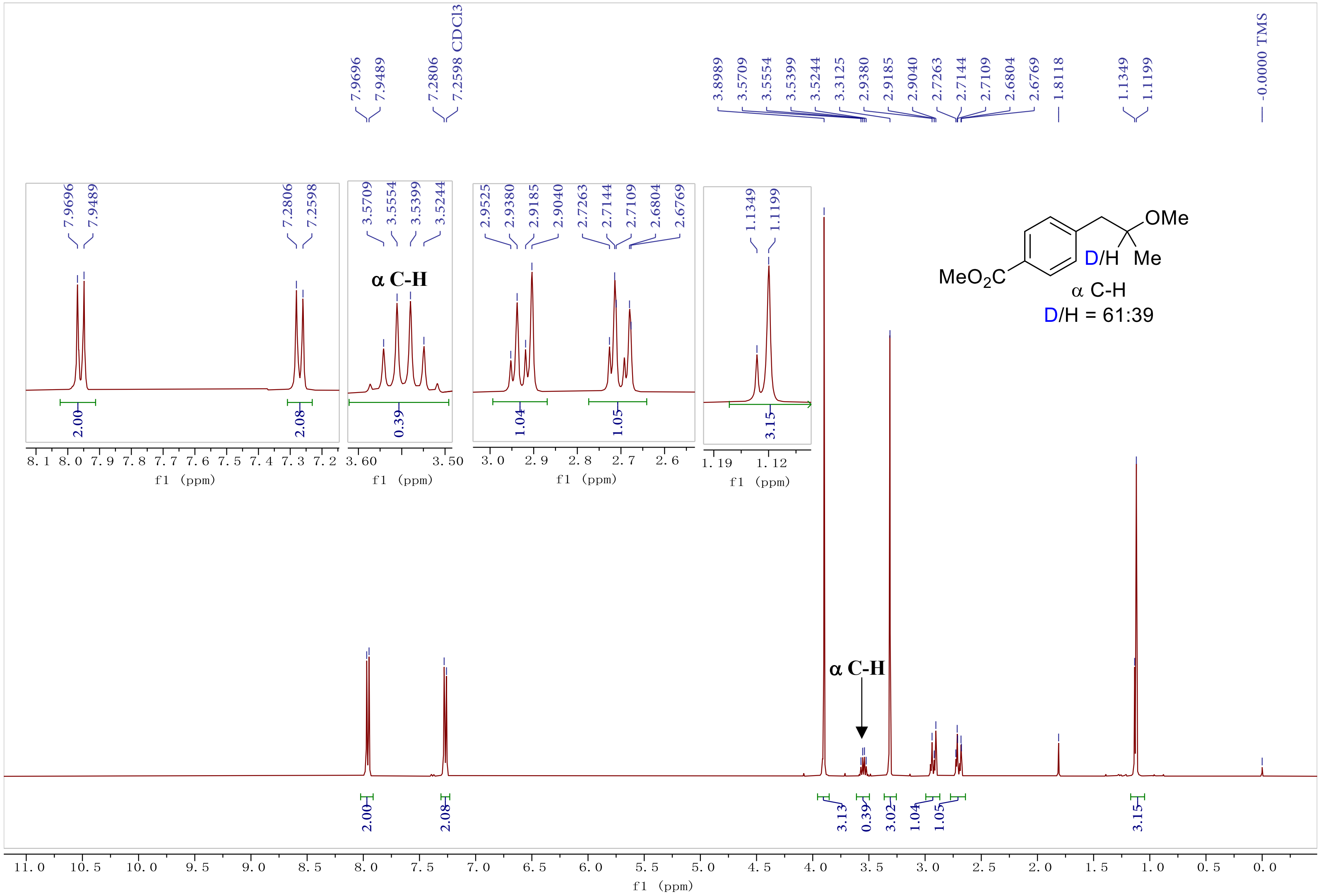
Crude ^{1}H NMR Spectrum (400 MHz) in CD_3CN



7.52. Deuterium labelling experiments using D_2O with 2-methoxypropene (11)

Methyl 4-(2-methoxypropyl)benzoate

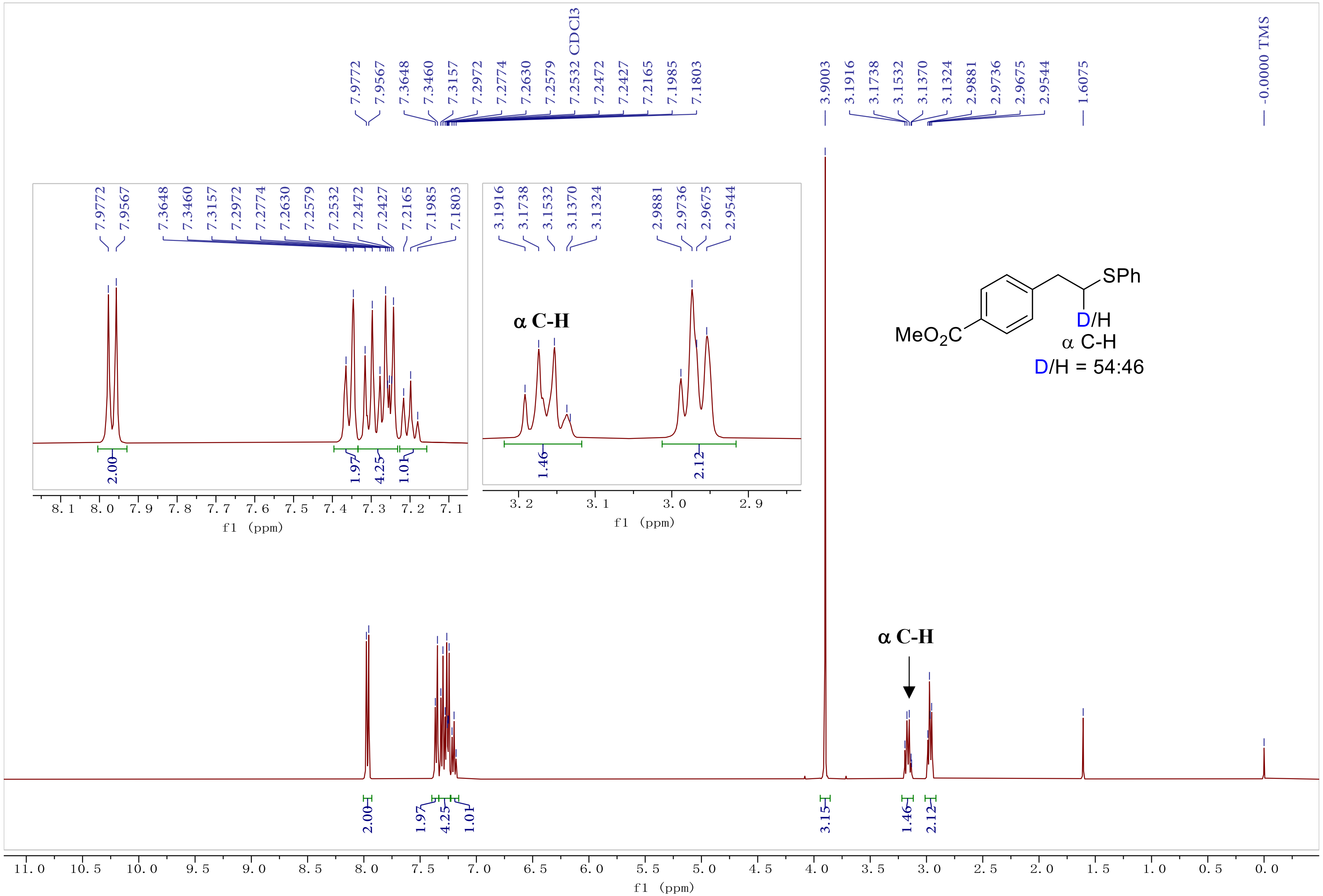
^1H NMR Spectrum (400 MHz) in $CDCl_3$



7.53. Deuterium labelling experiments using D_2O with phenyl vinyl sulfide (13)

Methyl 4-(2-(phenylthio)ethyl)benzoate

^1H NMR Spectrum (400 MHz) in $CDCl_3$



7.54. Deuterium labelling experiments using D_2O with 2-methyl-3-buten-2-ol (17)

Methyl 4-(3-hydroxy-3-methylbutyl)benzoate

^{1}H NMR Spectrum (400 MHz) in $CDCl_3$